Chemistry of Cement

Proceedings of the
Fourth International Symposium
Washington 1960

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UNITED STATES DEPARTMENT OF COMMERCE • Luther H. Hodges, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

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Fourth International Symposium
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Preface

Symposia on the chemistry of cements have become established through a succession of international assemblies held at irregular intervals. More than a half century ago such meetings among researchers, covering various materials including cements, were sponsored by the International Association for Testing Materials.

The first international congress dealing exclusively with the chemistry of cements and related materials seems to have been a meeting sponsored by the Faraday Society and held in London on January 14, 1918. Because of the priority of that meeting in this special field, it has come to be known as the First International Symposium on the Chemistry of Cement.

The First Symposium was designated as "A General Discussion" on "The Setting of Cements and Plasters." Ten brief papers were presented by eleven scientists from five countries. Twelve discussions followed the presentation of the papers. The Proceedings consisted of 69 pages published in the Transactions of the Faraday Society, Volume XIV, 1918–19.

The Second Symposium was sponsored by the Royal Swedish Institute for Engineering Research and the Swedish Cement Association. A three-day meeting was held in Stockholm in July of 1938 under the designation "Symposium on the Chemistry of Cements." Forty-seven persons from 13 countries participated in the presentation of 13 papers and 52 discussions. The Proceedings, consisting of 578 pages, were published in Stockholm in 1939 by the Royal Swedish Institute for Engineering Research.

The intervention of World War II delayed consideration of the next symposium. Preliminary plans for a general meeting in Washington were abandoned, but eventually arrangements were made for the Third Symposium to be held in London under the sponsorship of the Department of Scientific and Industrial Research and the Cement and Concrete Association. The five-day meeting was held in September of 1952, and was attended by 260 persons, 84 of whom participated with 23 papers and 102 discussions. The Proceedings, consisting of 870 pages, were published in London in 1954 by the Cement and Concrete Association.

Preliminary conversations on the organization of the Fourth Symposium were initiated in April 1956, at which time agreement was reached by the National Bureau of Standards and the Portland Cement Association that the Symposium would be jointly sponsored by those organizations. By the spring of 1959 a tentative program had been set up with the cooperation of leaders in cement research of several foreign countries. Later in that year the organization of the working committees was completed. The sponsors and members of committees are listed below.

Sponsors: National Bureau of Standards, Allen V. Astin, Director; Portland Cement Association, G. Donald Kennedy, President.

Executive Committee: I. C. Schoonover, and A. Allan Bates, Cochairmen; R. H. Bogue, Secretary, Robert E. Pflaumer, Douglas E. Parsons, Myron A. Swayze, W. S. Weaver, C. E. Wuerpel, and Hubert Woods.

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Papers for presentation at the Symposium were received at the Secretary's office, beginning in January 1960, and continuing to September. After review by the Program Committee and some preliminary editing by the Editorial Committee, they were reproduced by a photoduplicating process, and copies were mailed, as they became available, to the Symposium members.

The Fourth Symposium was held at Washington, D.C., October 2–7, 1960. Invitations to membership in the Symposium were accepted by 362 persons, including 169 from the United

States and 193 from 34 other countries. The number actually in attendance was 271. All sessions of the Symposium were held at the National Bureau of Standards.

At the first session, held on Monday morning, October 3, Dr. I. C. Schoonover, Associate Director of the National Bureau of Standards, and Dr. A. Allan Bates, Vice President of the Portland Cement Association, acted as cochairmen. Dr. A. T. McPherson, Associate Director of the National Bureau of Standards, welcomed the guests on behalf of the Bureau, and Mr. G. Donald Kennedy, President of the Portland Cement Association, indicated his pleasure in cosponsoring this important gathering. Dr. Eberhard Spohn, President of the Heidelberg Cement Company, responded on behalf of the members of the Symposium.

The first formal address, given by Dr. Wallace R. Brode, formerly Science Advisor to the Secretary of State, was entitled "Some Problems Associated with the Growth of Science." This was followed by an address, given by Dr. F. M. Lea, Director of the Building Research Station of the United Kingdom, entitled "Cement Research, Retrospect and Prospect."

Succeeding sessions were devoted to technical papers, grouped under seven general topics related to the chemistry of cement.

The titles of the individual papers will not be given here, as they are listed in the table of contents. The program included the following sessions.

Session II—Chemistry of Clinker; Monday afternoon, October 3; Dr. Henri Lafuma and Dr. R. H. Bogue, presiding.

Session III—Chemistry of Hydration of Cement Compounds; Tuesday morning, October 4; Dr. Fritz Keil and Mr. Charles E. Wuerpel, presiding.

Session IV—Chemistry of Hydration of Portland Cement; Tuesday afternoon, October 4; Dr. Niko Stutterheim and Mr. Myron A. Swayze, presiding.

Session V—Properties of Cement Paste and Concrete; Thursday morning, October 6; Dr. Wolfgang Czernin and Mr. Hubert Woods, presiding.

Session VI—Destructive Processes in Concrete; Thursday afternoon, October 6; Dr. Arturo Rio and Mr. Douglas E. Parsons, presiding.

Session VII—Chemical Additions and Admixtures—was combined with Session VIII.

Session VIII—Special Cements; Friday morning, October 7; Prof. B. G. Skramtaev and Dr. A. R. Collins, presiding.

The technical communications were of three categories, as follows:

1. Principal papers by outstanding contributors to the literature of cement and concrete technology, who were invited to present their appraisal of the present state of knowledge in their assigned topics;
2. supplementary papers submitted by members of the Symposium, presenting new and original research dealing with the specific topics of the Symposium; and
3. discussion of principal and supplementary papers, presented by members of the Symposium.

Papers were presented in condensed form, but are given in full in these Proceedings. Some of the discussions were submitted prior to the Symposium, others at the time of the meetings or subsequent thereto.

After the Symposium, authors were invited to submit corrections to their papers, but did not have opportunity to read printers' proof. Readers of the Proceedings are asked to make allowance for this, as well as for the facts that some papers are the joint product of authors and translators, and that translations had sometimes to be edited without access to the original manuscripts.

Following the sessions in Washington, many of the members of the Symposium accepted a general invitation to travel to Skokie, Ill., to visit the laboratories of the Portland Cement Association and to attend a series of seminars there. A two-day expense-paid bus trip from Washington to the vicinity of the laboratories was arranged by the Portland Cement Association for foreign guests to enable them to see the countryside and to observe some typical highway systems, expressways, toll roads, and city streets in the United States.

The program at Skokie, October 10–12, included seminars on cement manufacture and on basic and applied research, as well as laboratory tours and demonstrations.

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Explanatory Notes

Abbreviations. The following symbols, which have been widely adopted by cement chemists for formulating more complex compounds, are used interchangeably with the respective oxide formulas throughout this book: $C=CaO$, $S=SiO_2$, $A=Al_2O_3$, $F=Fe_2O_3$, $M=MgO$, $N=Na_2O$, $K=K_2O$, $H=H_2O$. Less common abbreviations of this type are defined as they occur.

Commonly used abbreviations of more general nature include the following:

DTA=differential thermal analysis
FM=fineness modulus
IR=infrared
NMR=nuclear magnetic resonance
psi (or p.s.i.)=pounds per square inch
rh (or r. h.)=relative humidity
w/c (or W/C)=water-cement ratio

Identification Numbers of Papers. Each symposium paper has been assigned an identification number. Examples: Paper II–1 is the first principal paper of session II; paper II–S1 is the first supplementary paper of session II. With few exceptions, the numbers correspond to those assigned to the copies of the papers distributed in advance of the symposium.

Scale of Magnification. In micrographs, the scale of magnification frequently is indicated by a horizontal line. Where not marked, the length represents one micron.

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Proceedings of the Fourth International Symposium on the Chemistry of Cement

SESSION I. GENERAL ADDRESSES

Paper I–1. Some Problems Associated With the Growth of Science*

Wallace R. Brode

(Former Associate Director, National Bureau of Standards, and Former Science Advisor to the Department of State)

In an address [1],[1] as retiring president of the American Association for the Advancement of Science, made in Chicago last December, I stressed the need for a National Science Policy in our Government. The reactions and input to these suggestions provided the background for a presentation [2] before the American Chemical Society some four months later, in which I moved toward an international science policy and program, but still slanted toward the Governmental requirements.

Again there has been reaction, opposition and support, to the ideas which were presented, with the development of a still broader concept of the need for coordinated science planning and programing between governments, universities, industries, and research organizations, both within and between countries.

A measure of the advance of civilization of the world as a whole, and its concomitant parts, is the advance in science and technology. Advance in science and technology is at times a prestige method by which nations try to establish their influence and position. The spread of scientific and technical knowledge is a part of the program by which enlightened nations try to raise the cultural level of the world community. Much of the approximately three billion dollars of foreign aid which the USA annually provides is directed toward scientific and technological training and assistance. Yet we, and other nations who maintain a scientific and technical approach to a way of living, are beginning to realize that at the present rate of increase in our scientific production and activity, we are rapidly approaching limitations in personnel, facilities, and funds which will require establishment of priorities including their funding, location, emphasis, and support.

Predictions of the Future

Essentially there are two extremes in the kinds of events which we predict in advance. One is the event which is quite certain, and by reason of repetitive character or a limited possibility, can be estimated with reasonable accuracy. The other kind of event is that which requires a "crystal ball" and may be said to be at best an intelligent guess.

A good example of these two kinds of forecasts is to be found in an address by Harvey W. Wiley, a noted U.S. Government Chemist, who, on the occasion of the 25th anniversary of the founding of the American Chemical Society, which was celebrated in 1901, predicted that on the occasion of the 100th anniversary of the founding of the American Chemical Society, in 1976, the population of the United States would have grown from 71 to 225 million and the membership of the American Chemical Society would have grown from the then two thousand to ten thousand members. Census experts tell us that barring the unforeseen Mr. Wiley will be correct within about 3 percent on his population prediction, whereas in his prediction on the expansion of science the ACS now has 90,000 members, and we still have 16 years to go in which we can expect a further growth to about 150,000 members as compared with his underestimate of 10,000 members.

People talk of the "population explosion" of our civilization, with dire predictions of the time when there will be standing room only. It is true that

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960.

[1] Figures in brackets indicate the literature references at the end of this paper.

world populations are increasing at a logarithmic rate with an average annual world increase of 1.7 percent. This produces a doubling of the world population every 50 years and of course mathematically speaking this could lead to standing room only. By the year 2000 the earth will have about double its present population. Some areas are growing faster than the average. The United States, India, and Red China are growing at about the average rate of 1.7 percent per year. Europe is growing at a slower rate of 0.7 percent per year. Asia at 1.8 percent, Africa at 2.2 percent, and South America at 2.5 percent, are all growing slightly above the average rate of 1.7 percent per year. In contrast—for quite a number of years—the growth in number of scientists and engineers and the production of technical papers has been increasing at the rate of 10 percent per year with a doubling every 8 years, rather than doubling every 50 years as does the population.

Science Support

The U.S. National Science Foundation, in a release issued in September 1960, estimated that the total outlay in this country for research and development for this year (1960) would amount to about 13 billion dollars, of which about 1 billion would be spent for basic research. This amount of 13 billion is about double that expended four years ago for research and development. On the basis of gross national product (GNP) this is not too staggering a figure, for with a 500 billion dollar GNP this represents only about 2.5 percent of the GNP for research and development and only about 0.2 percent of the GNP for basic research. I am advised that these percentages of the gross national product devoted to research and development are roughly paralleled in a number of the leading technical nations. The actual support and use of research funds may vary from nation to nation. For example, in the United States our basic research funds are furnished to the extent of 36 percent by industry, 55 percent by the Government, and 15 percent by universities and foundations, whereas they are used for the performance of research to the extent of 17 percent by the Government, 35 percent by industry, and 48 percent by the universities and foundations.

The amount we are expending for research and development is not disturbing, but rather the rate at which these funds are being expanded each year compared with the growth of the gross national product and our population. At the present expansion rate of these funds we will, in 10 years time, be spending some 30 billion dollars a year on research and development. By that time our gross national product will have increased to about 700 billion and the percentage of the GNP devoted to research and development will have risen from 2.5 to 4 percent.

The growth of science and technology at a faster rate than our population, wealth, and facilities, implies a trend which if extended to the world at large may overload our abilities to cope with the demands and most certainly will require some form of coordinated planning between governments, universities, and industries.

In addition to the problems of size and expansion rate, there is also a problem of the relative emphasis or direction of programs. The relative emphasis may be between government, industry or universities, or it may be between various areas of science and technology such as space, oceanography, health, nuclear physics, or the chemistry of cement.

It must be obvious that, as we approach saturation limits or shortages, there must be a rational program to conserve and distribute our research and development resources. Such planning requires the establishment of national and international goals and a serious consideration of the problems, not only by those who stand to profit by future developments in science and technology, but also more especially by those who are concerned over the long range prestige and advance of science and technology.

A century from now the world population will be four times what it is today, and this does not seem to be too complex a problem to prepare for. What requires more immediate attention is the expansion of science. The President of the American Chemical Society, Dr. Albert L. Elder, in his Presidential address in September 1960, considered the problem of the population explosion as viewed from the vantage point of the food chemist. For the moment the increasing world food requirements appear to be solvable, for science and technology have demonstrated through work in crop, breeding, and production techniques that yields can be increased at a faster rate than the population increase. In fact, the number of persons engaged in agricultural production in technologically oriented countries is reducing at a faster rate than the increase in the number of scientists and technologists. Today in this country, one person on a farm, with the aid of modern technology and science, produces enough food for 20 persons whereas in the less well developed areas of the world one person feeds three on a lower level of subsistence.

The great crisis which looms ahead is science itself, a crisis which is far more imminent and threatening in the closing half of this century than the population, food, or wealth problems.

The Educational Explosion

In many of the less well developed areas of the world where educational facilities are inadequate, it is expected that in the next decade or two, in order to achieve an adequate status, educational facilities will have to be provided on a much greater scale than are now available. This is a problem in the United States, as well as many other areas of the world. Due to changes in birth rates during the past war, there will be nearly double the number of persons of college age in 1970 as are now in this age bracket. We may expect, with the general increasing percentage of persons electing to go to college that we will have somewhat more than double the number of college students in 1970 than we have today. There is also a trend to gravitate towards science as a major, so that we may also expect a higher percentage of these students to major in science. We may in fact have three or four times as many science students in 1970 as today. There is a problem in the United States as to where we will be able to obtain the essential teachers for our own schools and also for other areas which we wish to help. The teaching problem may well be answered in part by research in mechanical devices, tape recordings, motion pictures, closed television, and other facilities. Space may be created through the use of three shifts on a 24-hour day, seven day a week schedule.

Some good may always accompany overcrowding, for it may be necessary to reduce enrollment and in doing so we can be selective and retain the higher quality of student.

Chemical Abstracts as a Measurement of Scientific Growth

The membership of individual scientific societies in each nation is a reasonable measure of scientific interest in that nation, but the foreign membership in such a society is not a good measure of the interest in the field since foreign membership is often one of convenience and may be induced by the availability of publications under a membership arrangement. While the American Chemical Society has 90,000 members, only about 6,000 are foreign, and the distribution is not at all proportional to known scientific strength of some of these foreign countries.

On the other hand the well-known magazine published by the American Chemical Society, known as Chemical Abstracts, uses the nationality of the authors of papers abstracted to provide a mechanism to measure the relative scientific production of a given area. Chemical Abstracts is only concerned that all acceptable contributions to chemistry are properly abstracted and indexed.

The so-called population explosion of the world with its annual expansion of 1.7 percent per year and a doubling of the world population every 50 years, is inconsequential when compared with the 10 percent per annum growth of our scientific literature with a doubling every 8 years. As much has been published in science in the past 10 years as in the preceding time since the discovery of the printing press, and it is a well-quoted phrase that 90 percent of all the scientists who have ever existed are alive today. The growth curves do not show any sign of having reached an inflection, and in fact they may well be on the accelerating growth side rather than the decelerating growth area which must be reached eventually before we reach the time when every citizen must be a scientist and the annual production of chemical abstracts equals the weight of the earth.

Science is expanding at a faster rate than our population, yet the contributions of science and technology are not distributed in proportion to populations. There are many highly populated areas of the world that are currently providing little to our scientific advance. What will be the effect on our scientific growth if these areas are brought into a state of fertile production? The ethnologists and anthropologists advise us that the entire human race is so nearly alike intellectually that we should expect relatively the same distribution of intelligence quotient (IQ) patterns in all areas of the world, and that if the mentally competent and alert individuals are given educational opportunities we should expect from them a relative number of important discoveries and scientific papers.

We have in the United States about 0.5 percent of our population as scientists and engineers (1 million out of 180 million), and with our population increase and even greater numbers of students and the increased proportion of these in science, we can still hardly expect to maintain a 10 percent increase per year so as to maintain our proportional contribution to the 10 percent world increase which has been a reasonably constant rate for the past 50 years.

At the present time the United States produces about 30 percent of the material in Chemical Abstracts, whereas the Soviet Union produces about 16 percent but the rate of increase of the United States contributions is about 8 percent per annum whereas the Soviet increase is about 15 percent per annum. By language in Chemical Abstracts 50 percent of the world's physical science literature is in English, 16 percent in Russian, 9.5 percent in German, 6.5 percent in Japanese, 5 percent in French, 4 percent in Italian, and 1 percent in Spanish.

Yet all of us realize that these percentages are not proportional to world populations, and while each of us would probably like to see a minimum number of scientific languages, each would like to see his own language retained as one of the principal mediums of scientific communication. It must be obvious that only a limited number of languages can be effective in promoting the interchange of science, and hence many scientists choose a language of communication which is other than their native tongue but which is comprehended by a larger audience.

For example, it should be noted that the population of South America is essentially the same as that of North America, and if the ethnologists are right, and we have no reason to doubt them, we should expect that with equivalent education and opportunity, their production in science could be equivalent to our own. It is this accelerating increase of production in these less well developed areas of the world which will keep the total rate of world annual increase in science at 10 percent or higher for a long time to come.

The amount of material distributed to the registrants of this symposium in advance of this meeting should convince one of the expanding character of our scientific literature. It might be worth while to quote a few statistics so as to impress on you the enormity of this scientific explosion which we are experiencing. Chemical Abstracts published abstracts on 120,000 papers last year and will publish about 135,000 abstracts this year, and by 1975 this will be 500,000 and it will be 1 million by 1985. There is now being published a 10-year cumulative index for Chemical Abstracts, the 5th Decennial, which consists of 19 volumes of 1,500 pages each. This covers the years from 1947 to 1956 and will cost about 2.5 million dollars to edit and publish.

We will not be able to publish another decennial index on account of the size, but the next 5-year cumulative index covering the years 1957 to 1961 will be just as big as the previous 10-year index of about twenty 1,500-page volumes, and the next 5-year cumulative index for the period of 1962 to 1966 will be forty 1,500-page volumes and will cost about 8 million dollars to produce. The annual edition in 1967 will have 250,000 abstracts, will require about 40,000 pages of text and 20,000 pages of index, and to publish this will require about 500 employees in addition to several thousand abstractors. The floor space for this staff will amount to about 40,000 square feet, and the budget for operation will be about 10 million dollars.

At some time between the years 2000 and 2050, we must reach an inflection point, for by the year 2000 about 10 percent of our population will be scientists and engineers if we are to maintain the present rate of increase. More probably other areas of the world will be approaching a technological level at a more rapid rate so as to maintain the world advancing rate of 10 percent. By the year 2050, however, even these areas may be saturated or tending towards a lower growth rate. In the past, wars were quite effective in providing a retardant or moratorium on basic scientific advance. The world is changing and it seems likely that we may be in for intellectual competition, rather than armed conflict, to establish prestige and technological advantage in such areas as space, health, food, new materials, and transportation. This may well result in greater acceleration in scientific production.

The same staggering increases face us in nearly every area of science and in some of the new and popular areas, such as electronics, space, nucleonics, biophysics, and health; the acceleration rates are greater than in the chemical areas.

These increases are not the result of publishing poorer work so as to increase the volume, but rather our information is to the contrary, for with competition to obtain publishing space and backlogs in journals the rejection rate has risen, and the quality of our published material is also rising.

The limiting factors which we are approaching are the ceilings on available personnel, financial support, and facilities. It becomes increasingly important that our communication be improved so that adequate planning and priorities can be effected to conserve our capabilities to realize a maximum production for our efforts.

Just how this improvement of efficiency is to be effected is in a measure dependent on good coordination and planning within each country or state and then across the boundaries by direct exchange and communication on all levels, but with reasonable direction through coordination boards or commissions in the international unions, trade combinations, exchange agreements, symposia, and conferences such as this International Symposium on the Chemistry of Cement, where world experts can exchange ideas and information.

In part, this desired coordination is being effected through better scientific liaison between nations. Some 25 nations have scientific attaches here in Washington, and the program of scientific attaches which I promoted in the major science centers of the world has demonstrated that it is possible to accelerate the flow of information and improve our scientific contacts so as to lead to a closer scientific coordination of our research programs.

I sincerely hope that I have not left the impression that we are approaching a tower of Babel or an imponderable mass of data, for a part of our scientific research program both here and abroad is directed towards the improved methods of literature storage and retrieval. The enormous mass of data to be handled in the future does not disturb me for I have confidence that scientific research will find a method to cope with it. The early monks who prepared the hand lettered manuscripts of the past would also have been disturbed if they had thought that our present day printing demands would require the issuance of weekly magazines in color with 5 to 6 million copies for their circulation.

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[1] Wallace R. Brode, Development of a science policy, Science **131**, pp. 9 to 11 (1960).

[2] Wallace R. Brode, National and international science, Chem. and Eng. News **38**, pp. 140 to 143 (April 18, 1960).

Paper I-2. Cement Research: Retrospect and Prospect *

F. M. Lea

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It is most appropriate that we should meet for this International Symposium on the Chemistry of Cement in the City of Washington and at the Bureau of Standards. Here in this city, in a neighbouring laboratory, there were commenced over 50 years ago those studies on the nature of rocks, that have contributed so much also to our knowledge of the constitution of industrial silicates. The Geophysical Laboratory and the names of its earliest workers on the phase equilibria between lime, alumina, and silica—Rankin, Shepherd, Wright—are familiar to all cement chemists. We know our present meeting place, the Bureau of Standards, as the laboratory from which P. H. Bates made many of his contributions to cement chemistry, to be followed by many others from the staff of the Bureau, and where there was established in 1924 the Portland Cement Association Fellowship under the leadership of R. H. Bogue. To the many contributions that have come from this Fellowship, we have also to add those from the Portland Cement Association laboratory, first at Chicago and then at Skokie, where we are to continue our meetings next week.

The thread that runs through progress in any field of scientific endeavour is often easier to see in retrospect than in prospect. Looking at the past we can see how one step has built on another; looking at the present we can identify the obvious gaps in knowledge and form some idea of the kind of work that is needed; but looking to the future we can only foresee much more dimly where such work may lead us. At the Stockholm Symposium over twenty years ago, it was evident, for instance, that we needed to know much more about the distribution of water in set cement, but we could hardly then have foreseen how far the study of the vapour pressure of set cement was to lead us in an understanding of its physical structure and properties.

These symposia on the chemistry of cements give us an opportunity to review the advances that have been made, to evaluate and discuss the evidence, and to mark out some of the problems that need attention.

The fulfilment of these purposes is the function of the later sessions and in this opening address I can only look broadly at the state of the science and the trends that can be seen emerging, and try to suggest some cross-connections between different parts of the subject matter. If, in doing this, I fall into speculation, perhaps this is an occasion on which it may be permitted.

When we met in London in 1952 we were all impressed by the notable advances that had been made in knowledge of the structures of the cement minerals, considered as idealised chemical entities, and of the phase relations to be expected if conditions of equilibria were maintained. The basis of the constitution of portland cement, and to a rather less extent of high alumina cement, was well-established. Not a great deal that is new is now to be found on such matters but rather has attention been directed more to the deviations from ideality that occur in practice. Variability in clinker structure and the effect of impurities and crystal imperfections on the cementing properties of cement minerals are questions of important practical significance that are discussed in our papers. It is evident that minor oxides in solid solution have significant effects on the atomic arrangements, crystal form, and hydraulic properties of alite and β-dicalcium silicate. We cannot therefore perhaps attach such constant characteristics to the four main clinker minerals as has been implicitly assumed in the past. The relations that can be derived between compound content and the properties of cements are statistical in nature and we have to recognise that the deviations which arise come not merely from experimental error but also from the ignoring of some variables. But may we not expect that with greater knowledge of such matters it may be possible to adjust the production of cements more closely to particular desired ends? We may well look to the further refinement of the analyses of crystal structure and to the application of the concepts of defects and dislocations in crystals, to enhance our understanding.

As always, advances in techniques open up new possibilities. Methods of X-ray diffractometry are now offering a direct means for the quantitative determination of the compound content of portland cement, in place of calculation. We still have to improve this method, since the separation of overlapping peaks, and the discrimination of weak peaks from the background, at present requires a considerable amount of personal judgment. This problem presents itself most acutely in the determination of low amounts of tricalcium aluminate and this is of much practical importance in the further development of sulphate-resisting cement. Perhaps a theoretical study of the shape of diffraction maxima could lead to methods whereby complicated patterns could be analysed by computers. On the other hand better techniques may lead to sharper peaks and increased resolution, and human error might be reduced by improved counting methods such as pulse height

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960.

discrimination or by the use of monochromatic sources.

Perhaps the most notable feature of this Symposium compared with that held in London in 1952 is the increased proportion of papers that bear on the hydration of cements. Infrared spectroscopy, nuclear magnetic resonance, and microwave absorption are all techniques which now offer possibilities, not only for determining the way in which water is bound in set cement, but also for following the hydration process. Advantage has been taken of improvements in electron microscopy and diffraction to study further the structure of set cement, though perhaps not all the high hopes placed on this powerful instrument have yet been realised. The difficulties in interpreting results on hydrates and materials subject to phase change because of the high vacuum and the heating effect of the electron bombardment need no stressing. Sometimes these can be turned to advantage by observing dehydration and decomposition phenomena in the microscope, the changes being followed by lapsed time photography and the diffraction pattern of the selected area.

Differential thermal analysis, with improvements in technique and in methods of interpreting the results, enables hydrated compounds to be differentiated by their water loss at low temperatures, though here again we encounter the difficulty of separating overlapping peaks. This method, combined with X-ray diffraction data, is giving much information on the hydration products in set cement, as, for example, on the composition of the calcium sulphoaluminates formed and the way it changes with age.

It is questionable if any phase equilibria in aqueous systems have received so much attention as those of CaO-Al_2O_3-H_2O and CaO-SiO_2-H_2O. The former at least we can say is now largely resolved over a wide range of temperatures and many of the gaps in knowledge of the latter have been filled. We cannot yet say, however, that full agreement has been reached on the lime-silica ratio of the tobermorite-like compounds formed in the hydration of cement and there is the curious anomaly that the hydration product of dicalcium silicate appears, according at least to some authors, to have a higher lime-silica ratio than that from tricalcium silicate. Is this perhaps linked with the idea that hydration of the tricalcium silicate is controlled by the rate of diffusion of water through overlying hydrate films, but that of the dicalcium silicate by its slow intrinsic hydration rate? We know of various quaternary hydrated calcium alumino-silicates, and have evidence for the formation of a gehlenite hydrate from the action of lime on a calcined kaolin pozzolana and from the hydration of slag glasses in the presence of lime, but we have not as yet positive evidence of its presence in set cement, and still less that of a hydrogarnet, at normal temperatures. There are many problems here still to be resolved.

Hydrothermal reactions have been much studied, both because of their practical importance and the hope that they would indicate without question the final equilibrium products in the lime-silica-water system. This hope has not been realised, for we now know that even under the severe conditions of autoclaving there are many intermediate stages and that metastable products can be formed. The variables governing these reactions are nevertheless important, since the properties of autoclaved products depend much on the constitution and crystal growth of the phases formed.

The role of carbon dioxide in the aging of cement products has now come again to the fore. There was a long period, following the first report nearly thirty years ago of the effect of carbonation on the shrinkage of set cement, during which interest remained dormant. Not only does the rate and time of carbonation affect shrinkage but it is also of importance in relation to the corrosion of reinforcement. The discovery of combined carbon dioxide in forms other than calcite in set cement is of much interest and there is scope for more work on equilibria in aqueous systems containing lime, alumina, ferric oxide, sulfur trioxide and carbon dioxide.

Pozzolanas were not considered at the 1952 Symposium but it is evident from the review on this occasion that the products formed from the reaction of their silica and alumina constituents with lime are essentially the same as those formed in the hydration of portland cement. Little is still known about the part played by iron and alkalies. Similarly, work since 1952 has given more information on the hydraulic properties of slag glasses. We are concerned here with two factors, the intrinsic reactivity of the slag glass towards water in the presence of activators and the strength-forming properties of the reaction products. The interaction of these two factors produces regions of high and low strength in slag composition with the position of the maximum varying somewhat with the type of activator. Though experiments with too many variables become very involved, it seems necessary to include as a variable the relative proportions as well as the nature of the activators used. In supersulphated cement, for example, a slag of low lime-silica ratio requires more clinker and less calcium sulphate than one of high ratio.

Knowledge of the hydration products of high alumina cement has advanced in parallel with that of the CaO-Al_2O_3-H_2O system and there are suggestions for ways of inhibiting the inversion of the hexagonal plate to the cubic aluminate. If this could be prevented at the higher temperatures that can be attained in use it would have much practical importance.

Though many details remain to be clarified we have now a fair picture of the chemical and physical nature of set cement and of the chemical reactions involved in the initial hydration. Despite much work there is still much to learn of the kinetics of the initial reactions, of the part played by surface forces, and of the mechanism by which the initial framework of setting cement is developed. We still know much less about set cement at very early ages than about the more mature product.

We know that both the strength and drying shrinkage of set portland cement are influenced by the proportion of gypsum added and that the optimum content varies with the composition of the cement. Does not this suggest that the initial framework established in setting determines the way in which the subsequent structure of hydration products is set up? If this is so, then it should influence the gel-space ratio and such properties as shrinkage and strength. Again it is evident that surface forces and particle charge determine the rheological properties of a cement paste and that these can be altered by surface active agents. Is this a merely transitory influence or do such forces predetermine the subsequent development of structure? In the absence of an adequate theory there is no guide to indicate how additives might be tailored to produce specific effects. We might contrast this with the part that the theory of polymers has played in the development of plastics.

Solution followed by precipitation and topochemical solid reactions are alternative suggestions for the mechanism of the initial hydration reactions. Do these leave their own specific marks on the physical framework of the set cement or is this primarily dependent on the chemical nature of the reaction products? The rapid initial reactions are dominated by the hydration of aluminates and their combination with gypsum, but initial setting and the development of structure is often attributed primarily to the tricalcium silicate. Sulphoaluminates can produce a structural framework, as is evidenced by supersulphated cement, and false set is attributed to the reformation of gypsum from its dehydrated forms. We have also the suggestion from electron microscopy that plate crystals from the tricalcium aluminate play an active part in the formation of structure by acting as a kind of template for other structures forming in their vicinity. If this kind of concept is valid then the framework of set cement, though composed predominantly of hydrated silicates, may still have its form, and to some degree its properties, predetermined by other products. There is much in the papers presented to this Symposium bearing on this topic but, as one of our authors says, a true understanding of the mechanism of thixotropy, setting and hardening, still lies in the future.

An allied theme running through many of the papers is the nature of the cement bond and its attachment to the aggregate. Here our ideas are derived from electron microscopy, considerations of crystal structure, and of specific surface. We can recognise that the conflict between crystal and colloid theories of set cement has been replaced by a more detailed description in which the large surface area underlying colloidal behaviour and crystal bond both play their part. We still are not clear about the relative importance of surface forces and chemical bonds; we cannot say that a large surface area is a necessary condition for hydraulic properties for this does not hold for the well-crystallised products that act as the bond in cement cured in high pressure steam. The evidence on the influence of crystal shape is also more conflicting now than it appeared in 1952. There is evidence that the bond of cement to aggregate is improved by mild reaction of the aggregate surface and this may be due to some rearrangement of the lattice in the contact phase. This would seem similar in principle to the welds that Bernal suggested are formed in set cement by the intergrowth of the lattices of crystals in contact.

There are various theories of the mechanism of deformation and rupture of concrete under load, but, on the principle of economy of hypotheses, we should not be content until these can be related to the bond within the cement paste and between the paste and the aggregate. Some theories of rupture are statistical derivations from the weakest-link theory, while others depend on the analysis of stress distribution and elastic and plastic deformations before, and at, failure in idealised models. Precracking in compression is often attributed to local breakdowns in adhesion between cement and aggregate caused by local shear stresses arising at the interface, and subsequent failure either to tensile failure of the cement crystals, or of the bond between them and aggregate, in a direction perpendicular to the applied load, or to the development of inclined shear planes. Has not the nature of the cement bond a direct bearing on such conceptions? The gradual reduction in the magnitude of the wet-dry movement of concrete on successive cycles of wetting and drying, and the observation in one of our papers that the irreversible element in the first drying shrinkage disappears after prolonged wet curing may point to the gradual creation of additional valence bonds. May not this be reflected in some change in the mode of rupture? The strength of a heterogeneous material like concrete is a complex property, but there is a need to try to link the physical and engineering approaches to the problem. It is of interest to see such an attempt made in another of our papers.

In many problems we tend to seek solutions in terms of phenomena which are specific to portland cement. There are, however, many properties of cement and concrete which do not differ materially when the concrete is made from quite different cements. Strength, elasticity, shrinkage and creep, for instance, show essentially similar characteristics in concretes made from portland cement, slag cements, or high alumina cement. If the shrinkage of a test specimen made from ground calcium monoaluminate is essentially similar to that of one made from ground tricalcium silicate then we must be tempted to seek the fundamental cause of shrinkage in the physical chemistry of the pore space assembly rather than in its chemical and mineralogical character. If we press this too far it may lead us into error, for there is good evidence that shrinkage has not a single source but rather several that come into play at different stages of drying. Capillary theory, gel sorption, and changes in the interlayer water probably all play their part at different relative humidities. The difficulty is to disentangle them. More attention has been paid to changes in the capillary and adsorbed water than to the interlayer water, but we now know that not only the tobermorite-like hydrates, but also hydrated tetracalcium aluminate and calcium sulphoaluminate all show changes in lattice spacing with changes in water content. There is scope for some comparative studies on the vapour pressure-water content-shrinkage relations of various kinds of hydraulic binders and the way that these are influenced by the surface area of the set cement. The results might in turn also help to clarify the nature of the structural framework of set cement.

There is much empirical knowledge of creep in concrete and an understanding of the rheological models, combining viscous and elastic elements in series or parallel, that will give mathematical expressions for it, but it is well recognised that such models only represent the behaviour and do nothing to explain it. Thus, such models can be used as a physical representation of creep in both concrete and coal, though the mechanism of creep in the two cases is probably quite different. There is still a lack of the basic fundamental data that alone can provide a critical test of the various theories that have been advanced to explain the mechanism of creep. The data on creep in water-stored concrete seem free from ambiguity but not so for that of concrete stored in air. One reason for the lack of progress has been the common assumption that creep and shrinkage are independent and that values for the former can be deduced by subtracting from the total deformations observed the shrinkage measured contemporaneously on unloaded specimens. This may well be a valid approach for purposes of structural engineering analysis, but not for the theory of the mechanism of creep. If it is now accepted that creep and shrinkage are interdependent phenomena the implications for the kind of further experiment needed are self-evident.

The more the quality of concrete can be controlled the more disturbing become the unidentified causes of deterioration. As long as deterioration could be vaguely ascribed to poor concrete, no further remedy than to make better concrete seemed needed. The marked advances in knowledge of alkali-aggregate reaction, of dimensional change in aggregates, and of frost resistance, have enabled not only failure from these causes to be identified, but also the remedies prescribed. There still remain arguments about the theory of these actions but the general picture is clear. Though diagnosis of causes of deterioration is not always easy—map-cracking, for example, can arise either from expansive reactions or aggregate shrinkage—there are reports from various countries of deterioration believed to be due to unknown reactions between cement and aggregate. It is evident that we are still far from running out of problems.

In the papers to this Symposium attention is directed mainly to the more basic aspects of the subject, with the purpose of explaining observed phenomena. This is the first step to the control of events which is the object of technology, but between explanation and control there is often a gap to be bridged. If we look back at the matters discussed at earlier Symposia and consider later developments in cement and concrete technology we find many examples of the accomplishment of this operation. We need have little doubt that the new knowledge being discussed here will be recognised by the time of the next Symposium to have formed the basis for new advances in practice.

SESSION II. CHEMISTRY OF CLINKER

Paper II-1. Phase Equilibria and Constitution of Portland Cement Clinker*

R. W. Nurse

Synopsis

A short section on new methods of research mentions high temperature microscopy, high temperature X-ray diffraction, and X-ray absorption microspectroscopy as significant advances in technique.

New and modified phase diagrams of interest to cement chemists are then reviewed. The principal advances have been in the phase relations of the iron-containing solid solutions and in alkali-containing systems. Some interesting problems remain to be solved even in the well-studied binary and ternary systems. The effect of water and other volatile components on phase relations requires more study.

Experimental studies on the clinker components themselves have given more data on alite and β-C_2S. Studies of hydration and gain in strength show the importance of the minor oxides in solid solution in the clinker minerals. Evidence is also reviewed showing that the strength of cement may be affected by the size and shape of the crystalline components in the clinker.

Among methods for the direct estimation of clinker constitution, X-ray diffractometry is of most interest. The method is still under development but is already giving useful and interesting results. The most significant finding is that the ferrite phase is much richer in iron than would be expected from simple theory, and nevertheless exists in contact with C_3A.

In reviewing the present position the author draws attention to the frequent observation that the clinker has not reached equilibrium at the clinkering temperature and still contains free CaO. The consequences of this have been discussed earlier by Swayze, with the conclusion that liquids will be formed more saturated with CaO than predicted from the equilibrium diagram. Such liquids can crystallise to form C_3A and an iron-rich ferrite, in agreement with the X-ray findings.

Finally some suggestions for further research are made, including an exchange of carefully selected clinker samples between national laboratories.

Résumé

Un paragraphe rapide sur les nouvelles méthodes de recherche mentionne l'important progrès d'ordre technique que constituent la microscopie à température élevée, la diffraction des rayons X à température élevée et la microspectroscopie de l'absorption des rayons X.

Des diagrammes de phase nouveaux et modifiés, susceptibles d'intéresser les chimistes du ciment, sont ensuite passés en revue. C'est dans les relations de phase des solutions solides contenant du fer et des systèmes contenant de l'alcali que les progrès principaux ont été réalisés. Certains problèmes intéressants sont encore à résoudre même dans les systèmes binaires et ternaires, cependant bien étudiés. L'effet de l'eau et d'autres composants volatils sur les relations de phase nécessite une étude plus poussée.

Des études expérimentales sur les composants mêmes du *clinker* ont fourni plus de données sur l'alite et β-C_2S.

Des études de l'hydration et de la résistance accrue montrent l'importance des oxydes mineurs en solution solide dans les minéraux du *clinker*. Également passés en revue sont des témoignages qui montrent que la résistance du ciment peut être affectée par la taille et la forme des composants cristallins dans le *clinker*.

Parmi les méthodes pour l'estimation directe de la constitution du *clinker*, la diffractométrie des rayons X est des plus intéressantes. La méthode est encore à l'étude mais elle donne déjà des résultats utiles et intéressants. La découverte la plus importante est que la phase ferrite est beaucoup plus riche en fer que ne le laissait attendre la simple théorie, et n'en existe pas moins en contact avec C_3A.

Passant en revue la situation présente, l'auteur attire l'attention sur l'observation fréquente que le *clinker* n'a pas atteint sa position d'équilibre à la température à laquelle il se forme et contient encore du CaO à l'état libre. Les conséquences de ceci ont été discutées précédemment par Swayze, qui conclut que les liquides formés seront davantage saturés de CaO que le diagramme d'équilibre ne le prédisait. De tels liquides peuvent se cristalliser pour former C_3A et un ferrite riche en fer, conformément aux découvertes des rayons X.

Enfin sont faites des suggestions pour des recherches ultérieures, en particulier l'échange entre laboratoires de différents pays d'échantillons de *clinker* soigneusement sélectionnés.

Zusammenfassung

Die neuen Forschungsmethoden werden kurz besprochen, wie die Hochtemperaturmikroskopie, die Hochtemperaturröntgenstrahlenbeugung und die Mikrospektroskopie der Röntgenstrahlenabsorption, welche die bedeutsamsten Fortschritte der Technik darstellen.

Dann werden neue und modifizierte Phasendiagramme besprochen, die den Zementchemiker interessieren. Die größten Fortschritte wurden hier für die Phasenbeziehungen der eisenhaltigen festen Lösungen und der alkalienenthaltenden Systeme erzielt. Sogar in den binären und ternären Sytemen, die doch so gründlich studiert worden sind, sind immer

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noch einige interessante Probleme ungelöst geblieben. Die Wirkung des Wassers und anderer flüchtiger Komponenten auf die Phasenbeziehungen muß noch untersucht werden.

Die Experimentaluntersuchungen der Klinkerbestandteile haben neue Werte für Alit und β–C_2S geliefert. Hydratationsstudien und Messungen der Festigkeitserhöhung haben die Bedeutung der Oxyde, die nur in kleinen Mengen vorkommen, in der festen Lösung der Klinkermineralien bewiesen. Andere Untersuchungen werden auch besprochen, aus denen es sich ergibt, daß die Zementfestigkeit durch die Größe und die Gestalt der kristallinen Bestandteile im Klinker beeinflußt wird.

Von den Methoden zur direkten Bestimmung der Klinkerkonstitution ist die Messung der Röntgenstrahlenbeugung die interessanteste. Die Methode ist noch in der Entwicklung begriffen, hat aber dennoch schon nützliche und interessante Ergebnisse gezeitigt. Die größte Entdeckung war hier, daß die Ferritphase viel mehr Eisen enthält, als man es der einfachen Theorie gemäß erwarten würde, und daß sie in Berührung mit C_3A nichtsdestoweniger existiert.

In der Besprechung der modernen Kenntnisse weist der Author darauf hin, daß der Klinker sein Gleichgewicht bei seiner Brandtemperatur nicht erreicht hat, wie daß ja so oft beobachtet worden ist, daß er immer noch freies CaO enthält. Die Folgerungen, die man daraus ziehen muß, sind schon früher von Swayze besprochen worden, der nämlich gefunden hat, daß flüssige Phasen entstehen, die im Sättigungszustand mehr CaO enthalten, als vom Zustandsdiagramm vorausgesagt wird. Solche Flüssigkeiten können unter der Bildung des C_3A und eines Ferrits, der sehr viel Eisen enthält, kristallisieren, was durch die Röntgenbilder bestätigt wird.

Am Ende werden einige Vorschläge für zukünftige Untersuchungen gemacht; es wird unter anderem vorgeschlagen, daß verschiedenen Regierungslaboratorien sorgfältig ausgewählte Klinkerproben miteinander austauschen sollen.

Introduction

The purpose of this paper will be first to review briefly those phase diagrams or modified phase diagrams of interest in the field of portland cement chemistry which have appeared since the 1952 Symposium. Work on the clinker components as such will then be discussed, and then direct studies on clinker or cement. Finally an attempt will be made to assess the present situation and outlook with regard to the constitution of portland cement.

Since the last Symposium, Bogue's book [1] [1] has appeared in a new and revised form, and also a new edition of Lea and Desch [2]. The existence of these two authoritative works will considerably lighten the present author's task. Structural questions will only be dealt with in so far as they have a direct bearing on the constitution of clinker.

A very brief reference will first be made to methods and techniques.

Methods

The principal advance since Bogue's review of 1952 [3] is in the wider use of high temperature microscopy. This method has not only proved to be faster than conventional quenching, but also more reliable. Only occasionally (in order to gather more material for examination, or to avoid too rapid volatilization) is it necessary to revert to the quench method. Up to 1,800 °C. the thermocouple loop can be used, and by means of a plain iridium loop observations can be made up to 2,200 °C. Temperatures are then measured by optical pyrometry or estimated from the voltage drop across the heater [4].

When the primary phase will grow as a single crystal, it is sometimes possible to separate the crystalline matter from residual liquid and to make separate observations on each.

The same technique of holding the specimen in a thermocouple loop forms the basis of a useful and reliable method of high temperature powder X-ray diffraction [5]. With 20/40 rhodium-platinum thermocouples a temperature of 1,850 °C can be reached. The general utility of high temperature X-ray methods has been discussed by Trömel [6].

In many systems subsolidus reactions are of importance. Frequently these present considerable difficulty because of the very slow rate of reaction. It is sometimes convenient to study the equilibria at high pressures and in the presence of water, extrapolating to NTP and 'dry' conditions [7, 8]. McConnell has used a kinetic method in which the dependence of rate of reaction on temperature for both forward and reverse reactions is used to find the transition temperature [9].

Roy [10] has described a convenient method of preparing mixtures for study.

A new technique which holds out much promise for application to the problem of clinker constitution is X-ray absorption microspectroscopy. This enables an estimate to be made of the mass of an element present in an element of a thin section from 1 to 10 μ square; alternatively a microphotograph can be taken of the surface in which the blackening of the photographic image is proportional to the amount of a given element present in the original surface [11]. Such methods could be used to find the composition of liquids and of the phases in contact with them. Oxides in solid solution in crystalline phases could also be determined.

Replicas of clinker surfaces have been studied in the electron microscope [12, 13].

No outstanding advances have been reported in conventional microscopy. It does, however, appear to the present author that the point counting method developed by A. A. Glugolev has many advantages over the intercept method still employed by many workers [14].

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[1] Figures in brackets indicate the literature references at the end of this paper.

The Calcium Silicates

That part of the system $CaO\text{-}SiO_2$ of importance to portland cement has been revised by Welch and Gutt [15]. Their diagram shows (fig. 1) that C_3S does not decompose at 1,900 °C as previously thought, but melts incongruently at 2,070 °C, forming CaO and liquid. It follows that C_3S has a small field in the binary system where it is stable in contact with liquid (fig. 2).

The metastable inversions at 923 and 980 °C (pure C_3S) and 850° (alite) found by Nurse and Welch have been confirmed and further studied by Yamaguchi, Ikegami, Shirasuka and Amano [16]. It is of some importance that the significance of these inversions should be established because of current interest in the conditions of occurrence of alite in various systems. If the original suggestion of Jeffery is correct, then the phase in contact with liquid near the melting point will in most systems be trigonal C_3S or alite and a phase field for triclinic C_3S will probably only appear at subliquidus temperatures. In studies on the solubility of impurities in C_3S it is important therefore to state the temperature at which the preparations have been processed. The solubility of oxides in C_3S and the stabilization of alite will be further discussed later.

Welch and Gutt actually observed and recorded photographically the incongruent melting of C_3S, and earlier workers had also doubted the original conclusions of Shepherd and Rankin; it appears therefore that ternary and higher order systems involving CaO and SiO_2 require revision in the higher temperature regions involving C_3S.

Yannaquis [17] has thrown some doubt on the lower decomposition point at 1,275 °C, stating that only impure C_3S is decomposed.

There have been no suggestions for revision of the thermal relationships of C_2S in the system $CaO\text{–}SiO_2$ except for unconfirmed reports of a cubic form at high temperatures [18] and a β' form at low temperatures [19].

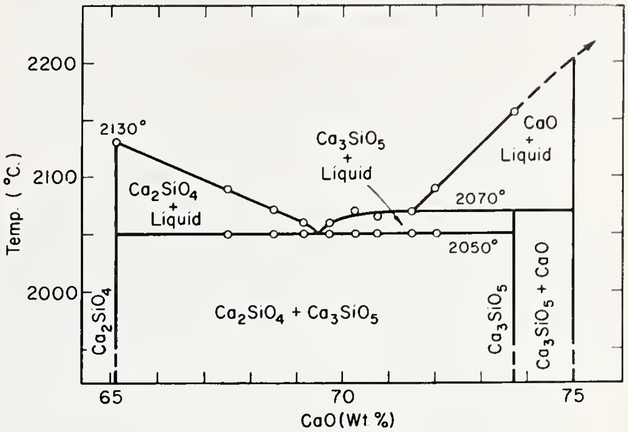

FIGURE 1. *Portion of the system* $CaO\text{–}SiO_2$.

FIGURE 2. *Photograph (x170) of* C_3S *crystals stable in contact with melt in the system* $CaO\text{–}SiO_2$ (*Temperature 2,060 °C*).

The Calcium Aluminates

The painstaking optical observations on the system $CaO\text{-}Al_2O_3$ by Wright have been vindicated by the isolation of single crystals of unstable C_5A_3 enabling the parameters of the unit cell to be measured [20]. From these measurements and the determined density it would appear that the unstable mineral is truly of C_5A_3 composition in contrast to the stable form which is now agreed to be $C_{12}A_7$. Nurse and Welch [21] find the melting point of the latter can be as low as 1,391°C; the higher values which have been obtained by the quenching method are explained by the amazingly rapid growth of this compound during quenching and by the effect of furnace atmosphere. Unless special precautions are taken, the normal furnace atmosphere contains enough water to be able to influence the melting curve. In drier atmospheres the field of stability of $C_{12}A_7$ narrows, and although it has not been observed to disappear it seems likely that it may do so in the complete absence of water. At 1,000 °C $C_{12}A_7$ can take up just over 1 percent of water. Further work is required to relate this behaviour to the suggested structure.

Neither unstable C_5A_3 nor $C_{12}A_7$ has been confirmed as occurring in portland cement, and they will not be discussed further at present. Equilibria involving $C_{12}A_7$, must however, be considered as part of the cement quaternary system and further study of the binary system $CaO-Al_2O_3$ is therefore essential.

The Ferrites and Aluminoferrites

While it can now be considered as established without question that the browmillerite (ferrite) phase of importance in portland cement is of variable composition, there still remains some uncertainty as to the range of this composition, and more particularly as to the relationship between bulk composition, temperature and solid solution composition.

The earliest paper describing the solid solution was that of Toropov, Merkov, and Shishakov [22], and this was followed very closely by that of Yamauchi [23]. Only very recently, however, has an attempt been made to establish enough tie lines to enable a calculation of crystallization paths to be made and this only for the pseudoternary system $CaO-CA-C_2F$ [24]. This system, as described by Newkirk and Thwaite is reproduced in figure 3, and is based in part on earlier works by Swayze, McMurdie, and Yamauchi. Figure 3 is a corrected version of the original, kindly provided by F. Ordway.

The solid solution is shown as a shaded area extending from the C_2F composition to point L. The width of this area was established by means of quantitative measurement on the X-ray spectrometer and may therefore possibly in part represent experimental error. Structural considerations [25] suggest that the series should follow a line joining C_2F to a hypothetical C_2A; such a line on figure 3 would follow closely the high CaO boundary of the shaded area.

Newkirk and Thwaite found C_3A in a devitrified C_6A_2F glass in agreement with the position of C_6A_2F as shown in the diagram. At the Building Research Station we have tried to decompose C_6A_2F to give C_3A but without success. On the contrary, a partially reacted melt containing a little C_3A absorbed it completely on annealing at 1,200 to 1,250 °C. It therefore seems likely that the solid solution line does run from C_2F towards C_2A.

Toropov and Boikova in a revision of the first author's work [26] consider the solid solution to be formed between C_4AF and the orthorhombic C_5A_3. However, in their conclusions these authors revert to the conception of a structure in the series C_2F-C_2A and round off their limiting solid solution to C_8A_3F, containing only 17 percent of Fe_2O_3 and not comprised within the system with C_5A_3.

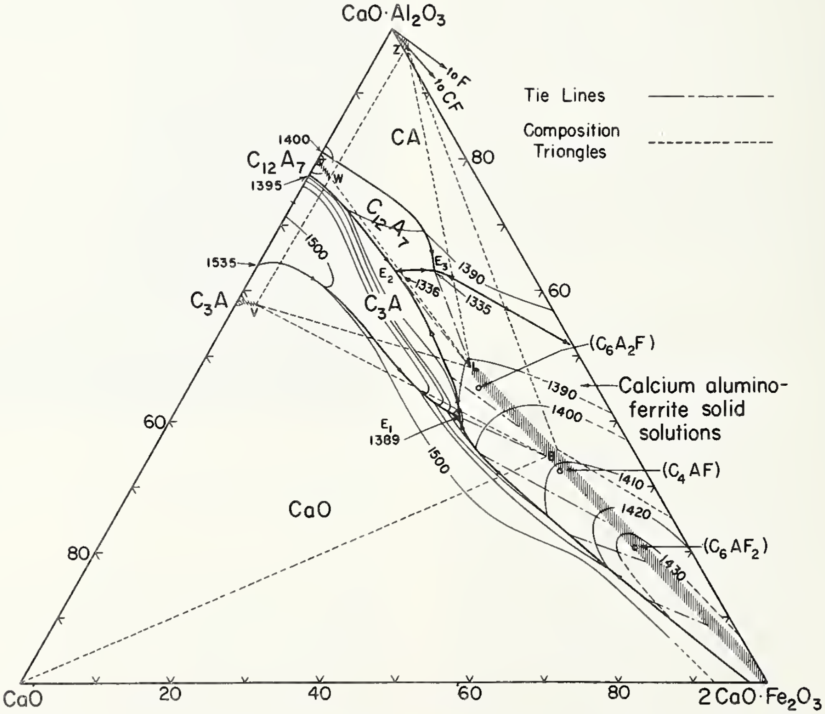

FIGURE 3. *The pseudo-ternary system* $CaO-C_2F$, *after Newkirk and Thwaite.*

Compatibility triangles within the pseudosystem CaO-CA-C_2F according to Newkirk and Thwaite are as follows:

$CaO+C_3A+Fss(B)$
$C_3A+C_{12}A_7+Fss(L)$
$C_{12}A_7+CA+Fss(L)$
$CA+Fss(B)+CF$
$CA+Fss(L-B)$
$C_3A+Fss(L-B)$
$CaO+Fss(B-C_2F)$
$CF+Fss(B-C_2F)$
2 solid solutions $(C_3A+C_{12}A_7)$
2 solid solutions $(C_{12}A_7+CA)$

where Fss(B) and Fss(L) represent solid solutions of compositions B and L in figure 3 respectively.

If the solid solution relations between C_2F and C_2A do not involve quaternary equilibria, the solid solutions L′ and B′ representing the compositions in solid equilibrium with C_3S, C_2S, and C_3A, and CaO, C_3S, and C_3A, respectively, should coincide with L and B in figure 3. The evidence provided by Swayze is that the solid solutions in equilibrium at the quaternary invariant points as shown by the lines 1 to 8 and 2 to 9 in figure 4 do differ in composition from points L and B. For an exact analysis of crystallization paths it will therefore be necessary to know the location of a sufficient number of tie lines within the tetrahedral volume. Some of these tie lines will undoubtedly terminate in solid solutions relatively rich in C_2F, even though the final products of crystallization do not involve C_2F–B solid solutions. The Alkemade spaces inside the larger system will be:

(1) CaO–C_2F–B–C_3S
(2) C_2S–C_2F–B–C_3S
(3) CaO–C_3A–B–C_3S
(4) C_2S–C_3A–L–C_3S
(5) C_3S–C_2S–L–B
(6) C_3S–C_3A–L–B

In this list L and B are used to represent the high and low A/F solid solutions so that the relationship to figure 3 is clear; the actual compositions may depart appreciably from those at points L and B.

Leaving aside assemblages (1) and (2) which are not true portland compositions, the composition of the ferrite phase is fixed for assemblages (3) and (4) and has the A/F ratio of the clinker for (5). Only in assemblage (6) is C_3A found in contact with a variable iron phase, and C_2S is then absent. As will be seen later, these conditions are not those found in practice.

The accepted authority for the relation in the bounding plane CaO–C_2F–CA is Burdick [28]. A C_3F compound does not appear in this system as it has hitherto only been observed as a result of solid state reaction. According to Burdese and Gallo [29] it decomposes at 800° and it is therefore unlikely that it will ever appear in the presence of liquid even in systems higher than quaternary. It may conceivably appear as a product of devitrification of glass of high iron content and in this case would be confused with C_3A in X-ray examinations (a_0 for $C_3A=15.2A$, for $C_3F=15.4A$).

It will be noted that the series Fss(B)—C_2F cannot exist in equilibrium with C_3A in completely solid preparations. Compositions which solidify containing C_3A and CaO, and are therefore potentially of interest as cement compositions, can, however, yield solid solution richer in C_2F than point B at temperatures above that of point E (1,389 °C). By interpolation of tie lines it can be seen that the solid solution richest in C_2F involved in such crystallization paths would be just beyond C_6AF_2. Under conditions of fairly rapid cooling one would therefore expect to find in contact with C_3A a zoned solid solution extending from C_6AF_2 towards point B. Similarly in the triangle C_3A—B—L rapid cooling may result in zoning from B towards L. These conclusions will not necessarily be valid however for equilibria in the presence of silicates.

The Basic Quaternary System

The most recent investigation of the quaternary system CaO–C_5A_3–C_2S–C_2F remains that of Swayze [27] (fig. 4). If we accept the revisions of the bounding planes which have already been discussed, Swayze's diagram requires amending in respect of the high temperature and of the C_3S volume and to take account of Newkirk and Thwaite's limitations to the ferrite solid solution series. However it does not seem likely that the fixing of the invariant points (1 and 2 in Swayze's terminology, T_1 and T_2 of Lea and Parker) can be very much in error, and these will probably lie as they do at present, outside their corresponding tetrahedra of compatibility, so that the iron compounds formed at the invariant points will be members of the solid solution series. Swayze identifies them as having Al_2O_3/Fe_2O_3 ratios of 0.50 and 0.85 for invariant points (1) and (2) respectively.

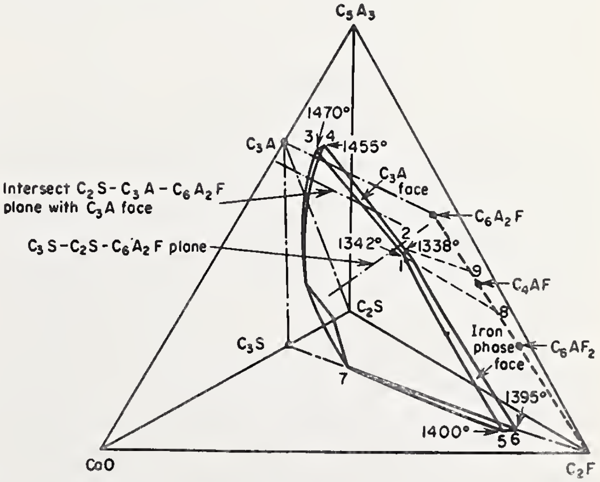

FIGURE 4. *The* C_2S *phase volume in system* CaO-C_5A_3-C_2F-C_2S (*after Swayze*).

Systems With Magnesia

The system CaO-C_2S-C_5A_3-C_2F as modified by 5 percent of MgO has been explored by Swayze [27], who showed that the compositions of the invariant points move in the direction of higher A/F ratio to such an extent that the plane through C_3S, C_2S and the limiting iron phase solid solution passes on the high Fe_2O_3 side of these points (in contrast to the situation in the unmodified quaternary). Since the same uncertainty as to tie lines remains in this case, all that need be noted at present is that in the presence of MgO the iron phase will be more likely to be of higher A/F ratio and of fixed composition.

Some recent work in the ternary system CaO-MgO-Al_2O_3 by Welch [30] should be mentioned, since, although it is of more interest in connection with high alumina cement, the new compounds discovered do affect the triangulation of the system. A ternary compound C_3A_2M has been found with a very small phase field in the system. It melts incongruently to form first MgO, CA and liquid, and then MgO and liquid. Invariant points are approximately as follows:

Equilibrium phases	CaO	Al_2O_3	MgO	Temperature	Type
				°C	
CA, $C_{12}A_7$, C_3A_2M, liq	44	51	5	1344. 5	Eutectic
MgO, $C_{12}A_7$, C_3A_2M, liq	44	50	6	1346	Eutectic
MgO, CA, C_3A_2M, liq	43	51	6	1350. 5	Reaction point

Another new compound, C_7A_5M, is itself stable only below the lowest solidus temperature in the ternary system. It forms a series of solid solutions with gehlenite within the quaternary CaO-MgO-Al_2O_3-SiO_2; with increasing gehlenite content, incongruent melting is first established, to be followed by a range of congruent melting extending towards gehlenite. The "unstable C_5A_3" compound of high alumina cement tentatively identified by Parker as C_6A_4MS [31] is almost certainly associated with compositions in the C_2AS-C_7A_5M solid solution series.

The join from C_2S towards merwinite, C_3MS_2, has been studied by Gutt [33]. As merwinite is added to C_2S, the liquidus temperature falls slowly; below the liquidus separate fields of existence are found for α'-C_2S and merwinite.

Liquidus temperatures in the system CaO-MgO-Al_2O_3-SiO_2 have been studied by Osborn, de Vries, Gee, and Kraner [34] and by Prince [35]. Phase equilibria, especially in the high alumina part of the system, have been reviewed and amplified by de Vries and Osborn [36].

Alkali Systems

The systems CaO-Na_2O-Al_2O_3 and CaO-K_2O-Al_2O_3 have been studied by Brownmiller and Bogue [37] and Brownmiller [38] respectively. In the high CaO portions of interest in cement chemistry the systems differ in that no potassium compound analogous to C_8NA_3 was found. The synthesis of the potassium compound was however recently reported by Suzukawa [39]. Whereas C_8NA_3 has a smaller unit cell than C_3A, C_8KA_3 has a larger. It seems possible that a small amount of SiO_2 is necessary for the formation of C_8KA_3.

The same author has reinvestigated the compound $KC_{23}S_{12}$ and confirms the view of the present author that it is α'-C_2S stabilized by K_2O.

Thilo and Funk [40] have investigated the effect of small amounts of sodium and potassium on the stabilization of C_2S. They find that even the small amount of alkali absorbed from the furnace atmosphere can markedly affect the polymorphism of this compound.

The systems K_2O-Al_2O_3-SiO_2 and Na_2O-Al_2O_3-SiO_2 have recently been investigated by Schairer and Bowen [41, 42].

In Eubank's study of the quinary system Na_2O-CaO-Al_2O_3-Fe_2O_3-SiO_2 the quinary invariant point was located and found to be at 1,310 °C [43]. No estimate of the composition of the iron phase in equilibrium at this temperature was made. It was thought that the addition of MgO to the system would have lowered the temperature of first liquid formation to about 1,275°.

Systems of Minor Components

Phosphate as a small amount of P_2O_5 is present in the analysis of most portland cements, but in recent years has become of greater interest because of the exploitation of difficult limestone deposits, or the desire to use various trade wastes as raw material in cement manufacture. The effect of phosphate in portland cement has recently been reviewed by Steinour [44] who concluded that the rules put forward by Nurse [45] are a sufficiently accurate guide to practice. Nurse showed that the major part of the P_2O_5 is combined in solid solution with the C_2S, and that as a consequence the amount of C_3S is markedly reduced. Nurse, Welch, and Gutt have since published the phase diagram of the system C_2S-C_3P [46], showing a series of solid solutions between α-C_2S and a new high temperature form of C_3P isomorphous with α-C_2S. At subliquidus temperatures two compounds are formed, but are not likely to be met with in cement compositions.

The system CaO-C_2S-C_3P has been further studied by Gutt [33] who has explored the liquidus surface covering the temperature range 1,640 to 2,150 °C and has established the primary crystallization fields of the phases present which include C_3S. The field of C_3S extends to about 13 percent P_2O_5. Work is continuing to determine the compatibility triangles and suggests at the time of writing that a small amount of C_3P is soluble in C_3S.

In the system CaO-Al_2O_3-P_2O_5 a mixture of C_3P and C_3A appears to decompose forming C_4P, C_3A, and C_5A_3 [47]. The high lime portions of the system were not explored by Stone, Egan, and Lehr [48] but they do indicate their belief that C_3P and C_3A can exist in equilibrium together.

Fluorides are occasionally found as impurities in limestone. They may also be added deliberately as a flux or whitening agent or to offset the deleterious effect of P_2O_5.

Eitel's original studies on the systems CaO-CaF_2-$2CaO{\cdot}SiO_2$ and CaO-CaF_2-$5CaO{\cdot}3Al_2O_3$ showed that in the former there was no field for C_3S and in the latter none for C_3A. Later evidence however suggests that both C_3S and C_3A can exist in the presence of small amounts of calcium fluoride [16]. The system CaO-CaF_2-$CaO{\cdot}SiO_2$ includes a field for cuspidine, $3CaO{\cdot}2SiO_2{\cdot}CaF_2$. Cuspidine decomposes at 1,450 °C into CaF_2 and $2CaO{\cdot}SiO_2$ [49]. Toropov, Volkonskii, and Sadkov [50] confirm that C_3A is decomposed by 5 percent of calcium fluoride and show the same effect with 5 percent of sodium or potassium fluoride. When members of the ferrite solid solution series are acted upon by calcium fluoride, they decompose into $C_{12}A_7$ and a ferrite near to $6CaO{\cdot}Al_2O_3{\cdot}2Fe_2O_3$ in composition [51].

In a study of the system of reciprocal salt pairs SiF_4-SiO_2-CaO-CaF_2, the region of two liquids formation was delineated; it does not reach to probable cement compositions [52].

Experimental Studies on Individual Clinker Components

Alite

There have been several studies on the C_3S—alite relationship, but none have yet been extensive enough or sufficiently precisely controlled to establish the phase field of alite in the cement system. It can now be shown that at least one reflection due to C_3A appears in diffractometer traces of both the single crystals of alite used by Jeffery and the synthetic powder preparation $C_{54}S_{16}AM$. It appears likely therefore that the alite structure can be formed with a deficiency of Al. Another possibility is that there is slow unmixing of C_3A at low or even room temperatures. In early studies on alite the solubility of C_3A in C_3S was given as 6 to 7 percent at 1,400 °C; Naito, Ono, and Iiyama [53] report the maximum substitution of Mg and Al in the series $(Ca_{1-x-y}Mg_xAl_y)_3(Si_{1-3y}Al_{3y})O_5$ to be $x=0.025$ and $y=0.0075$, but do not state the variation with temperature; and Yamaguchi, Ikegami, Shirasuka, and Amano give details of alite containing either MgO or calcium fluoride [16]. Alite containing CaF_2 in solid solution has also been studied at the Building Research Station, and small scale strength testing on the product shows that the strength is greatly inferior to that of pure C_3S.

It is by no means obvious whether, in the work done so far on the range of composition of alite, a sufficiently clear distinction has been drawn between lattice changes in the triclinic structure of pure C_3S brought about by solid solution and the assumed transformation, triclinic $C_3S \rightleftharpoons$ monoclinic C_3S (alite). No synthetic work at all has been done on the further transformation monoclinic $\rightleftharpoons$ trigonal. Existing methods of X-ray diffraction at high temperatures would not discriminate between the three suggested forms. Films taken at 1,500 °C by Trömel for the present author show no difference in structure as compared with room temperature. Volkonskii [54] however reports an inversion in pure C_3S at 1,375°, giving an α-C_3S with d-values at 2.94, 2.78, 2.32, 2.00, and 1.47 A. Tröjer also has distinguished two forms of C_3S in the microscopic examination of clinker [55].

The practical significance of this question is of course the question of reactivity towards water. It appears possible that the reactivity may depend more on the nature of the substances in solid solution than on their effect on the crystal structure (which in any case is slight). There is some evidence too of the part played by physical characteristics. Jander [56] has stated that the reactivity of C_3S depends on (1) substances in solid solution, (2) structural defects, (3) cracks and irregularities of colloidal dimensions. Grzymek [57] believes that small and elongated crystals of alite can hydrate more rapidly, even if ground to the same specific surface as larger and more equant crystals. Both of these theories could account for the frequent observation that the strength obtained from a cement is not always a function of its C_3S content.

Dicalcium Silicate

Investigations on the polymorphism of C_2S have been very numerous, but most of them would more appropriately be discussed under the heading of "Structure." Metzger [58] has observed small quantities of α'-C_2S in cement, and it seems probable that under unusual conditions of composition such as high K_2O, or P_2O_5, combined with quick cooling, larger quantities of α' will be formed. Azelitskaya [59] finds that the strength is lowered as a consequence.

There is still some confusion as to the hydraulic properties of the forms of C_2S. At the Building Research Station we find that γ is almost inert, β hydrates at a rate depending on the kind of stabilizer, α' gives very poor strength, and α is nonhydraulic. In stabilizing α' and α, increasing quantities of $3CaO{\cdot}P_2O_5$ were used. Budnikov and Azelitskaya [60] however declare that γ-C_2S has hydraulic properties.

The evidence given by Nurse [61] to show that the strength obtained from β-C_2S depends on the nature of the stabilizer has been extended by Kukolev and Melnik [62]. The same authors show that a mixture of BaO, P_2O_5, and B_2O_3, which gave the best result in experiments with C_2S alone, is also effective in increasing the strength of a cement, provided the potential composition is high in C_2S [63].

Ferrite Phase

The ferrite phase has been studied by Midgley [64, 65, 66]; Cirilli and Brisi [67, 68]; Santarelli, Padilla and Bucchi [69]; Fratini [70]; and Fratini and Turriziani [71]. Yamaguchi and Kato [72] agree with Midgley that because of zoning effects the X-ray reflections from the ferrite are not always sharp. Sanada, Miyazawa, and Tazawa [73] quote the solubility of MgO in C_4AF as 1.5 percent and in C_2F less than 1.0 percent. Fratini uses a chemical method and Midgley magnetic separation in order to concentrate the ferrite before X-ray examination. According to Royak [74] Na_2O can enter into solid solution with C_4AF.

Tricalcium Aluminate

Tricalcium aluminate has been observed zoned by Tröjer [55]. As previously mentioned, the two alkali compounds, C_8KA_3 and C_8NA_3 will be recorded as C_3A in X-ray examinations, as will any C_3F which may be formed. No estimate of the kind of solid solution present in C_3A can be made from the *d*-values of lines which are visible in clinker X-ray diagrams. As will be shown later, it is important in quantitative work to realize that the spacings are slightly variable. Muller-Hesse and Schwiete [75] give the solubility of MgO in C_3A as 2.5 percent.

The only effects observed on heating C_3A to 1,500°C in the high temperature X-ray camera were caused by thermal expansion [54].

The Direct Determination of Constitution

Microscopy

The results obtained up to 1948 by the direct microscopic estimation of compound content have been reviewed by Lea [2]. He concluded that in general, measured C_3S contents were higher than as calculated from the Bogue formula, and those for C_2S were lower, especially for high A/F ratios. The measured C_3A and C_4AF contents are lower. Quick cooling tends to eliminate MgO; commercial clinkers are in general cooled fast enough to be intermediate between the quenched and fully crystalline conditions.

Some of the more recent papers on microscopy of cement clinker have drawn particular attention to the inhomogeneity of clinker, caused by insufficient grinding of the raw meal, by the taking up of fuel ash, and by the blending of clinkers from different periods of production or from different kilns. Tröjer [55] finds C_3S to be lower than calculated and C_2S higher, and ascribes this to coarseness of the raw meal. Schwarz [76] makes only qualitative microscopic observations, but points out the poor correlation between calculation and observation, especially with regard to glass content. In a detailed study Alègre and Terrier [77] finally conclude that for properly burnt clinker the agreement between microscopic observation of C_3S, C_2S, and interstitial matter and the Bogue calculation of C_3S, C_2S, and (C_3A+C_4AF) is very good.

Broadly it may be stated that the conclusions drawn by Lea are still valid. Many authors point out the seriousness of discrepancies in estimates of C_3A, having regard to the importance of this constituent in determining resistance to chemical attack.

X-ray Diffraction

The apparatus and technique of X-ray diffraction have been developed considerably since the early studies of Brownmiller and Bogue. It is universally agreed that for quantitative work diffractometry is essential, but photographic methods have also been greatly improved and at least one recent quantitative study [78] has employed photographic methods. Using an internal standard of NaCl and a Guinier type camera and measuring intensities by means of a photodensitometer, von Euw claims the following standard errors: alite ±2 to 3 percent, C_4AF ±1 to 1.5 percent, C_3A ±0.5 percent, C_2S ±6 to 9 percent. The author states that in general results are obtained close to those calculated from chemical analyses, but draws attention to the discrepancy with regard to C_3A. He does not consider the complications introduced by the variable composition of the ferrite phase.

H. G. Midgley [64, 65, 66] has used powder methods to determine the composition of the ferrite phase. He finds a range from about C_6A_2F to C_6AF_2 with a median composition a little higher in C_2F than C_4AF.

A chemical method was employed by Fratini and Turriziani for separating the ferrite phase from cement before X-ray examination using a diffractometer. Although unwilling to draw firm conclusions, they pointed out that although the ratio of A/F in their cements varied from 0.98 to 2.90, the A/F ratio in the ferrite phase never exceeded 1.0.

The most comprehensive study to date is that of Copeland, Brunauer, Kantro, Schulz, and Weise [79]. They employed a North American Phillips Geiger counter diffractometer with Cu $K\alpha$ radiation, in an attempt to measure directly the percentages of the phases present in portland cement. Unfortunately they were forced in the long run to rely also on chemical data.

As an internal standard they used metallic silicon or potassium bromide, intimately mixed with the cement or clinker sample by pulverization in a vibratory ballmill. The difficulties they had to overcome included:

(1) The existence of C_3S in clinker as alite, including in its composition some MgO and Al_2O_3.
(2) The presence of stabilizers (concluded to be principally MgO and Al_2O_3) in C_2S.
(3) The overlapping of the most important lines in the C_3S and C_2S patterns.
(4) The variable composition of the ferrite phase.
(5) The partial overlapping of ferrite and C_3A lines.

These difficulties were dealt with by a method of calibration using synthetic mixtures of alite and β-C_2S in one case and ferrite and C_3A together with alite and C_2S in another. These mixtures were made up from the oxides and burnt to equilibrium. They were not mechanical mixtures of the individual constituents. In order to separate overlapping peaks an empirical relationship was deduced to correct for the error in C_3A caused by the ferrite peak. Before planimetering, the peaks were separated by a geometrical construction based on the symmetry of the C_3A line at 2.71 A. The composition of the ferrite phase was obtained either directly from the *d*-spacing of the 200 reflection as described by Midgley or by including in their final calculations (which were done with the aid of a computer) a determined relationship between the A/(A+F) ratio of the ferrite phase and the *d*-value. An apparent discrepancy between Midgley's data and that of American authors is caused by a drafting error on Midgley's figure (1) (reference 65) in which the left-hand ordinate should be lowered by one division (i.e., the 200 spacing for C_4AF should read 2.64).

One method the American authors used for computing the A/F ratio of the ferrite phase and the absolute contents of ferrite and C_3A in the clinker was independent of a knowledge of the chemical analysis of the clinker. A second method for obtaining the same data however required a knowledge of the Fe_2O_3 content. The alite and C_2S contents were computed by two methods, one involving a knowledge of the CaO and the other of the SiO_2 content of the original cement or clinker.

Agreement between the different methods was quite good in regard to the content of constituents; there were rather larger discrepancies between the two methods of estimating the A/F ratio of the ferrite phase.

Comparing the results obtained by diffractometry with the potential phase composition, Copeland, Brunauer, Kantro, Schulz, and Weise conclude that the median value for the molar ratio of A/F in the ferrite phase is about 1.0 and that therefore agreement with a calculation which assumes the ferrite is C_4AF should be good, provided complete crystallization has taken place. In fact the average difference between the two estimates of ferrite content was only 0.7 percent and the maximum difference 2.2 percent. For C_3A the comparison was not considered satisfactory, the determined value being lower than calculated. In part this was ascribed to the Al_2O_3 in solid solution in the silicates. For alite the mean difference between the X-ray results and calculation was negligible, although the average absolute difference between the two sets was 3.6 percent. A similar average difference was noted for C_2S, but in this case the X-ray value almost consistently exceeded the calculated value. The authors also compare their results with earlier microscopic examination of the same cements.

A Phillips counter diffractometer has also been employed at the Building Research Station to determine cement constitution. A fuller account of this work will be given in a supplementary paper [82]. Briefly, the experimental methods employed give a somewhat better resolution of the X-ray spectra than was obtained in the foregoing investigation, permitting a much simpler approach to the problem.

The radiation used was CuKα and the specimen with its KBr internal standard was milled in a vibratory rod mill to less than 5μ, as checked by microscopic examination. The composition of the ferrite phase was measured on an X-ray photograph of the magnetic fraction, using the 202 spacing. A check was made on the position of the 200 peak on the diffractometer trace. Standard calibration curves for the peaks used in measurement were prepared from mechanical mixtures of alite (Jeffery's composition, found to contain a small amount of excess C_3A), β-C_2S stabilized with B_2O_3, C_3A and various ferrites.

Where peaks overlapped, either in the calibrating runs or in the trace from a cement, it was generally possible to allow geometrically for the error involved. The peaks were assumed to be symmetrical and were drawn in, referring when necessary to the nearest peak of the same size on the calibration chart for the same constituent. Alite was estimated directly from the peak at about 29½° 2θ and β-C_2S from that at 31°. An indirect estimate of these two components was also available from the combined intensities at 32½° and 34½°. When the two independent estimates of alite and C_2S differed, the cause was investigated and the error was usually found to be due to the presence of calcium carbonate or hydrated substances. An important difference from the American method in estimating C_3A was that the 2.71 A peak of pure C_3A was found to wander over a range in various cements; the smoothing of the peak was therefore done on the trace as found and not around a hypothetical 2.71 A maximum.

Three runs were made on each cement using a newly made specimen each time, and three independent measurements of peak areas were made. As an illustration of the accuracy obtained, the following standard deviations were obtained on a typical cement; alite 60±4 percent, C_2S 18±5 percent, C_3A 11±1 percent, ferrite 6.5±2 percent.

Particularly for low A/F cements, the C_3A tended to be higher than as calculated from the Bogue formula, the reverse of the results found by the American workers.

Assessment of Results and of Future Needs

Even the earliest workers in the field of portland cement constitution arrived at a fairly accurate assessment; namely that four mineral constituents C_3S, C_2S, C_3A, and C_4AF, with possibly some glass, constitute the major part of cement and that the relative amounts of these govern such properties as strength and durability. Since that time the emphasis in research has been to try to replace tedious and inaccurate microscopic examination by sets of rules, deduced with the aid of the phase rule, connecting constitution with bulk chemical composition.

More recent work, some of which is summarized in the foregoing sections, has tended to challenge the basic assumptions on which this approach is founded. In the first place it has been shown that the four constituents enter into solid solutions, not only between each other but also with the minor constituents or impurities of the cement. For the ferrite phase the range of composition is considerable, and the relative success of the earlier estimates of constitution must be explained by the fact that the average composition turns out to be very near to C_4AF. Secondly, calculations based on the phase rule must necessarily start with the assumption that equilibrium is obtained at clinkering temperature and maintained thereafter. This conception has been challenged for some time and has led to modified versions of the Bogue calculation such as those of Lea and Parker or Dahl.

At the present stage improvements in microscopic technique and the development of X-ray diffractometry offer hope of more exact direct determination of constitution. For control and specification purposes, however, it will always be desirable to avoid as far as possible determinations requiring expensive apparatus and highly skilled operators.

A further difficulty appears with the suggestion that the properties which the various constituents confer on the cement as a whole may vary with the detailed nature of those constituents.

It seems that both C_3S and C_2S exist in definite polymorphic forms in cement, but may be stabilized by varying amounts of varying kinds of impurity. There is good evidence that these stabilizers affect the cementing power of C_2S and some evidence that this is the case with C_3S also. It has also been shown that crystal habit and size may affect the reactivity of the anhydrous components.

The regulation of the tricalcium aluminate content of cement is now considered vital in producing sulfate-resisting portland cement. For specification purposes it is highly desirable that the accuracy of predicting or determining C_3A content should be improved. Unfortunately the discrepancies between different methods of estimation are greater for C_3A than for other components. The question of C_3A is linked closely with that of the ferrite phase, and this has led to methods involving either (a) some arbitrary assumption of a composition for the ferrite phase or (b) an independent determination of the ferrite composition.

Using Midgley's method for obtaining the composition of the ferrite phase, the compound composition can be worked out using the same principles as for the Bogue method, but first calculating all Fe_2O_3 as C_2F. From the experimentally determined ratio of C_2F/C_2A in the ferrite phase the total quantity of ferrite can be found, and also the CaO and Al_2O_3 combined as ferrite. The rest of the calculation then follows Bogue. In this way estimates of C_3A have been obtained at the Building Research Station more in agreement with the results of diffractometry (table 1).

TABLE 1.—*Data of H. G. Midgley comparing Bogue (B), modified Bogue (M.B., see text) and diffractometer estimates of* C_3A *and ferrite contents*

Sample		540	539	AS	AF	A40
C_3A	B.	0.9	0.7	15.4	2.5	9.9
	M.B.	3.4	3.0	13.6	2.3	13.3
	Diff.	4.5	4.8	13.5	3.7	11.5
Ferrite	B.	19.3	18.8	10.2	18.0	9.2
	M.B.	17.4	16.9	12.2	18.3	7.9
	Diff.	16.5	17.5	10.5	17.5	8.5

The list of phase assemblages previously given shows that cements containing C_3S and C_2S should either crystallize ferrite of the composition at the invariant point or of the same A/F ratio as the clinker. While relatively few results have yet been published, it is clear that in practice the A/F ratio of the ferrite phase is not simply related to the A/F ratio of the cement and that the distribution of A/F ratio is not that expected. (See for instance the histogram given by Midgley [65].)

This fact needs to be considered in conjunction with the observation that C_3A is found in contact with ferrites of A/F ratios lower than that of C_6AF_2. Cirilli and Brisi [67, 68] with laboratory clinkers found that C_3A disappeared at A/F=1.0 when MgO was absent and at A/F=1.2 when MgO was present. The evidence therefore seems to point to lack of equilibrium as an explanation of the facts. Astreeva [80] states that the composition of the ferrite phase depends on rate of cooling, a slowly cooled clinker having *lower* C_3A because more aluminate is dissoved in the aluminoferrite phase.

Consideration of the cooling conditions brings us to the question of glass. It is here that the results of X-ray methods conflict most with the older assumptions. Glass in quantity should be detectable by X-ray methods either by the increase of diffuse scattering in certain bands or by low totals for the other constituents. On either count, the indication is that the glass content must be very low. Devitrified glass might well give an X-ray pattern when optical examination fails to resolve any structure. It is possible that the heat content of such a finely crystalline mass might be appreciably higher than that of material in the fully crystalline condition and would give anomalous values for glass determined by heat of solution methods.

The independent crystallization of glass has of course been considered earlier by Lea and Parker. If the liquid from which the glass was formed were in equilibrium with the solid phases, the iron compound formed would however be in equilibrium with $C_{12}A_7$ and therefore of a high A/F ratio.

It seems that more consideration needs to be given to a suggestion of Swayze. He showed [27] that the crystallization of liquids saturated with regard to CaO would differ from that of liquids in equilibrium with C_3S and C_2S. Saturation with CaO could arise because of oversaturation of the cement composition with regard to CaO, or because there had been insufficient time for all free CaO to be completely reacted. Swayze showed that such liquids would crystallize to give some C_3A and an iron phase lower in A/F ratio than C_4AF. Such a theory seems to fit the facts as yet available very closely.

This review has been written at a time when X-ray diffractometry is only just being applied to the problem of cement constitution. It offers great possibilities but as yet results are scanty and in some respects contradictory. It seems clear however that greater attention must be paid to the question of homogeneity and equilibrium in clinker. The microscopic method necessarily reveals these defects if enough samples are examined, while the careful blending of specimen and standardizing substance required in diffractometry conceals them. Hitherto we have thought of lack of equilibrium in terms of the attainment of equilibrium at the clinkering temperature and departure therefrom during cooling. Swayze's work and the results of X-ray determination of the ferrite phase reveal the importance of the fact that in most clinkers equilibrium has never been attained.

I would like to conclude by offering for discussion certain problems and methods of study.

(1) Obtaining more data on constitution and the possible errors involved in computing it

It would be desirable to organize the exchange between cooperating laboratories of one or two carefully taken samples of clinker from each country. The clinker should be sampled from the kiln discharge so that no blending of clinker representing differing kiln conditions takes place. Each laboratory would examine the clinkers by whatever methods they choose to employ and circulate the results to the other laboratories.

(2) More research on minor components and solid solutions

I have indicated in this paper how small amounts of oxides such as P_2O_5, K_2O, BaO, and fluorides such as CaF_2 can influence cement properties. Many other minor constituents have not yet been considered. Important among these are sulphur as SO_3 and sulphide, and FeO. The interaction between SO_3 and alkalies has been adequately studied [81], but there is evidence that not only does SO_3 go into solid solution with the silicates, but it strongly influences the solubility of other groups at the same time. The method of X-ray absorption microanalysis seems promising for work of this kind.

(3) Experiments in the heat treatment of clinker

If the explanation given for the unexpected results on the C_3A and ferrite content of clinker is correct, then it should be possible by the laboratory heat treatment of both real and synthetic clinkers to bring about true equilibrium, and a more "normal" distribution of the interstitial phases.

These subjects are by no means academic ones. As Swayze has already pointed out, many specifications contain restrictions on the A/F ratio which are no longer realistic. The current demand for cements of low C_3A content makes consideration of this question urgent. At the moment C_3A is regulated in specifications by the Bogue calculation. Can a better method be found? Let us hope that these questions will find an answer by the time of the next Symposium.

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Discussion

N. Yannaquis and A. Guinier

The following contribution is of interest in connection with the problem of the stability of dicalcium silicate.

It was established [1] [1] in 1955 that dicalcium silicate prepared synthetically from products of analytical purity may be obtained in its β-modification without a trace of γ, and will be indefinitely stable; the synthesis is accomplished by repeated heating in the range of α' stability (for example, 1,100 to 1,200 °C).

We have, on one hand, confirmed that the pure β-modification is not due to an excess of CaO in the solid solution, because one obtains without difficulty the γ-modification containing 0.5 percent of this oxide; on the other hand, we established that impurities such as Na$_2$O and K$_2$O, normally present in the initial products, have no effect on the β-γ inversion [2, 3]. The study of powder diagrams of the α', α, β and γ forms, obtained at temperatures at which these forms are stable, carried out either on Geiger-Müller counter diffractometer recordings or through microphotometry on photographic diffraction patterns, reveals a decisive effect of the fineness of the crystalline grains as a stability factor.

The α' phase always becomes transformed during cooling into the β phase at 675 to 650 °C. If the β grains are smaller than a certain critical size of the order of $(5\mu)^3$, the probability that such a grain contains a γ nucleus is very slight; thus the metastable phase can be preserved at ordinary temperature. On the other hand, when the grains are large (for example, $>(30\mu)^3$), a nucleus of γ is always present in the grain and grows as the temperature decreases sufficiently below the point of the α'-β inversion, producing a transformation of the entire β grain into γ. Among the experimental facts which confirm this interpretation, the most outstanding is the following: two identical specimens of β-dicalcium silicate are brought to a temperature definitely above the point of the α'-α inversion (about 1,460 °C), such as 1,550 °C; one of these is quickly quenched while the other is permitted to cool slowly to below the point of this inversion, or 1,400 °C for example, before it too is quenched in the same manner. In the first case one obtains 90 percent β-C$_2$S; in the second 95 percent γ-C$_2$S. In the first case the α' crystals, not having had time to grow, have yielded the β modification consisting of small crystals which have remained stable, while in the second case the α' crystals have had time to grow during the α-α' inversion, so that—in spite of quenching—the β-γ inversion is almost complete.

The nature of the stability of the β modification can now be defined more precisely, thanks to the results of a recent investigation based on the effect

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[1] Figures in brackets indicate the literature references at the end of this paper.

of pressure on the β-γ inversion. Pellets of β-C_2S powder agglomerated into disks with a thickness of 2 mm were subjected to percussion (drop of a mass corresponding to the energy of several tens of kilogram-meters) or to crushing between the platens of a hydraulic press operating with a maximum pressure of 10,000 kg/cm^2. We have observed that under these conditions it is possible to produce a partial β-γ inversion in the cold.

Percussion (shocks, blows), producing work of about 40-kg-m on a pellet of uniform density, results in a transformation at a low rate, which can attain 30 percent if the percussion is repeated several times. The proportion of β transformed by crushing in a hydraulic press is an increasing function, especially of the pressure, of the number of cycles of pulverization-compression, and of the fineness of the crystalline grains. It increases very fast as a function of the duration of applied load during the first 10 min and only slightly beyond this time; it is independent of the rate of pressure increase. In contrast, if the β powder is subjected to *hydrostatic pressure* (in an oil-filled compression chamber) which can even be very high (9,600 kg/cm^2), no transformation is produced.

We have compared the effect of pressure on silicates of different compositions.

In the case of *pure silicate*, for a given granulometric range (of the order of 0.5 to 10 μ) and a given pressure, the maximum proportion of transformed crystals increases with the number of pressure applications, tending, however, towards a limit of the order of 50 percent; this limit decreases rapidly with the proportion of larger grains greater than the critical volume defined above, which is of the order of $(5\mu)^3$; if the largest grains remain above this figure, the proportion transformed drops to 25 percent.

In the case of silicates containing additions, the results permit us to define three types of behavior:

(1) Transformation as if *the addition had no effect*. This is the case of the oxides Na_2O and K_2O at a concentration of 0.3 percent.

(2) *No transformation*. This is the case with silicate synthesized with B_2O_3 (even only 0.5 percent), with natural silicate [4], and with belite in clinker. These different products have a crystalline lattice which is different from that of pure β-silicate or the silicates mentioned in the preceding paragraph. The displacements of the lines, measured on Debye-Scherrer diagrams are very weak, but measurable. The lattice has a monoclinic cell which is slightly different from that of β. It should be noted that the D.-S. diagrams of β-C_2S + 0.5 percent B_2O_3 and of larnite show the same modifications and that that of belite is similar to the diagram of β-C_2S + 2 percent B_2O_3.

(3) Transformation *in greater proportion than* for pure silicate. This is the effect of an addition of 1 percent of P_2O_5 in the form of $CaNaPO_4$ [6]. The product obtained with this admixture, the D.-S. diagram of which does not differ from that of the pure silicate, becomes transformed to the extent of 85 percent.

Numerous examples are known of allotropic transformations produced by compression of the unstable phase. Thus Burns and Bredig [9] have observed the transformation of calcite into aragonite with prolonged grinding. In our case, the γ phase is less dense than the initial β phase. An increase in pressure can not favor this transformation, and this is exactly what we have observed in our experiments with hydrostatic pressure [10].

The transformation is actually produced by *deformation* of the crystal under the influence of the compression. The transition from the β to the more stable phase is always thermodynamically possible. But this transformation does not begin unless nuclei are present; these nuclei are formed during shearing of the crystal during the percussion or the crushing of the crystal in a press.

The effectiveness of compression in producing the transformation depends on a number of factors. First among these is the size of the powder grains. It is natural to think that the fine grains will have more chance to resist the pressure without shearing. Moreover, each nucleus which is produced in a small isolated grain can transform only this grain, thus only a very small volume.

Our experiments also shed light on the effect of so-called stabilizing admixtures. The only admixtures that have a stabilizing action are those which modify the lattice of pure silicate. Alkaline oxides that do not change the lattice have no effect, and the oxide P_2O_5 even favors the β-γ inversion. It seems that addition of phosphorus has the effect of making the β-crystals more deformable, a fact which would explain the higher proportion of transformed crystals. This idea is suggested by the observation that γ-crystals mixed with β-crystals before application of pressure, and initially rather coarse, are crushed and reduced into very small crystals following application of pressure. This does not happen with other silicates. One could imagine that—on the contrary—silicates with modified lattices (as by addition of B_2O_3, etc.) become less deformed, decreasing the number of possible sites for the nuclei, or that the formation of a nucleus is less easy in a modified lattice than in a lattice of pure silicate; indeed the two effects could be additive.

These different effects could be related to the modifications in the redistribution of interionic fields which are due to the introduction of anionic groups more electronegative, $(BO_4)^{5-}$, or less electronegative, $(PO_4)^{3-}$, than $(SiO_4)^{4-}$; or groups of different kinds such as $(AlO_4)^{5-}$ and $(FeO_4)^{5-}$, associated with cations having a more highly polarizing effect than Ca^{2+} or Mg^{2+}. This is the case of larnite, and possibly of belite in clinker [8].

The effect of B_2O_3 must also be due to the fact that the $(BO_4)^{5-}$ groups, being less voluminous but having a higher valence than $(SiO_4)^{4-}$, cause formation of vacancies through maintenance of electric neutrality in the lattice by elimination of Si^{4+} ions, probably in the form of silica. At 0.5 percent B_2O_3 we would have a missing Si for 160 molecules of C_2S, or for 40 unit cells of β; the existence of such vacancies is easier to accept than the insertion of supplementary Ca atoms into as compact a lattice as that of β.

A mechanism based on the same principle, but apparently more complex, could be responsible for the behavior of larnite which contains Al_2O_3, Fe_2O_3, and MgO [4]. Nevertheless, systematic studies are needed to reveal the various effects of cations and anions in variable concentrations.

Although industrial grinding is largely a percussion process, it is not improbable that shearing forces might be applied several times to a given crystal and might provoke a limited transformation in insufficiently homogeneous clinkers containing grains with an excess of silica or phosphorus.

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Discussion

A. J. Majumdar and Deane K. Smith

This discussion of Dr. Nurse's paper will be restricted mainly to brief descriptions of our recent work in the areas of polymorphism of dicalcium silicate, stability or metastability of pentacalcium trialuminate, and compositional variations in the iron phase crystallizing in the quaternary system C_2S—C_3S—C_3A—Fss. (Fss=calcium aluminoferrite solid solution.)

Polymorphism in Dicalcium Silicate

The presently accepted picture of the thermal transformations in the dicalcium silicate phase is due to Bredig [1950] and was reviewed by Nurse in the 1952 Symposium. An alternative interpretation of changes taking place when Ca_2SiO_4 is heated to and cooled from clinkering temperatures has been put forth by Toropov et al. [1957]. Figure 1 shows both interpretations. They differ significantly both in the sequence of appearance of phases and in the temperatures of the phase changes. In addition to suggesting a new phase, β', Toropov claims that the β phase has a stable field at atmospheric pressure.

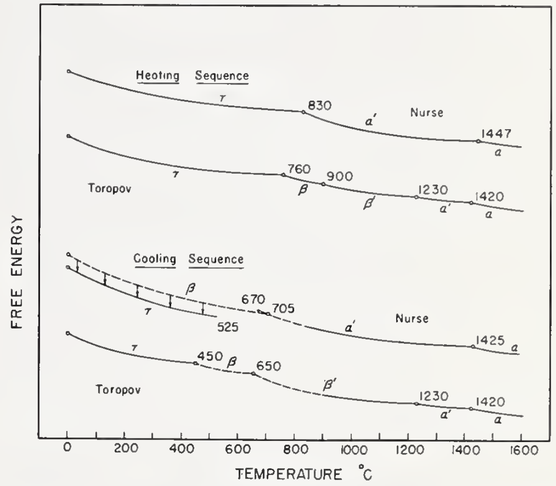

Figure 1. *Schematic free energy-temperature curves after Nurse (1952) and constructed from Toropov's (1957) data.*

The dashed portions on the cooling curves indicate regions where the phase is not the same as on heating.

In our recent paper (soon to be published in the Journal of the American Ceramic Society) we have neither confirmed the existence of Toropov's β' phase nor verified a stable field for the β modification. Instead, our work indicates that Bredig's diagram more nearly represents the true relations in this one-component system. If our interpretation of the dependence of the $\beta \rightarrow \gamma$ transformation on the thermal history of the sample is correct, the system is complicated by the presence of heretofore unreported metastable (?) phases as diagrammatically shown in figure 2.

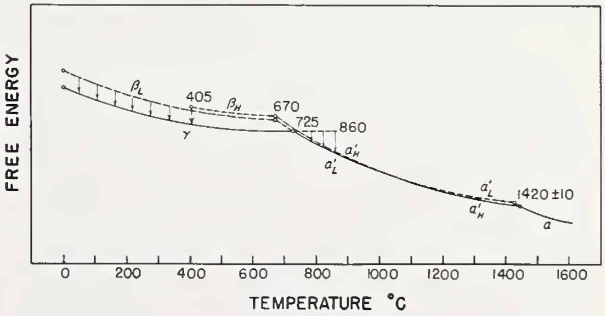

Figure 2. *Hypothetical schematic free energy-temperature curves for the phases of* Ca_2SiO_4.

Solid lines indicate stable phases; dashed lines, metastable phases.

We used samples of Ca_2SiO_4 prepared by three different methods; the $CaO:SiO_2$ ratio was very close to 2:1 in all samples. Some samples had additives up to 0.1 wt percent representing common impurities in clinkers. High-temperature powder diffractometry and differential thermal analysis were the principal techniques used in the investigation. The important results of this work are as follows:

(1) A critical heating temperature of 1,420 ± 10 °C was found which had a marked effect on the $\beta \rightarrow \gamma$ transformation on cooling. Samples cooled from above this temperature "dusted" and converted completely to the γ form, whereas samples cooled from below this temperature showed only partial conversion of β to the γ form and no dusting. Guinier and Yannaquis [1957, 1959] have observed that samples cooled from 1,500 °C produced the pure γ modification while samples cooled from 1,100 °C produced a mixture of β and γ forms. They suggested that growth of larger crystals at the higher temperatures resulted in an increase in lattice strain energy on cooling, thus promoting complete inversion to the room-temperature stable γ form. Our work indicates that, although grain-size effects may be present, they are minor for particles larger than 40μ, and the effect of thermal history on the completeness of $\beta \rightarrow \gamma$ inversion is much more complex.

The critical heating temperature of 1,420° coincides with the α'–α inversion temperature. Apparently if the α phase forms during the heating of a Ca_2SiO_4 sample, the room-temperature product is all in the γ form. The X-ray patterns of the α' phase formed on cooling from a Ca_2SiO_4 sample below 1,420° show slight differences when compared with the patterns of the α' phase formed on heating. Although these differences may be due to the shifting and growth of grains at the elevated temperature, structural differences may be indicated. The phase formed from α has been designated α'_H in figure 2. Yamaguchi [1957] has shown that the X-ray pattern of the β form can be completely indexed only if the a axis is multiplied by four and the c axis by three. Perhaps this superlattice is reflected in α'_H, although our high-temperature X-ray patterns have not been sharp enough to verify the hypothesis.

The β_H phase formed from α'_H–Ca_2SiO_4 likewise indicates some structural differences. If the $\beta_H \rightarrow \gamma$ transformation has a lower activation energy barrier than the $\beta_L \rightarrow \gamma$ inversion, the dependence of this transformation on the α–α' transformation can be explained.

(2) The sluggishness of the γ–α' inversion on heating does not appear to be due completely to reaction rates. A range of over 100 °C has been found where both forms appear to coexist. If a sample starting as all γ is heated to 725 °C, some α' appears in the first 15 min, but a 20-hr heat treatment does not promote continued conversion to α'. Even at a temperature of 850 °C extended heating does not increase the $\alpha':\gamma$ ratio over that formed in the first 15 min. These observations are contrary to the effects expected if the sluggishness of the transformation is due to slow reaction rates.

The presence of two phases of the same composition over a range of temperatures violates the phase rule unless the compositions shift slightly from the single-phase compositions. No evidence for a mixed-crystal phase in this region of coexistence was found in the X-ray patterns. The presence of impurities, which did not stabilize the β form, did not affect the β–γ transformation in any marked manner.

The "C_5A_3" Phase

We have attempted to establish the field of stability for the "C_5A_3" compound reported by Aruja [1957], but so far our experiments have not yielded any positive evidence for the existence of such a field. Five mixtures ranging in composition from 100 percent C_5A_3 to 100 percent $C_{12}A_7$ were prepared. The C_5A_3 and $C_{12}A_7$ starting mixes were synthesized by coprecipitating calculated amounts of $Al(OH)_3$ and $CaCO_3$ from solutions, followed by ignition at an elevated temperature. Chemical analysis shows 51.53 percent Al_2O_3 and 48.47 percent CaO for the $C_{12}A_7$ preparation (theoretical—51.47 percent Al_2O_3, 48.53 percent CaO) and 52.30 percent Al_2O_3 and 47.70 percent CaO for the C_5A_3 preparation (theoretical—52.17 percent Al_2O_3 and 47.83 percent CaO). Thus, the compositions of the mixtures correspond within experimental error to the desired values and are distinguishable as two separate compositions. Both X-ray and optical examination revealed the presence of a trace of CA in the C_5A_3 mixture whereas the $C_{12}A_7$ was found to be homogenous.

The mixtures were placed in platinum capsules which were then sealed and subsequently heated above 1,500 °C in a furnace. It was assumed that complete melting had taken place in all the samples at this temperature. The charges were then cooled slowly at a rate of 50 °C per day to 1,000 °C whence they were quenched. X-ray and optical examination of these quenched samples failed to show the presence of the "C_5A_3" compound of Aruja. Compositions other than $C_{12}A_7$ yielded CA in addition to the cubic $C_{12}A_7$, the former being more abundant in C_5A_3-rich mixtures. Therefore it does not seem likely that "C_5A_3" and $C_{12}A_7$ are compatible phases.

The experiments of Welch with the hot-wire apparatus as reported by Aruja have been recently repeated at the Fellowship Laboratory with success. There is very little doubt that a phase with the optical and X-ray diffraction characteristics almost identical with those of "C_5A_3" can be grown reproducibly following the procedures described by Aruja [1957]. In our experiments we have not yet succeeded in growing "C_5A_3" alone. In all our runs other crystalline phases, mainly CA and $C_{12}A_7$, were found to be present in conjunction with "C_5A_3" and glass. In addition we have not yet been able to grow this orthorhombic phase from the C_5A_3 composition. Thus, the phase relationships at or near the liquidus temperature also cannot be successfully explained on the basis of our present data.

The possibility that "orthorhombic C_5A_3" is a high-temperature modification of $C_{12}A_7$ has also been explored. Thermal analyses of $C_{12}A_7$ have not shown any evidence of change in heat content of the sample below its melting point. High-temperature powder diffraction has also failed to indicate that any rapid polymorphic inversion exists in $C_{12}A_7$ up to 1,375 °C. On the other hand, "C_5A_3" has been grown from a $C_{12}A_7$ melt. Thus the original assumption of Rankin and Wright [1915] that "C_5A_3" is a metastable phase seems to be supported by the recent work.

The Fss Phase

The most recent work on the composition of the Fss phase in quaternary equilibrium with C_2S, C_3S, and C_3A is due to Swayze [1946]. By directly estimating the proportions of the siliceous phases in the equilibrium four-phase assemblage, Swayze calculated the composition of the Fss phase using a knowledge of the chemical composition of the mixture investigated. This method, although theoretically valid, can yield only approximate results for two reasons. First, the accuracy of estimating the amount of a phase by microscopic method in the system under consideration is not too good. Second and more significant, the three phases, C_2S, C_3S, and C_3A, are not "pure" compounds but rather contain marked amounts of the other components in solid solution.

When one speaks of the compatibility tetrahedron as having C_2S, C_3S, C_3A, and C_4AF at the apices, one assumes that the compositions of the phases are stoichiometric. Actually the true tetrahedron has its corners displaced a significant amount from the hypothetical positions, and the question whether the invariant point is inside or outside the true tetrahedron requires not only locating the invariant point but locating the true apices as well. On the basis of their experimental data Lea and Parker [1934], in their classic study, were still uncertain about the location of the invariant point. It remains doubtful even today whether one has definitely established that the invariant point lies outside the tetrahedron of compatibility as stated by Nurse in the present Symposium paper. As a matter of fact, this question cannot be solved until precise data on the chemical compositions of the compatible phases at the invariant point are available; the presently accepted equations due to Dahl [1939] for calculating the amounts of potential compounds have to be modified in the light of the true compositions of "impure" compounds that make up the corners of the compatibility tetrahedron. The composition of the Fss phase at the invariant point can be definitely established only when compositions of the other phases coexisting with it are more accurately known.

The exact nature of the invariant point is important in any discussion of the paths of crystallization of a mixture from above the invariant point temperature. If the invariant point happens to be a eutectic, the compositions of the final products of crystallization below the invariant temperature will be identical, at each temperature, for all mixtures within the compatibility tetrahedron. If equilibrium is maintained throughout the cooling cycle, no phase would show zoning. In the crystallization of the ternary Fss phase, we have not detected any evidence of zoning, even in deliberate attempts to develop zoned crystals by rapid cooling from the melt. Zoning might occur in the quaternary system if the presence of silica increases the viscosity of the melt and appreciably affects the diffusion rates of the mobile ions. Evidence of zoning in the Fss phase in actual clinkers cannot be taken as positive proof for zoning occurring in a true four-component system. Aside from the presence of many minor impurities whose effects are not well established, a clinker rarely reaches equilibrium due to temperature inhomogeneiety in the kiln and compositional variations in the raw materials. These variations may account for the range of reported compositions for the Fss phase in clinkers.

If the invariant point is a peritectic, most mixtures having the proper bulk composition will complete crystallization at the invariant point under equilibrium conditions, and the final liquid to crystallize would have the composition of the invariant point. However, for some mixtures the liquid will be used up before the peritectic point is reached on cooling, and the Fss phase from such mixtures might show zoning because it would be different compositionally from the phase that would crystallize at the invariant point. Thus, it can be seen that the composition of the equilibrium Fss phase may depend on the nature of the invariant relationship in the system.

In the Fellowship Laboratory we are attempting to establish the unique compositions of the four compatible phases at one temperature below the liquidus. Seven quaternary mixtures were equilibrated at 1,275±5 °C for a period of 72 hr. The work is far from completion at this stage, but careful X-ray diffractometry measurements by interval counting at 1/50th of a degree 2θ indicate that in each sample the Fss phase has interplaner spacings almost identical to those of C_4AF. This identification agrees well with the observations of Copeland and coworkers [1959]. It is not yet established how much silica is dissolved in the Fss phase, but apparently not enough is taken into the structure to change the unit cell dimensions appreciably.

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Discussion

N. Yannaquis and A. Guinier

The interpretation of Majumdar and Smith rests entirely on the existence of two crystalline forms of α'-C_2S. As the authors, in their contribution, did not specify their experimental evidence, it is difficult to discuss their conclusions.

(1) We wish to make it known that we have sought long and carefully to show the existence of an abnormal form of the α' phase, and that we have finally had to admit that all the differences apparent in the diagrams obtained with the diffractometer could be explained by a variable granulometry *of a single crystalline phase*. The difficulty in the diffractometer study of the phases formed within the apparatus at high temperature results from the inability to give to the specimen the grain fineness indispensable for good registry. When the crystals are too large, it is known that the individual diffraction spots are never all aligned on the center of the line given by the fine powder. If the number of spots registered by the counter is small, the line observed may be displaced. In addition, the measured intensities are subject to fluctuations, considerable and not always erratic, if there is a preferential orientation of growth of the crystals. For this reason it is not possible to establish the existence on the diagram of an α' phase of slightly different structure.

We therefore believe that one must hold to the hypothesis, pointed out as well by the authors themselves, that the differences observed are due to the form of the grains. The correlation found between the aspect of the diagrams and the production of the β or the γ phase arises from the fact that the two phenomena are influenced by the same factor: the form of the grains of the α' phase.

(2) It is not exactly correct that when the silicate has been heated above the point of transformation $\alpha' \to \alpha$, the product obtained on cooling is *always* the γ phase. One can obtain the pure β phase if the silicate is quenched rather than slowly cooled.

(3) It is possible to index all the lines of the β phase [1] on the basis of a monoclinic lattice very close to that given by C. M. Midgley [2]. The difference between the values of d, calculated and observed, is at most a few thousandths of an angstrom unit.

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Discussion

Myron A. Swayze

The following remarks are on two sections of Dr. Nurse's excellent report: one concerning the influence of other clinker minerals on the composition of the series of aluminoferrite solid solutions; the other some practical suggestions to govern the selection of clinker samples for use by a group of laboratories in further studies of clinker constitution.

The 1959 report by Newkirk and Thwaite [1][1] on the ternary system $CaO—CA—C_2F$ and the 1946 report by Swayze [2] on the system $CaO—C_5A_3—C_2F$ differ in some details that concern the series of ferrite solid solutions. Where Swayze pictured this series as a single straight line running from C_2F to C_6A_2F, the Newkirk-Thwaite report considers the series to be a band of compositions including the compounds C_2F, C_6AF_2, and C_4AF, but on the low lime side of C_6A_2F and running beyond it towards $C_{12}A_7$ to an assumed point L, in relative agreement with previous reports by Yamauchi [3] and Malquori and Cirilli [4]. This assumed endpoint composition was not tested by Newkirk and Thwaite, nor is there any clear evidence that previous authors made similar checks of their assumed endpoints of their lines or bands. It is therefore interesting to note that while Newkirk and Thwaite found the composition C_6A_2F to contain C_3A in addition to the ferrite phase, Nurse in his present paper finds it to be a homogeneous compound.

The principal and serious difference between these two reports on the ternary system is in the location of the correct $CaO—C_3A—Fss$

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[1] Figures in brackets indicate the literature references at the end of this paper.

invariant point composition, and in the composition of the ferrite phase crystallizing at this point. Swayze reported an A/F ratio of 0.50 for the ferrite phase at this point, while Newkirk and Thwaite show an A/F ratio of 0.77. While to the operating cement chemist this difference may seem academic, it becomes of practical significance if the same alumina-iron oxide relations carry through into the more complex systems approaching commercial portland cement compositions. The only evidence we have [2] is that these conditions do prevail. Therefore this present inconsistency in available data on compositions in the ternary system should be resolved by a more careful and thorough study. Nurse's present remarks to the effect that crystallization of a ferrite phase with an A/F ratio of less than 0.64 in the presence of free CaO "seems to fit the facts as yet available very closely" indicate that such a restudy is badly needed. In this connection I would recommend that mixtures of raw materials be held down to a maximum of 1.5 g ignited basis and that homogeneity of the final mix preparations be checked thoroughly. Also, more reliance should be placed on petrographic and X-ray examinations of quenched burns at critical temperatures on closely spaced mixtures than on differential thermal analysis readings, which can show similar responses for several different compositions in small critical areas. This is brought out clearly by Toropov, in his paper on solid solutions of the clinker minerals [5].

It is evident that presence of free CaO as a primary phase in liquids of the ternary system shrinks the length of the ferrite line or band down to a range from 0.00 to 0.50 A/F ratios, or if preferred to the range from 0.00 to 0.77. It should be equally evident that in such a case the band of ferrite compositions will shrink to a line over these A/F ranges, since the low limed portions of the band should not be compatible with liquids saturated with CaO. Similarly, in the CaO-C_5A_3–C_2F–C_2S system, the full range of ferrite compositions is impossible, since the principal invariant points are outside the phase volume in which C_6A_2F is stable. The top limit on A/F ratio in this case appears to be about 0.85 when CaO is absent. The presence of solid C_3S in the cooling liquids of this system should again reduce the band of stable ferrite phases to a line, since C_3S is reduced to C_2S during cooling by liquids unsaturated with CaO. While the modification of this quaternary system with MgO shifts the principal invariant points towards the CaO-C_5A_3 boundary far enough to make C_6A_2F crystallization possible, it is still doubtful if a band of ferrite phases can exist in the presence of solid C_3S, or if the line of ferrite phases can extend past the composition C_6A_2F any appreciable distance. The further addition of alkali oxides to the system should make such an extension possible, although the band of ferrite phases would still be doubtful.

The other section in Nurse's report on which practical comment should be made concerns the selection of commercial clinker samples for tests on constitution by an international group of cooperating laboratories. Clinker composition from interior to exterior can be affected materially by contamination from coal ash on clinker surfaces which have come through the kiln in nodular form. It is therefore suggested that selection of these important samples should be limited to kilns using oil or gas for fuel.

Another point on selection of clinker samples is with regard to differences in the silica/(alumina + iron oxide) ratio that exist between large and small clinkers from the same lot. Our research laboratory has been aware of this for some years, although it has not been noted in the literature. This segregation is evidently due to the very low silica content of the clinker liquid and to differential rates of clinker cooling after leaving the burning zone of the kiln. Since small sized clinkers lose their temperature more rapidly to the relatively cool secondary combustion air on leaving the kiln hot zone, their liquid content shrinks during its crystallization and leaves solid C_3S crystals out in relief on the surface. This faster cooling of small clinkers permits them to have a blotting action on larger hot clinkers whose liquid is still at the surface due to slower cooling. The result is a reduction of the silica ratio in the fine clinkers and an increase of it in coarse clinker, due to this transfer of the low silica liquid. It should therefore be advisable in sampling clinker for this important research that all laboratories be supplied with the same size of clinkers, preferably in the intermediate range of diameters.

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Discussion

H.-G. Smolczyk

At the end of his excellent paper Dr. Nurse suggests that some laboratories in different countries should carry out X-ray investigations of the same clinkers. I am very optimistic and should like to add to this broadminded proposal another further suggestion to be put forward for consideration. In this discussion I also want to address all those who at the Symposium showed X-ray diagrams of any

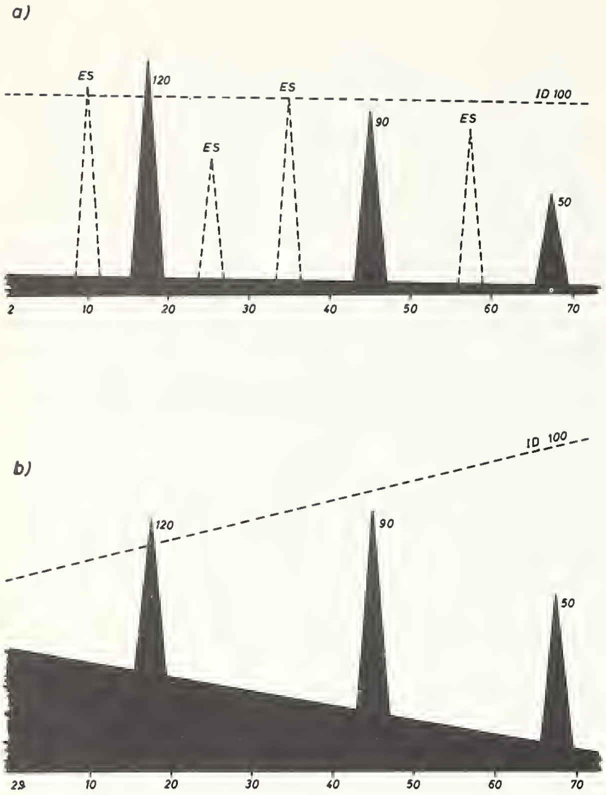

FIGURE 1. *Two examples of different intensity distribution (ID) in X-ray diagrams.*

kind. (As done by the workers of the Portland Cement Association, the Building Research Station, and by H. E. Schwiete, G. Malquori, H. zur Strassen, J. H. P. van Aardt, R. Turriziani, F. W. Locher, Y. Suzukawa, N. A. Toropov, and myself.)

Many of those diagrams were in perfect accordance with one another, others seemed to differ. Much trouble could be saved and many a misunderstanding could be avoided if we could compare qualitative X-ray diagrams or even rough sketches or X-ray intensity tables of different laboratories by a simple method and in a nearly quantitative way. But to this very moment we have not found a standardized reference system. The complicated method using internal standards would not serve this purpose, for it demands a different standard or a different concentration of the standard for every new case, and if for instance the complete diagram of a partly hydrated clinker is to be described, one single diagram with only one internal standard would be of no help.

Now I simply want to describe how, for about two years, we have tried to overcome this difficulty. Beforehand I want to say that at our institute two X-ray diffractometers are continuously busy producing diagrams of different minerals, slags, pastes, mortars, and concretes. Every time the X-ray tubes are changed or some repair is done, some new adjustment must be performed. But often we do not have the time to adjust both diffractometers so that afterwards they will show exactly the same intensities and the same intensity distributions. Especially in the course of long-time studies with fixed testing periods there has been little time available, and our adjusting procedure has then been limited to the exact peak position and to the maximum intensity of each of the diffractometers. To be able to compare each of the 6,000 diagrams already produced with all the others, in spite of all the above mentioned impediments, I have developed the following method:

Each peak height of a diagram is expressed as percentage of an "Intensity Distribution 100," that has been fixed experimentally. This "ID 100," is measured anew and in accordance with the entire diagram of an "External Standard" after every change made on the diffractometer. Afterwards this "ID 100" is subject only to daily investigations of one single peak.

Figure 1 shows one normal (a) and one much exaggerated (b) possibility for the "ID 100" and also a way in which one and the same diagram could possibly change. One can clearly see that in spite of the different looking patterns the relative intensities have maintained the same values. For our purposes we have fixed as "External Standard" the following peak heights of α-Al_2O_3:

h_1: (102), $d=3.479$ A, ES-Int.$=65.6$
h_2: (014), $d=2.552$ A, ES-Int.$=100.0$
h_3: (116), $d=1.601$ A, ES-Int.$=83.9$

This α-Al_2O_3 has some advantages that serve this special purpose: It can be ground for hours without any change of intensities. Its X-ray diagrams are absolutely reproducible. The intensities are not too high. It is insoluble. It is available everywhere. For clinker and quartz analysis α-Al_2O_3 can also be used as an internal standard.

The three peaks of the external standard are to be seen in figure 1a. The peak h_4 at 10° is of a silicate used to fix the low-angle region of "ID 100." (For this special section of the diagram another substance should be found to serve as "Low-Angle External Standard.")

To obtain the "ID 100" of a certain X-ray diffractometer with a certain adjustment, it is only necessary to take an X-ray diagram showing these 4 lines, multiply their heights by $\frac{100}{h_{1-4}}$ and connect these 4 points. Every diagram produced by this diffractometer can be expressed in percentage of this newly constructed "ID 100," and can easily be compared with diagrams obtained for instance a year earlier.

As long as the adjustment of the equipment has not changed, i.e., as long as the shape of the new "ID 100" has remained the same, for daily checking it is only necessary to measure the height of one peak out of the α-Al_2O_3 diagram. For this purpose we measure the peak at 35° three times a day.

If the chemical composition of the substance that has been recorded in such a way is known, the diagram can also be used for a quantitative determination by applying the well-known theoretical equation

$$x=\frac{I_x}{I_0}\cdot\frac{\mu_G}{\mu_x}$$

x=the amount of the mineral in the compound; I_0=the intensity of 100 percent of the mineral; μ_x= the mass absorption coefficient of the mineral; μ_G= the mass absorption coefficient of the entire compound,
or better with the exact equation of Leroux, Lennox, and Kay [1]

$$x=\frac{I_x}{I_0}\cdot\left(\frac{\mu_G}{\mu_x}\right)^{-c}$$

wherein the constant c has to be fixed experimentally.

Now my opinion is this:

I should appreciate very much if we could do something similar on an international basis. That is, if, after thorough consideration, we could come to an agreement on an "International Standard" with entirely fixed intensities as "ID 100," we could express all our diffractometer diagrams in percentage of this "ID 100," and we should be able to compare all our intensities, no matter where they came from.

I thank Dr. R. H. Bogue, Dr. S. Brunauer, Dr. L. E. Copeland, and Dr. D. L. Kantro for valuable discussions on this subject.

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Discussion

Levi S. Brown

It is said that superlatives have no place in science, or that science has no place for superlatives. Exception surely should be taken with respect to hot wire microscopy, referred to in this paper, and to which this discussion is limited.

The merit of the exception can be best appreciated by those experienced in investigations of high-temperature phase equilibrium. To give this some sort of quantitative expression, consider the ternary diagram of the lime-alumina-silica system. More than 15 years of intensive research went into the building of this diagram. The eventual comprehensive report notes that the investigation comprised ". . . some 7,000 heat treatments . . . ." Realization that each one takes up at least a half a day brings some concept of the enormity of the accomplishment.

But then some concept of the enormous facility that could be conferred by the hot wire microscope is gained by realization that with it the same investigation could have been carried out with one-seventh to one-tenth of the 7,000 heat treatments, and probably better. Each one could take care of 7 to 10 quenches, at the same time directly establishing critical or invariant temperatures, with less time lost in assurance of equilibrium conditions. These original investigators surely would have looked upon this apparatus as superlative.

Of course the hot wire microscope is not all-sufficient in itself. From the very nature of the application, close working distances and high magnifications are proscribed. In the mapping of a new system, detailed determination and description of specific optical properties of new compounds must be worked out by more orthodox petrographic methods.

That however becomes a relatively slight insufficiency in the realization that it only has to be done once. That serves to point up further the practical utility of the instrument in present day industrial technology or control, in many and varied high temperature processes, as in glass making, and smelting operations. The capabilities and facilities offered are great.

Discussion

Rustum Roy

Dr. Nurse in his paper mentioned very briefly the new techniques which have been brought to bear on some of the problems of the structure of the individual clinker components. This discussion reports some of our work with high-temperature diffractometry, hydrothermal catalysis, and very high uniaxial pressures. In spite of the application of these and other new tools the understanding of the polymorphism of dicalcium silicate still leaves much to be desired.

The $\beta\rightleftharpoons\alpha'$ *Transition.* The *relative* ease of reversibility of this transition has been known from differential-thermal-analysis data for a long time. However, such data do not indicate much about the actual sequence of reaction, nor of the extent of conversion. In the high-temperature X-ray study by D. Roy [1],[1] a temperature of 670 °C has been assigned to the inversion. In the up-temperature direction 10 min at 680 °C is sufficient to convert most of the β to α' and the amount of α' increases normally with time. On cooling, holding for even 2½ hr at 640 °C fails to convert the α' to β while 30 min at 610 °C yields a larger percentage of β. One may, therefore, say that we obtain on our samples [1] a temperature of—very roughly—675 °C in the up-direction and 625 °C in the down-direction. Such a "hysteresis" is quite analogous to the similar anomaly in cristobalite studied by Hill and Roy [2], in which case in the well-ordered phase the

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[1] Figures in brackets indicate the literature references at the end of this paper.

up-temperature conversion is at 268 °C and the down-temperature one is at 225 °C. The reconciliation of these anomalies with phase rule necessitates some new hypotheses. Such a proposal is discussed later. *The $\gamma \rightarrow \alpha'$ transition* was located by D. Roy [1] at 675 °C at 2,000 psi (H_2O) pressure and was extrapolated back by calculation to 725 °C at atmospheric pressure. All investigators are agreed that the starting material determines the temperature at which the reaction proceeds fast enough to be detected. In the sample studied [1] the reaction runs rapidly only above 840 °C. While there is a tendency for the γ- phase to persist even 100 °C above the equilibrium temperature (as shown by high-temperature X-rays), this persistence probably does not require a special explanation. The kinetics of a reconstructive silicate transformation with a large volume change cannot be expected to be very different at such low temperatures. In the down-temperature direction, of course, the reaction $\alpha' \rightarrow \gamma$ has never been carried out, although one can cool the sample to nearly 500 °C for several hours before the alternative transition to β is accomplished.

The $\beta \rightleftharpoons \gamma$ Transition. This is, of course—according to present general agreement—the only really monotropic transition, since β is always less stable than γ in the temperature range of its existence *at atmospheric pressure.* Calculations by D. Roy [1] using available thermochemical data (Gronow and Schwiete [3]) show that the β—phase should be stable even at room temperature (see fig. 1) at about 2,000 atm.

The common failure of pure β—C_2S (i.e., omitting cases due to equilibrium stabilization by solid solution) to invert to γ may, in general, be ascribed only to the sluggishness of a rather complex reaction involving breaking nearly all Ca—O bonds and some Si—O bonds at such low temperatures ($<<$670 °C). Our data here reflect the remarkable stability of β—C_2S (prepared hydrothermally) since runs of 2 to 5 weeks near 400 °C failed to cause inversion to γ. Moreover, the data on the stability of "large crystals" of hydrothermally made β-crystals do not agree with those reported by Yannaquis and Guinier [4]. Crystals of the β-phase which have an estimated volume of 1000 A^3 appear to be quite stable—indeed, they survive inversion better than the smaller crystals. Furthermore, the phase made dry by heating gels at temperatures between 1,475 and 1,300 °C all inverted to γ with no change in behavior at the $\alpha \rightarrow \alpha'$ transition point.

The most recent of our data are those obtained under very high pressures. Dachille and Roy [5] have pointed out that, in many cases, so-called "grinding" in very simple laboratory devices such as mortars and pestles and Wig-L-Bug shakers can cause the attainment of pressures of 15-20,000 bars. In a later study, by the introduction of a simple apparatus which provided the means of applying shearing stresses superimposable upon quasi-hydrostatic pressures of up to 90,000 atm, Dachille and Roy [6] were able to separate clearly the effects of pressure alone, and the catalytic effect of shearing stresses which exceeded the strength of the material and caused fracture.

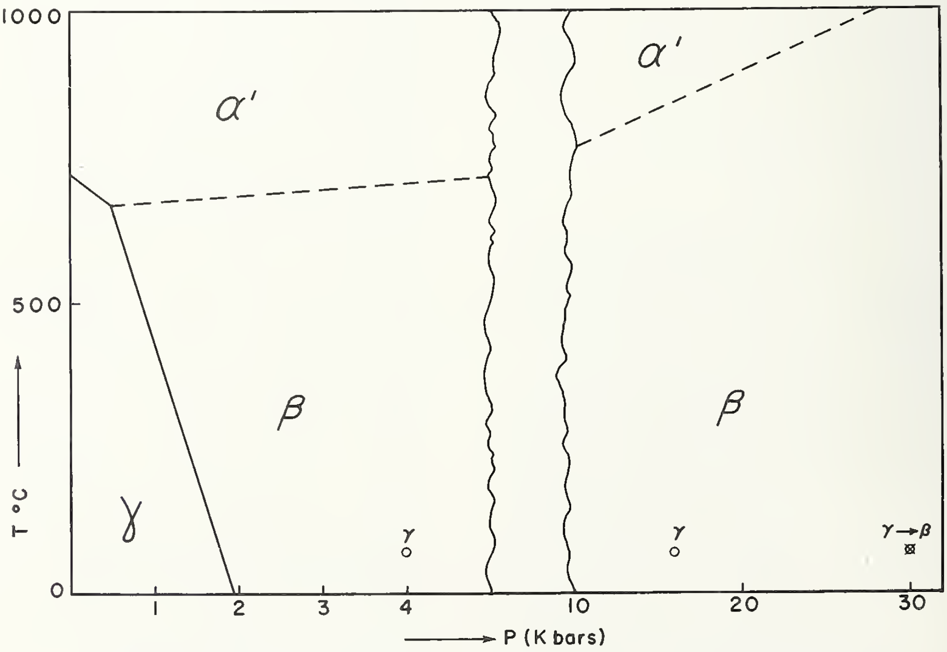

FIGURE 1. *Phase relation of C_2S as affected by temperature and pressure.*

Applying this same "displacive shearing" apparatus it is possible to convert γ to β at room temperature at 30,000 bars in 1 hr.[2] D. Roy was unable to convert γ to β at 17,000 bars without the shearing. Moreover, not only will a Wig-L-Bug type mixer convert β partly to γ (also described by Yannaquis and Guinier with a "percussion" of a different type) but it will also convert γ partly to β. The situation here is exactly analogous to that described by White, Dachille and Roy [7] for the PbO case which also has a negative *p-t* slope. The pressure + catalysis of bond breakage converts the γ to β, whereas the catalytic effect alone in those grains which are not necessarily at a high pressure causes them to invert from β to the γ phase *which is more stable at low pressures.*

Discussion—New Hypotheses on Transitions. The principle of parsimony demands restraint in the creation of new hypotheses to explain apparent anomalies. The apparent violation of the phase rule in the $ZrO_{2\ \mathrm{mono}} \rightleftharpoons ZrO_{2\ \mathrm{tet}}$ transition, due to the coexistence of the two forms over a 150 °C range (see, for example, Mumpton and Roy [8]), and the high-low cristobalite transition [2] is so well established experimentally by many different workers that an explanation is necessary.

When a small volume element of the less dense phase forms inside a crystal of the more dense form, the larger element of the latter containing it is, of course, also placed in compression. The simplest hypothesis is to assume that the transition is suppressed in such cases due to a pure pressure effect on the transition temperature. If we disregard for the moment the anisotropy inherent in the shape factor or that dependent on the mutual crystallographic relationship, one can easily see that the transition temperature of the phase under compressive stress is now altered by an amount determined by the Clapeyron relationship. Since the $\gamma \rightarrow \alpha'$ and $\beta \rightarrow \gamma$ changes involve large volume changes one can expect a substantial change of inversion temperature with pressure. In the latter case it has been calculated to be 350 °C per 1,000 atm. And, since the strength of such crystals is probably in the order of 10,000 atm the effect of the *pressure alone* may be quite enough to suppress the transition from proceeding further. This type of effect *can* account for the abnormal sluggishness of certain reactions and the apparent coexistence of two phases of the same composition over a temperature range, since the volume element of the matrix surrounding the less dense phase may be under sufficient pressure to actually be stable till the matrix crystals fracture.

A great deal has been written on the influence of "strain" in altering the mutual stability relations between two phases, while no clear cut experiments are at hand to demonstrate that it is strain and not "hydrostatic" pressure which is effective. If it is implied, for example, in a one-component system that Phase B will invert to Phase A at temperature T', this situation can be treated very simply by regarding the strained A as another polymorph A* with different free energy. On this basis hysteresis would be explained as being caused by the inversion, let us say, of A→B on the up-cycle at T °C and on the down-cycle of B→A* at a *necessarily lower* temperature, with subsequent change of A* to A. Hence, there is no question of pressure or coexistence of two phases, but merely the failure to distinguish between A* and A. This explanation may be applied to the high-low cristobalite case and possibly to the $\beta \rightarrow \alpha'$ case in Ca_2SiO_4.

In the case of the $\alpha' \rightarrow \gamma$ transition the failure to invert at all on cooling may be due to the pressure stabilization of matrix α' caused by pressure due to formation of γ within the α'. The sluggishness on heating has previously been ascribed to the usual difficulty of reconstructive transitions, but some apparent coexistence may be realized by having some α' crystals forming within γ crystals and requiring a *higher* temperature for the transformation of the resulting strained γ.

The $\beta \rightleftharpoons \gamma$ transition now appears to be qualitatively straightforward while anomalies may be found when the curve under pressure is determined quantitatively. While β is "very nearly" a stable phase at atmospheric pressure, it requires only quite low pressures ($\sim$2,000 bars) to stabilize it even at room temperature. γ can be converted to β even at room temperature but expectedly requires a bond breakage mechanism over and above the requisite hydrostatic pressure (to move γ into the β stability field). Likewise, the transformation of $\beta \rightarrow \gamma$ at atmospheric pressures requires mainly the formation of nuclei which can be provided by shearing stresses *which cause fracture.* It is as yet difficult to say whether or not the total strain energy which can be stored in such phases is sufficient to significantly alter the activation energy for nucleation.

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[2] It is worth noting that there was some evidence for the dissociation of Ca_2SiO_4 into CaO—SiO_2 under these conditions. This would be quite surprising.

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Discussion

H. Krämer and H. zur Strassen

Our recent investigations on the influence of minor components on clinker composition showed some surprising results. The influence of MgO and Na_2SO_4 is greater than that expected and indicated by the phase diagrams.

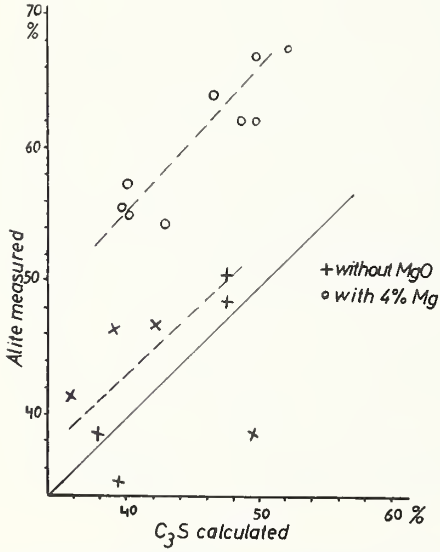

Figure 1. *Comparison between C_3S content calculated and alite content measured by microscope.*

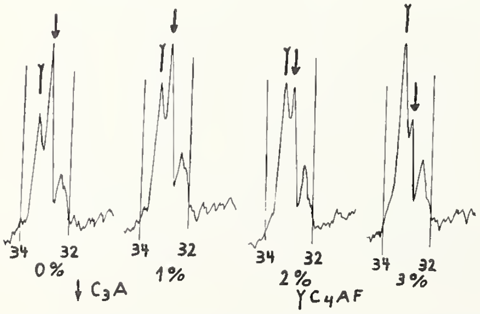

Figure 2. *Interstitial phase of clinkers burned with increasing MgO content.*

MgO influences the relation between all the four components and C_3S, and especially the iron phase. Figure 1 shows a comparison between the C_3S content calculated according to Bogue (on the abscissa) and the actual alite content (on the ordinate) which has been measured by microscope in polished sections (point counting method). The straight line would show the alite content if the Bogue formula gave the correct result. It may be seen that in clinkers without MgO the values calculated and measured coincide approximately. For clinkers with 4 percent MgO the average alite content is about 14 percent higher than calculated.

The X-ray diffraction patterns in figure 2 show the interstitial phase of clinkers burned with increasing MgO content. The silicates had been destroyed by ammonium chloride. The relation between the iron phase ($d \sim 2.64$) and the C_3A phase ($d \sim 2.69$) shows that the content of the iron phase with growing MgO content increases, whereas the C_3A phase decreases. These findings confirm both Swayze's melting diagrams and the observations of Cirilli and Brisi [1],[1] to the effect that the iron phase can take up more alumina in presence than in absence of magnesia. If the alumina content increases, the lattice dimensions should shrink [2]. But according to our measurements (table 1), based on the (200) reflection, the contrary is found.

Table 1.—*Spacings and intensities (I/sec) of C_3A and iron phase (according to figure 2)*

MgO content:	0%		1%		2%		3%	
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
C_3A	2.6922	115	2.6882	104	2.6882	93	2.6859	80
C_4AF	2.6367	57	2.6420	73	2.6481	80	2.6458	91

The increase in the alite content (fig. 1) is the result of all the phenomena which cause a reduced lime requirement of the clinker phase in the presence of MgO: the smaller lime content of the equilibrium melt as shown by the diagrams of Hansen and Swayze; the reduced C_3A content as confirmed by these studies; the substitution of CaO by MgO in the alite itself as shown by Locher [3].

The influence of alkali oxides and alkali sulfates is shown in figure 3. In these diagrams characteristic lines of CaO and alite are marked. It may be seen that the diagram of the clinker containing K_2SO_4 is very similar to that of the clinker without any addition, showing that K_2SO_4 does not influence the distribution of the other components. Very much in contrast to these diagrams is that one with sodium sulfate and you can see that the clinker has suffered a radical change. The alite peak has disappeared whereas the peak of the free lime has grown. This is similar to the effect obtained by adding potassium oxide to the clinker.

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[1] Figures in brackets indicate the literature references at the end of this paper.

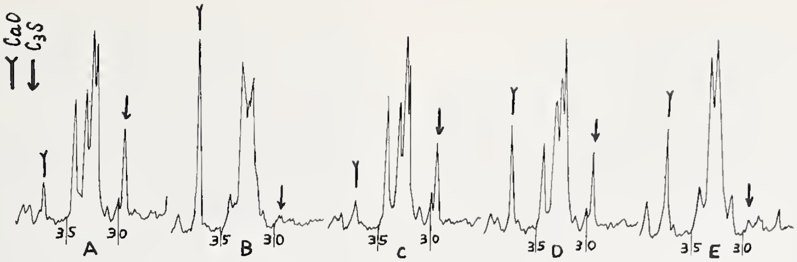

FIGURE 3. *The influence of alkali oxides and alkali sulfates on the clinker composition:*

A—without addition
B—2% K_2O
C—2% K_2SO_4
D—2% Na_2O
E—2% Na_2SO_4

In order to corroborate this statement a photograph of a polished section of this clinker is shown in figure 4. There are grains of C_2S with twin stripes together with plain grains of free lime, thus showing that in this case C_2S and free lime are stable without the formation of alite.

It is our opinion that the sodium sulfate is taken up by C_2S in solid solution, because the ionic radius from sodium and calcium is nearly the same and the SiO_4-group has nearly the same space requirement as the SO_4-group. This solid solution should prevent the formation of alite, in the same way as $KC_{23}S_{12}$ does.

These findings show the important influence of minor components on the phase equilibria of clinker, and the difficulty of drawing quantitative conclusions in particular from X-ray diagrams.

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FIGURE 4. *Polished section of a clinker containing 2% No_2SO_4.*

Discussion

Katharine Mather

Nurse [1] [1] has reported that at the Building Research Station it had been observed that "the 2.71–A peak of pure C_3A was found to wander over a range in various cements." The range was not cited in the paper by Nurse or the supplementary paper by Midgley, Rosaman, and Fletcher [2.] Midgley et al., report that they used the "2.699–A" peak to identify C_3A. The Index to the Powder Data File [3] shows 2.70 A as the strongest line of pure C_3A. With copper radiation, the line falls at 33.14 deg 2θ.

In diffractometer charts made here of portland cements and clinkers, the location of the intense spacing of C_3A has ranged from 33.10 deg 2θ (2.704 A) to 33.20 deg 2θ (2.696 A), in charts where the position of the alite spacing indexed as (20·2) [4] fell in the range 29.90 to 30.04 deg 2θ (2.986 to 2.972 A). The reproducibility of this alite spacing from chart to chart was taken as indication that the specimen surfaces were flat and accurately positioned. It is difficult to attach meaning to discussion of the change in position of spacings unless some criteria are provided of the reproduction of flat specimens with their front surfaces in the same plane.

Nurse, and Midgley and his collaborators, also reported that the latter found C_3A contents by X-ray diffractometry in cements of low A/F ratio that were higher than those calculated according to the Bogue formulas—the reverse of the situation reported by Copeland [5], Brunauer [6], and their collaborators. The A/F ratios of the cements in which Midgley and his collaborators obtained these results were not reported. The finding is also the reverse of that reported by Insley [7], by Ward [8], and by Brown [9] from quantitative determinations of clinker compositions by light microscopy.

It seems possible that both the reported wandering of the location of the most intense C_3A spacing, and the reported finding of C_3A contents above those indicated by the Bogue calculations in cements of low A/F ratio, may arise from the presence of a constituent (or constituents) detected here that gives rise to a spacing at slightly lower diffraction angle than the 2.70–A spacing of C_3A, a spacing which easily may be misinterpreted as C_3A. The best evidence that this spacing (or spacings) at slightly lower diffraction angle (32.84 to 33.00 deg 2θ with copper radiation) is not tricalcium aluminate in a substituted form, lies in the fact that cements whose diffraction charts show this peak do not produce calcium sulfoaluminate in quantities to support this interpretation when the cements are hydrated with excess SO_3. We have found this spacing in cements meeting the requirements of type I and type II of Federal Specification SS–C–192b; the spacing has been much more frequently found in type II cements. We have not examined enough cements of type III and type V to form an opinion on how often this spacing occurs in X-ray diffraction charts of those types.

While we have several pieces of information about this spacing, we have not made a coordinated study of it. We first recognized it in a review of data in which we plotted the spacings of the most intense aluminoferrite peaks and what we took to be the most intense C_3A peak, against the A/F ratio of the cement or clinker for 49 samples. The positions of the (20·2) alite spacing and the combined silicate peaks at about 34.3 deg 2θ with copper radiation were also plotted against A/F ratio as controls of the planeness and position of the specimen surface.

The means and standard deviations of each kind of spacing in each range of A/F ratio were also computed, and the following surprising results for the "C_3A" spacing emerged:

A/F by weight	Mean position of C_3A	Standard deviation	Number of observations
	A		
3.10–2.40	2.7010	0.0030	11
2.40–1.70	2.7018	.0041	12
1.70–1.00	2.7080	.0083	17
<1.00	2.7002	.0042	4

It was reasonable to separate the group containing 17 values into two subgroups, one of 9 values ranging from 2.696 to 2.704, with a mean of 2.7018 and standard deviation of 0.0030, and a second of 8 values ranging from 2.707 to 2.725, with a mean of 2.7150 and a standard deviation of 0.0075. A fifth value of 2.715 in the group with A/F ratio below 1.00 was rejected. We then interpreted these results as showing that the C_3A spacing was 2.700±0.004 A, and that the spacing at approximately 2.715 A arose from some other constituent. We later found that spacings at 2.707 to 2.712 can be resolved by manual scaling into pairs of spacings at 2.700 and at 2.715 or 2.720 A respectively. We did not interpret the 2.715± as the second most intense peak of the aluminoferrite, because of the intensity relations in the charts.

Later, eight type II cements were examined [10] on the diffractometer and also tested according to the ASTM method of test for potential sulfate resistance of portland cement [11]. In studying the diffractometer charts C_3A was regarded as present when some or all of the following features appeared: a spacing at 2.70±0.004 A; presence of any of the less intense spacings of C_3A that are not interfered with in portland cement, especially those of 4.24 and 4.08 A or at 1.558 A. By these criteria, small amounts of C_3A were found in five of the cements. Four had a line that fell in two instances at 2.72 A (32.90 deg 2θ) and in the others at 2.725 A (32.84 deg 2θ).

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[1] Figures in brackets indicate the literature references at the end of this paper.

In the ASTM test for potential sulfate resistance of portland cement, the expansion of mortar bars, containing added calcium sulfate to bring the total SO_3 content by weight of cement to 7.0 percent, is measured at various ages after water storage of the bars. In this particular group of tests, all of the cements appeared to be potentially sulfate resistant, since the expansions were essentially negligible at the usual end point, 28 days, were still small at one year, and were more clearly related to the magnesia content of the cements, as determined by X-ray diffraction or chemical analysis, than to any other feature of the cement composition. When the bars were one year old the test was discontinued and one bar from each set was examined. Only very minor amounts of calcium sulfoaluminate could be found in any of the bars; the relative amounts did not agree with the hypothesis that the 2.720 or 2.725–A, constituent was contributing to the production of calcium sulfoaluminate; therefore it was concluded that the 2.720– or 2.725–A constituent was not a substituted form of C_3A. It appeared probable that it was a modification of one of the calcium silicates.

It is therefore suggested that the most definite way of establishing whether the tricalcium aluminate spacing wanders is, first, to establish reference spacings in the diffraction patterns, by setting tolerances for certain silicate spacings or by adding a substance with precisely known spacings. Second, if the tricalcium aluminate spacing then apparently departs from the value for the pure substance, some of the cement should be hydrated with an excess of sulfate to determine whether the amounts of calcium sulfoaluminate produced are compatible with the amount that should be produced if the wandering spacing arose from a substituted tricalcium aluminate.

It is quite possible that more than one substance may produce a spacing or spacings confusible with that of C_3A. Suzukawa [12] reports that C_3A containing either sodium or potassium can occur in clinker under some circumstances; he agreed with Greene and Bogue [13] that NC_8A_3 had a longer spacing of its most intense line than C_3A. Brownmiller and Bogue [14] on the other hand, found a shorter spacing for NC_8A_3 than for C_3A. Potassium-substituted C_2S or $KC_{23}S_{12}$, the stabilized α' form of C_2S, can exist in portland cement [15]. The cements in which we have found the spacing or spacings confusible with C_3A have generally been cements with more K_2O than Na_2O, but this is the case with most cements made in the United States; they have not been the cements of higher alkali content in the groups in which we have found them.

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Closure

R. W. Nurse

In replying to the discussion it will be easier to deal with specific subjects than to analyze each contribution separately.

At the time of drafting my paper I had not seen the recently published work of Yamaguchi and Miyabe [1][1] which identifies the reactions at 920 and 970 °C in pure C_3S and 830 °C in alite, reactions which were discovered at the Building Research Station and reported by Jeffery at the 1952 Symposium. This work shows quite clearly that preparations processed at such temperatures as 1,500 °C will take up impurities to an extent dictated by the solubility in the trigonal phase; these solubility limits cannot therefore give any quantitative information on the unit cell contents of alite (the monoclinic form). Since the transition temperature of $C_{54}S_{16}$-AM was lower than that of pure C_3S, MgO and Al_2O_3 are presumably more soluble in the trigonal

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[1] Figures in brackets indicate the literature references at the end of this paper.

form than in alite. Differences in heat treatment can therefore readily account for the different results obtained by the author and by Locher, Krämer, and others. The practical importance of pursuing this line of research is brought out by Welch and Gutt.

The important contributions concerned with effects of ash and reducing conditions and with reaction velocities (Heilmann, Kondo, Longuet, Suzukawa, Woermann) raise the question of the low temperature decomposition of C_3S. This reaction is normally very sluggish, but it is suggested that various impurities will catalyze the reaction until it becomes a serious problem to the cement chemist. This may well be so, and the possibility was considered by many of the earlier authors who studied the problem. I wish however to draw attention to the fact that secondary free lime can form from the decomposition of C_3S by other processes. In the first place, where the impurity oxide has more than one possible valency, the metal may change from an anionic to a cationic role and so displace a certain amount of CaO. In the second place, if the impurity forms a high temperature solid solution with C_2S, as so many do, then the phase assemblage C_3S–CaO–C_2S solid solution may become stable. If rates of reaction were fast enough all the free lime would be present as primary crystals, but in many cases long processing at high temperature is necessary to form the solid solution; in such mixes the C_3S forms first and later decomposes, giving secondary free CaO. Thus many impurities such as barium and strontium silicates (Toropov) sodium sulphate (Krämer and zur Strassen) will behave in a manner analogous to that of P_2O_5 as described in the studies of the present author and his colleagues. FeO, as Woermann shows, decomposes C_3S, and this must in part be caused by the fact that fayalite goes into solid solution with C_2S as established by Bowen, Schairer, and Posnjak [2].

The discussion on C_2S shows that we still are not able to control all the variables affecting the transformations of this phase. Thus Yannaquis finds that alkalies do not stabilize the β-γ inversion, but many other workers disagree; he very correctly draws attention to the importance of nucleation and crystal size.

Majumdar and Smith point out the range of coexistence of γ and α' and suggest that this implies a differing chemical composition for the two phases. I think this is an additional reason to suspect solid solution with CaO necessarily present as one of the reactants from which the C_2S is formed. For instance de Keyser's reaction (Symposium 1952) at 900 °C could be interpreted as exsolution of CaO from part of the γ-C_2S with a corresponding rise in the γ-α' inversion temperature. This is confirmed by his observation of increased free CaO in the X-ray pattern. Material prepared hydrothermally or by dehydration will tend to contain free CaO because the lime/silica ratio in any hydrate formed is likely to be less than 2.0. As with alite, we must be careful to determine the solubility of impurities by heat treatment within the range of stability of the polymorph under study. The enlargement of the β-C_2S unit cell suggested by Majumdar and Smith is confirmed by work in progress at Cambridge [3] and this suggests that the anomalous X-ray patterns for β-C_2S recorded by Toropov and also by Majumdar and Smith may arise from ordering reactions taking place during cooling.

I was very glad to read the contribution from R. Roy, since it repeats and confirms so many observations in my paper on C_2S, presented to the 1952 Symposium. The temperatures given at that time are all somewhat higher than those of Roy; this may be due to the kinetic nature of the DTA results, but may also be caused by the difficulty of maintaining a known and uniform temperature in a diffractometer specimen. Roy's figure confirms part of my figure 6, but he is able to put a calculated scale on the ordinates; his first hypothesis of the effect of pressure on the C_2S inversions is also described in my 1952 paper (pp. 67–8). The second part of his hypothesis is very interesting and it may be that the small and as yet unexplained breaks found in some DTA curves of C_2S can be attributed to "strained" phases, or what is almost the same thing, order-disorder changes.

Most of the hysteresis in phase changes can, I am sure, be explained by nucleation theory.

The aluminates $C_{12}A_7$ and C_5A_3 have been mentioned by Suzukawa and by Majumdar and Smith. I would like to reaffirm the importance of atmospheric water in experiments on these compounds. At the Building Research Station we have been trying to finalize the phase diagram for CaO-Al_2O_3 over the last 10 years or so. It was not until we recognized that the ternary behavior of this system was caused by atmospheric water that some consistency was obtained. Even now, we do not feel able to publish all the results, but since they complement some data given later in this volume by Roy (paper III–S9) some details observed by Welch will be given.

$C_{12}A_7$ prepared by crystallization in bulk from the liquid on cooling from 1,450 °C in air was found to have the following properties: density 2.68; refractive index 1.61 (Na light). During subsequent reheating in air of the pulverized material a gradual gain in weight took place which reached a maximum of about 1.3 percent at 1000 °C. This reheated material was then cooled quickly and on further examination by microscopy and X-ray diffraction was found to have an increased refractive index of 1.62 and reduction of the unit cell volume amounting to 0.3 percent; the density had also increased to 2.73. It was shown conclusively that water had been taken into the structure, by reheating this material in a dry oxygen-free nitrogen atmosphere. In these circumstances a sample heated to 1,450 °C lost 1.33 percent in weight, of which 1.20 percent was recovered by absorption in $Mg(ClO_4)_2$. The sample was maintained in the same atmosphere during cooling and crystallized essentially as orthorhombic C_5A_3. The presence of water vapor in the atmosphere in which $C_{12}A_7$ is heated has a marked effect on the melting point. In moist air the $C_{12}A_7$ liquidus temperature is at 1,391.5 °C whereas in dry argon $C_{12}A_7$ melts incongruently to CA + liquid at 1,374 °C. Since C_5A_3 melts incongruently at 1,361 °C in air and at 1,352° in dry argon it must necessarily be regarded as a phase which is metastable with respect to $C_{12}A_7$ at temperatures close to its melting point.

The question of the ferrite phase is so closely linked with the general question of cement constitution that I will deal with both together. It follows from the published work of Swayze, Newkirk, and Thwaite that the quaternary cement system must be subdivided into the phase assemblages I have listed in my main paper. Some important conclusions follow. For instance a cement may be formulated for high sulfate resistance, with a low A/F ratio. If the lime saturation factor is not too high, it will fall within the assembly C_3S–C_2S–ferrite solid solution and contain no C_3A; a rise in the L.S.F. can however throw the composition into the assembly C_3S–C_3A–ferrite solid solution,[2] when the sulfate resistance will presumably be lessened. In order to judge adequately the importance of such calculations we need to know with confidence the values of the limiting ferrite solid solutions. Krämer and zur Strassen in their contribution reaffirm the opinion of earlier workers that these compositions will be altered by the presence of minor components. It is to be hoped that it can be shown that the compositions will be essentially constant for all normal portland clinkers, but they must be determined on clinker, as well as of course for various pure oxide systems. The experimental approach outlined by Majumdar and Smith seems very promising for this study.

The ferrite system is so difficult experimentally that it should be attacked by all the methods available. I agree with Toropov and Swayze that the microscopic method should not be neglected, but the results should be checked and compared with X-ray determinations. On the theoretical side it seems unnecessarily restrictive to insist on stoichiometric end members for the series; if Toropov is correct in saying there is a series from C_2F towards C_5A_3 as well as "C_2A", then there are ternary solutions which cannot comply with the structural formula. Single crystal X-ray work would throw some light on this.

It is difficult to believe that the assemblage C_3S–C_3A–ferrite solid solution occurs in real clinker, since it implies the disappearance of C_2S in favor of C_3A, and it is very rare not to find C_2S in a clinker. However, most clinker contains free CaO, and potentially therefore, if equilibrium were achieved, the C_2S could disappear. The basic question is the composition of the liquid at clinkering point; will this correspond to an invariant point with CaO and C_3S or C_3S and C_2S? Provided none of the phases are "protected" as described by Swayze, I would suggest that the composition of the liquid will be determined by the ratios of anions and cations and will not be materially affected by the fact that full combination between CaO and SiO_2 has not yet been reached for the solid matter. If this is so, in clinker where uncombined CaO is still present, the assembly C_3S–C_3A–ferrite will be replaced by CaO–C_2S–C_3S–C_3A–ferrite, which is frequently observed.

Since the conclusion from our discussion can only be that much more remains to be done, it would be appropriate to conclude by discussing techniques. However, the method of X-ray diffractometry has been thoroughly discussed at many points in the program, so that I will only thank those experts who have contributed to this question. The standardizing procedure suggested by Smolczyk seems attractive. I would also agree with Mrs. Mather concerning the need to look for substances interfering with C_3A. I have found in certain clinkers substantial quantities of α'-C_2S, and in such cases the C_3A peak at 32.9° 2θ is confused. I am glad to say that the suggestion to exchange standard clinker samples has been well received and we may all hope that the studies of the next few years will solve many of our problems.

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[3] J. D. McIver, Private communication.

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[2] This had previously been suggested by H. H. Steinour in unpublished correspondence with L. Dahl and F. Ordway.

Paper II–2. Crystal Structures of Clinker Constituents*

Fred Ordway

Synopsis

The concepts of a phase, a compound, and a solid solution, based on the mathematical abstraction of a continuum bounded by discontinuities of infinitesimal width, are discussed in relation to the known characteristics of the structures of real solids. Present knowledge of the structures of clinker constituents, as revealed by the literature, is outlined.

Résumé

Les concepts de phase, composé, et de solution solide, basés sur l'abstraction mathématique d'un continu limité par des discontinuités de largeur infinitésimale, sont discutés par rapport aux caractéristiques connues des structures de solides véritables. La connaissance actuelle des structures des constituants du clinker, telle que la révèle la littérature, est brièvement exposée.

Zusammenfassung

Die Begriffe einer Phase, einer Verbindung und einer festen Lösung, wie sie durch die mathematische Abstrahierung eines Kontinuums, welches durch Diskontinuitäten unendlicher kleiner Weite begrenzt wird, hervorgebracht werden, werden in ihren Beziehungen zu den bekannten Merkmalen der Strukturen wahrer fester Körper besprochen. Die heutige Kenntnis der Strukturen der Klinkerbestandteile, wie man sie in der modernen Literatur findet, wird klargestellt.

Introduction

In the study of matter, its structure and its behavior are inseparable. Dr. Nurse probably found it difficult to exclude structural considerations from his paper on phase equilibria and clinker constitution, and the availability of his paper was almost a prerequisite to avoid duplication in preparing this one. Rather than ignore this close relationship, we should emphasize it. Accordingly, I take the liberty of repeating fundamentals well known to the student of phase equilibria, and others well known to the structural chemist, in order to depict a fundamental philosophy accommodating both.

Fundamental Concepts

The phase equilibria of the clinker constituents, their formulas, and their structures are all merely different aspects of the same phenomenon. We might describe this phenomenon from the viewpoint of statistical thermodynamics as the equilibrium behavior of a system of atoms of O, Ca, Si, Al, Fe, Mg, K, Na, etc., in a given range of temperatures, of compositions, and perhaps of pressures. The complete theory would contain both the chemistry of cement clinker, as embodied in the equilibria between phases, and the structures of all the phases. We cannot actually derive the phase equilibrium relations from fundamentals, but our observations of them must be interpreted in the light of theoretical concepts. To discuss the relation between our concepts of phase equilibria and structure we begin with the former.

Determinacy

The basic premise of a thermodynamic discussion is the assumption that any system to be discussed can have but one equilibrium state under any specified conditions. Whether this state is a result of inherent determination in all of nature, or of averaging the somewhat uncertain individual behaviors of very many atoms, is not initially important; modern statistical theories and the classical ideas of earlier days both justify the expectation of highly precise determinacy in macroscopic samples under most conditions.

The single "true" equilibrium is thought of as a state to which the system eventually returns, after any change in conditions, when restored to the original conditions. The equilibrium is called metastable if certain changes, such as high temperature or pressure, make accessible a new equilibrium state which the system assumes preferentially. The identification of any equilibrium as "true" rather than metastable must be regarded as provisional, limited by convenience and by the range of experimental conditions that has been explored at the time. We often discuss "true" equilibrium states in chemistry which, from the viewpoint of nuclear physics, are clearly metastable.

In the present discussion, we take equilibrium states to be definable in practice by allowing adequate time or choosing an appropriate sequence

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of conditions, so that confusion with possible metastable states is obviated. We assume in principle that every sample of specified composition, temperature, and pressure will attain in finite time a state that differs by less than experimental error from a true equilibrium, and that this true equilibrium depends only on the specified conditions, not on previous temperature, pressure, or compositions of materials from which the sample was synthesized.

Continuity and Discontinuity

The entire thermodynamic theory of phase equilibria is based on the fundamental assumption that we can distinguish between continuity and discontinuity in the intensive scalar properties (those properties independent of the quantity of material and the spatial orientation) of a sample of matter at equilibrium. The distinction is applied in two ways—firstly to the variations in properties with position within the sample, and secondly to the variations in properties with changing composition, temperature, or pressure.

Continuity With Position

We may examine a sample of matter by various experimental methods. Any such examination is basically a comparison of a property of the sample, or part of it, with the same property of another sample, or another part of the same sample. If the comparison is made with a standard that is related to some accepted units of measurement, and it yields a quantitative result, we say that property of the sample has been measured rather than merely compared. Intensive scalar properties are, of course, the only significant ones because we may take a sample of any desired size, within the limits of the experimental technique, and the comparison of properties must be independent of orientation.

From the given sample at equilibrium, we may select small portions of matter at various positions and examine these separately. Such examinations, in principle, form the basis for all statements as to the continuity or discontinuity of properties. Thus, any such statement must always represent definite limitations in the variety of properties compared, the sensitivity of comparisons, the smallness of the portions of the sample taken for examination, and the closeness of successive points at which they are taken.

Phases at Equilibrium

If there is no discontinuity in the variations of intensive scalar properties from point to point, the sample is said to be homogeneous, and to consist of a single phase. We suppose that composition, temperature, and pressure of the sample are the only significant variables, there being no gradients of magnetic, electric, or gravitational fields, for example; then the intensive properties of a single phase at equilibrium are not only continuous but constant throughout. The phase may be identified and distinguished from other phases by the precise values of these constants at stated conditions of composition, temperature, and pressure. If more than one phase is present, each is separated from the others by a surface across which at least one intensive property exhibits a discontinuity.

Arbitrariness of Distinguishing Phases

The intensive properties whose values and continuity identify a phase include, in principle, all the ordinarily measured properties such as density, refractive index, conductivity, specific heat, vapor pressure, lattice constants, etc. Moreover, they include all derivatives, of whatever type and order, of such properties with respect to the independent variables of composition, temperature, and pressure.

Clearly the choice of an experimental basis for deciding whether two portions of a given sample are the same phase must be fundamentally arbitrary. We examine the sample by certain methods and make those distinctions which seem profitable. Identity of microscopic appearance and X-ray diffraction pattern, for example, are common criteria by which two homogeneous portions of a sample may be identified as the same phase.

We must always understand that study by other methods may later reveal significant differences in physical properties. If there are significant differences in behavior in any process of interest to us, then the two phases must be distinguished, however difficult that may be. Fortunately we can usually expect significant differences in energy, which cause significant chemical differences, to produce significant differences in physical properties as well. Systems which can form several distinguishable structures of approximately equal energy may be far more difficult to elucidate than those forming a few widely different structures.

A second element of arbitrariness is spatial resolution of the experimental technique. Clearly the structure of a sample cannot be said to change discontinuously on an atomic scale at phase boundaries, any more than it does within a phase. The spatial resolution of our examination of the sample therefore must be coarse enough that we do actually recognize discontinuities at the phase boundaries; the resolution may be submicroscopic, but not atomic. Even with this restriction the results of differing techniques may disagree. A sample that is microscopically homogeneous, for example, may be revealed by the electron microscope as a matrix of one phase containing droplets [Sastry and Hummel, 1959; Krogh-Moe, 1959] or crystallites [Hsiao, 1958] of another.

The status of matter within the region of transition between phases is often ambiguous when details of structure are considered. We regard a polycrystalline sample as homogeneous if properties are identical within all grains, and we may treat the twin planes of a twinned crystal as the grain boundaries of a polycrystalline sample. We are assuming that any grain boundaries and imperfections (such as are described below in the section on "Real Crystals") not in equilibrium have negligible effects on the properties investigated. Whether this idealization is valid depends upon the phenomena and materials under discussion.

For example, we may find it profitable to identify two samples as β-dicalcium silicate even though the microscope reveals one to be very finely twinned, and the other not [Insley, 1936; Insley et al., 1938]. Two crystals of a metal which are identical in appearance, on the other hand, may be sharply distinguished for other purposes because one has many dislocations in its structure, and the other not.

Existence Regions

For each different phase capable of existence at equilibrium there is a volume in the $(N+1)$-dimensional space, corresponding to the range of conditions under which the phase is present in a mixture. We may call this entire volume the existence region for that phase. Clearly a part of the existence region must correspond to the presence of that phase alone; for if the phase is present in any proportion in a mixture corresponding to a given point in the $(N+1)$-dimensional space we can arrive at its solitary-existence region by moving the mixture point along those lines of constant temperature and pressure which correspond to removal of the other phases present. The N-dimensional boundaries of the solitary-existence region correspond to the phase changes that take place with various changes in the composition, temperature, and/or pressure of the homogeneous sample. The mixture point, in crossing one of these boundaries, may move directly into an adjoining solitary-existence region, corresponding to the complete transformation of the entire sample into a new phase; or it may move into a region where another existence region overlaps the first, corresponding to the appearance of a second phase without disappearance of the first.

Adjoining Existence Regions

When the mixture point crosses a phase boundary where two existence regions adjoin but do not overlap, the new phase has the same composition as the original phase. Such a situation may occur in a polymorphic transformation or the congruent melting of a solid.

Overlapping Existence Regions

If the phase change is appearance of a second phase without disappearance of the first, the principle of determinacy requires that the second phase must have a different composition from the first. Each phase is represented by a point in the $(N+1)$-dimensional space, and all possible mixtures of them correspond to the line segment joining these two points. Mixtures at different points along this line segment are in the same state, having the same temperature and pressure, and differing as to composition only in the proportions of the two phases. A family of such line segments, called tie lines, defines all the possible equilibria involving coexistence of the two phases.

Continuity With External Conditions

Our sample may also be examined by measuring its properties between successive changes in the externally imposed conditions of composition, temperature, and pressure, rather than at various points of the sample under fixed conditions. If each measurement represents equilibrium state, the series of measurements indicates the manner in which the equilibrium properties change with the external conditions. The relationships ascertained in this way are definitely limited in the variety of properties measured, the precision of measurement, and the smallness of the changes in conditions between measurements.

Phase Changes

When the composition, temperature, or pressure of a homogeneous sample is changed, we identify the sample as that same phase always, and only, if it remains homogeneous and its intensive properties exhibit no discontinuities. A discontinuity in any property with changing external conditions thus corresponds to a phase change.

Arbitrariness of Distinguishing Phase Changes

In recording any experimental study of phase changes we must always admit that future investigation, through more precise or more sensitive experiments, may detect a phase change where none had been thought to exist. Conversely, it may happen that a phase change already known may represent such slight departures from continuity, in all properties of importance to a given problem, that it can safely be ignored.

Geometrical Description of Phase Equilibria

Much of the power of phase-equilibrium theory resides in the development of geometrical ideas that are suggested by the foregoing discussion. The $N-1$ independent composition variables, together with temperature and pressure, form the $N+1$ coordinates of a space in which each point represents a unique choice of external conditions for a mixture of N components. The principle of determinacy requires that there be a single equilibrium state corresponding to each point. In that equilibrium state, the sample may be either homogeneous or heterogeneous; we identify the state by characterizing the one or more phases present. The totality of phase equilibria may be defined by prescribing, either from theory or from experiment, the region in the $(N+1)$-dimensional space corresponding to the existence of each phase that can exist.

Similarly, any coexistence region defined by the overlapping of two or more existence regions must be characterized by ties of constant temperature and pressure connecting the coexisting compositions. With the usual sets of composition coordinates, each tie is a line segment, a scalene triangle, an irregular tetrahedron, or a simplex [see Sommerville, 1958] in a higher-order space. Whatever its order, the tie represents a region within which the mixture point may move without a change in state.

The state is completely specified by the specification of any one of the coexisting phases. Thus any displacement of a mixture point that corresponds to a real change in state, within the same coexistence region, corresponds to a displacement of the point for each coexisting phase. The number of independent variables that can effect such a change must be the same as the dimensions of the boundary between the coexistence region and any adjoining solitary-existence region, since each of the individual phase points joined by a tie lies on such a boundary.

The Phase Rule

The number of independent variables determining the position of a mixture point in the $(N+1)$-dimensional space is $(N+1)$, but there are $(P-1)$ independent variables, corresponding to the subspace which is the tie for the P coexisting phases, that do not affect the state. Therefore the variance or number of independent variables affecting the state, in any region is $V=(N+1)-(P-1)=N-P+2$. This is the Phase Rule of Gibbs [1876–8] [Butler, 1936].

Phase Diagrams for Condensed Systems

The multidimensional space with a delimited region for existence of each possible phase constitutes the complete phase diagram of the system. Any intensive scalar property of a sample is continuous along any path that does not cross a boundary of one of the existence regions. Conversely, a discontinuity in even one intensive scalar property along any path in the phase diagram determines a point where that path crosses a phase boundary.

This fact is the fundamental basis for constructing phase diagrams. If the diagram is being constructed from theory, the boundaries are located where discontinuities occur in the calculated properties. If the diagram is determined by experiment, the boundaries of existence regions are located by detecting the discontinuties in the laboratory.

Instead of the full pressure-temperature-composition diagram, a section through it at a constant pressure value of 1 atm is ordinarily considered in clinker chemistry and many other fields. Strictly speaking, the clinker systems usually studied contain no vapor phase at atmospheric pressure. Any possible interactions with a gaseous phase must be considered carefully in the interpretation of experimental results. For example, the vaporization of an oxide constituent in sufficient amount to alter significantly the composition of a solid or liquid requires that the vapor phase be counted in determining P, and sufficient dissociation of an oxide to affect its composition requires that oxygen be counted in determining N.

If the idealization ignoring vaporization is satisfactory, we may restrict the discussion to condensed systems; the remainder of this paper is so restricted. The Phase Rule, with pressure fixed, becomes $V=N-P+1$.

A chosen mixture, at high enough temperatures, will be entirely liquid. For our purposes the liquid is taken to be a single phase, there being no immiscibility reported for the silicate liquids occurring in cement clinker. The liquid phase exists alone down to the upper limiting temperature for coexistence of a solid phase. This limiting temperature, or freezing point, is a function of composition. The boundary of the solid-phase existence region, defined by this function, is called the liquidus.

At a low enough temperature the mixture is entirely solid. As temperture rises from this point, melting begins at the low-temperature limit of the liquid-phase existence region. This limiting temperature, or freezing point, is also a function of composition. The boundary defined by this function is called the solidus. The most significant aspect of most of our phase diagrams, with respect to the character of the solid phase, is the relationship between the liquidus and the solidus.

Solids of Definite Composition

In cement clinker chemistry, as in most chemical studies of a prescribed realm of materials, we give first attention to the compositions that seem most important because they represent phases that are often found in the mixtures observed. That is, we are interested first in those phases whose existence regions are relatively large, but whose solitary-existence regions are comparatively small.

Of course the extent of these regions in composition is a function of the temperature. Above the highest melting point, for instance, the liquid phase has a solitary-existence region extending throughout composition space, and no coexistence regions. In this situation, no one composition can be considered more important than another.

At a eutectic temperature, on the other hand, the liquid's solitary-existence region is but a single point while its coexistence regions may range through almost the entire composition space. The eutectic point is one vertex of a tie that covers a sizable region of composition space, and thus has significance to a correspondingly sizable range of mixtures. Such liquid compositions, representing liquids present at the beginning of melting or the end of crystallization, have rightly been emphasized in Dahl's [1955] discussion of burnability and in studies of multi-component systems such as $CaO-5CaO\cdot 3Al_2O_3-2CaO\cdot Fe_2O_3-2CaO\cdot SiO_2$ [Swayze, 1946] and $Na_2O-CaO-Al_2O_3-Fe_2O_3-SiO_2$ [Eubank, 1950].

As with liquids, the solids may be rated in importance according to the range of conditions under which each is observed to be present in clinker. That is, a given solid might be considered important in proportion to the size of its existence region in composition space and, *ceteris paribus*, to the range of temperatures over which it can exist. Such a consideration would clearly emphasize the ideal conception of a chemical compound—a crystalline phase of unvarying composition, capable of existing in equilibrium with solutions (i.e., melts) of widely varying composition and temperature.

Compounds

The ideal compound, if it melts congruently, would necessarily be a composition at which the solidus and liquidus coincide. The shape of the liquidus temperature surface as a function of composition around the melting point of a compound has been argued extensively by many authors. A distinction has often been made between a "dissociating" compound and one that is completely stable. Gibbs [1876–8] showed that the chemical potential of a given component in a mixture must be negatively infinite if that component is entirely absent from the mixture, and finite if the component is present. As Wilson [1944] has reemphasized, the junction of liquidus and solidus at a congruent melting point must be a horizontal tangency, except where the chemical potential exhibits a singularity because a component disappears. Thus the liquidus maximum for an intermediate compound can be sharp only if the compound has an infinitely negative free energy of formation (i.e., infinite stability).

The assumptions we have stated regarding the attainability of equilibrium must rule out the presence of infinitely stable compounds and thus, in principle, the existence of sharp maximums in the liquidus. A compound of relatively high stability is not forbidden, however, and may in principle have a liquidus maximum of great curvature which appears sharp within experimental error. The shape of the maximum has been interpreted in terms of the "degree of dissociation" of the compound on melting [Kremann, 1904; Kendall and Booze, 1925; Bennett and Wain, 1936].

Different authors treat in different ways the experimental observations of apparently sharp liquidus maximums reported in the literature. Zernike [1955] speaks of the system of two substances that form a perfectly stable compound as "a simple combination of the systems of each of the substances with the compound . . . obtained by just placing side by side the corresponding diagrams of the two systems," and cites phase diagrams from the literature that appear to represent such relations. Ricci [1951], on the other hand, emphasizes the reversibility of formation of the compound, and says the completely stable compound "is not a binary compound in the phase rule sense. . . . It is merely a third substance . . . giving rise to two independent binary systems."

This view is consonant with the fundamental development of Gibbs [1876–8], and seems to avoid an inherent contradiction in Zernike's viewpoint. Discussing phase equilibria in any system involves the basic assumption of equilibrium in any mixture of the specified components—but there is no mechanism for equilibrium between a component in the perfectly stable compound and the same component elsewhere in the sample. One could scarcely treat the system H_2-H_2O-O_2 or H_2-H_2O-H_2O_2-O_2 as a binary system, for example, at such low temperatures that equilibria requiring molecular changes are inaccessible.

The basic rule of continuity that defines a phase, which we have discussed under "Continuity and Discontinuity" argues for the viewpoint of Ricci [1951] rather than that of Zernike [1955]. The free energy per unit mass and its derivatives, being intensive properties, must be continuous functions of composition, temperature, and pressure for a single phase. The geometrical derivation of the liquidus from the free energy surfaces [Gibbs, 1876–8; Butler, 1936] must lead to a liquidus temperature that is similarly continuous in value and slope. In principle, a sharp maximum in the liquidus temperature for a solid phase of unchanging composition would have to correspond to a discontinuity in the liquid phase. The binary solutions between the perfectly stable compound and its separate constituent substances must therefore be considered different phases. This appearance of a phase change as composition varies in the liquid (or even in the gas phase, for a sublimation curve with a sharp maximum) would be quite reasonable because the presence of the perfectly stable compound must lead to definite discontinuities in value or slope of certain properties of the fluid phase.

The compounds related to cement clinker chemistry do not approach perfection, as we have used the term with reference to stability. They are considerably, if not completely, dissociated in the high-temperature liquids. They may, however, approach ideality in our sense of the word—having an unvarying composition in the solid phase.

For such an ideal compound, the liquidus temperature must be continuous in value and slope, and pass through a maximum at a congruent melting point. The solidus, on the other hand, must be quite discontinuous. If our compound forms a eutectic with other ideal compounds, for example, the solidus temperature is equal to the eutectic temperature everywhere within the composition simplex joining the compounds, but at each vertex it rises abruptly to coincide with the liquidus at the melting point of the corresponding compound. At all the boundaries of the composition simplex it rises abruptly to coincide with the eutectic temperatures of the boundary systems.

For such an ideal compound, the well-known methods of purification (by crystallization from the solution), characterization (by the melting point), testing for purity (by sharpness of melting), and confirming identity (by mixed melting with a known sample) are applicable without reservation. Healthy skepticism as to the universal applicability of any idealization and the physical reality of the discontinuous solidus impels us to expect, however, that every solid phase will deviate from ideal behavior to some extent. If the deviations are insignificant, we may speak of "the small composition range called a compound" [Searcy, Williams, and Schissel, 1960]. If the deviations of the solid from fixed composition are significant, we must apply the more general term "solid solution."

Solid Solutions

Taking the more general viewpoint, we may regard every solid phase as stable over some finite range of composition. If the range is small, we may term the phase a compound and ignore its variability of composition—it is always observed to have the same identifying properties, within experimental error. If the range is larger, on the other hand, the variability of properties may render even identification difficult.

We refer to solid phases of variable composition as solid solutions without implying that their solitary existence regions necessarily have any particular shape or extension in composition space. The designation of "components" of the solid solution may often be profitless, or even misleading if it suggests unsound analogies to the properties of liquid solutions.

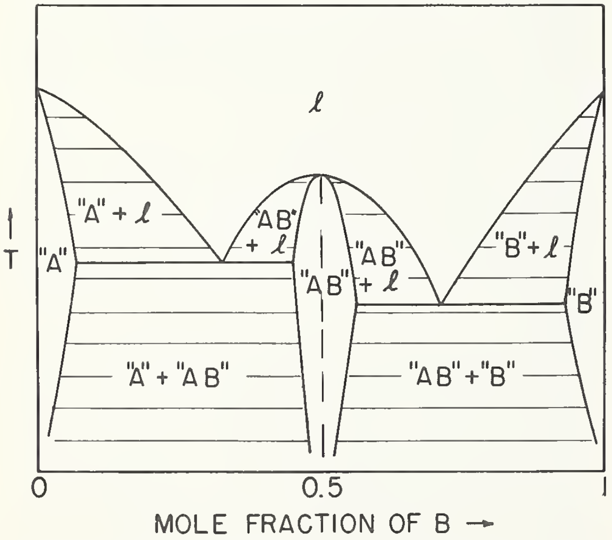

Figure 1. *Phase diagram for a hypothetical binary condensed system A–B, with tie lines in two-phase regions.*

A given solid phase might be called a solution "between" or "among" any set of linearly independent compositions that lie within its solitary existence region, but this usage is misleading if the same phase can have compositions outside the tie so defined.

Conversely, the solid phase of variable composition is sometimes called "a solution of *the solutes* in *the solvent*." The solutes may be any set of compositions defining a tie that encloses the solitary existence region, and the solvent may be any composition within the solitary existence region. In such a description, there is no particular basis in chemical data for naming any set of solutes other than the ultimate components of the system, but the unique composition of the solid solution that melts without decomposition might possibly be named as the solvent.

The idea that every solid phase has a solitary existence region of finite extent in composition is a satisfactory generalization because it includes the ideal compound as a limit. For example, the phase diagram in figure 1 for a hypothetical binary system A–B has finite solid-solution regions around the pure components A and B. Any of these regions might be broadened, or might be shrunk to infinitesimal width, without qualitatively changing the phase-equilibrium relationships. Any one that was reduced in width to a vertical line would represent an ideal compound. The phase could then be indicated by its formula without quotation marks.

The situation near the melting point of "AB" is shown more clearly in figure 2. A mixture point in the coexistence region ("AB" + l) below the melting point T_M can move along its tie line, as indicated under "Overlapping Existence Regions," without altering the state of the mixture. Only a change in temperature, moving it to a new tie line, produces a change in state. This being a two-phase binary equilibrium, the phase rule for condensed systems requires that the number of variables affecting the state be $V=P-N+1=2-2+1=1$.

At the melting point, the liquid and solid have the same composition. The phase rule requires

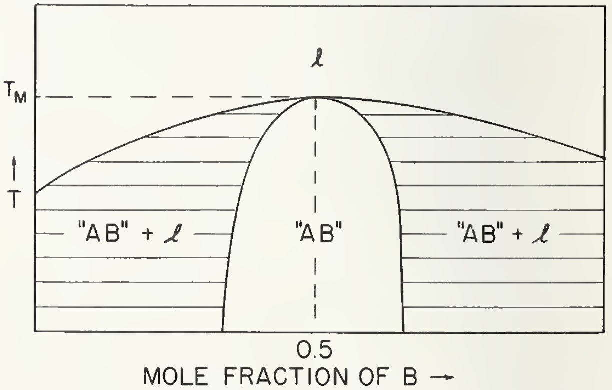

Figure 2. *The system A–B in the neighborhood of the melting point of "B," showing smooth maximum in liquidus and solidus.*

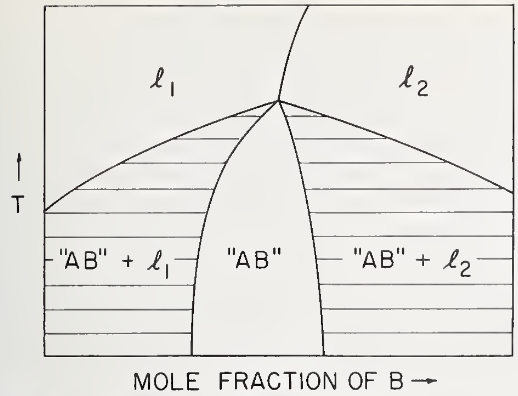

Figure 3. *Hypothetical phase relations for a sharp maximum in the liquidus of "AB": discontinuous liquid phase.*

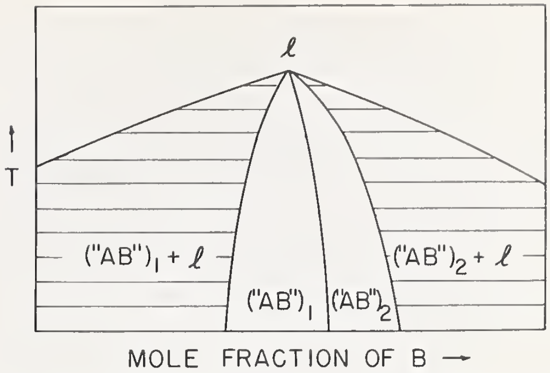

Figure 4. *Hypothetical phase relations for a sharp maximum in the liquidus of "AB": discontinuous solid phase.*

the same variance, since there are still two phases, but the principle of determinacy requires that one of the two phases disappear upon any infinitesimal change in temperature. Thus the coexistence region at T_M must be a single line of zero slope—the limiting tie line—and the liquidus and solidus must have smooth maxima which are tangent at the melting point.

The diagram would approach that for an ideal compound as the "AB" region narrowed, and the solidus increased in curvature at its maximum.

The existence of a sharp maximum in the liquidus of a congruently melting solid phase, as described by Zernike [1955], corresponds to a variance of zero at the melting point because there is no smooth curve passing through that point and lying in the solid-liquid coexistence region. The phase rule requires $0=N-P+1=3-P$. Thus the point must be one at which three phases coexist. Any such point must correspond to a discontinuity in either the liquid phase, as in figure 3, or the solid phase, as in figure 4.

The discontinuity in properties of liquid or solid with the composition that is associated with an observably sharp liquidus maximum would in general have to be found by experiment, but for systems of interest in clinker chemistry we expect the liquids to show no discontinuities, and therefore expect that any such phenomenon would be due to a discontinuity in properties of the solid solution. The origin of the unique compositions we think of as compounds, and the nature of the changes in solid solutions with composition, will have to be discussed in terms of the concepts of structural chemistry rather than the more abstract considerations of thermodynamics.

The Structural Basis of Definite Compositions

The traditional introduction to chemistry, for pedagogical simplicity, is a Daltonesque picture of a universe made of compounds in which the chemical elements are combined in definite, simple, and integral ratios of their atomic weights. The expectation of definite, simple, and integral chemical formulas has been of tremendous value in the understanding of chemical entities. In organic chemistry, hundreds of thousands of individual compounds have been characterized in these terms.

Although the ratios of the more complex organic compounds may no longer be simple, they remain definite and integral. The great success of research in this field is due in large degree to the existence of stable units of structure which can pass without destruction through solid and liquid (and also frequently gaseous) states. These units are called the molecules.

Molecular Structures

The hypothetical perfectly stable compound we have discussed as a limiting case is by definition a molecular compound, since its complete stability extends through the gaseous as well as the solid and liquid states. Many of the usual illustrations in introductory chemistry are molecular compounds approximating this limiting case, because the structural basis of their compositions is simplest and was therefore historically first to be elucidated.

The molecular compound consists of aggregates of relatively few atoms having relatively great stability. The forces between atoms in these aggregates (covalent bonds) are strong, specific, and directional. A unique configuration of atoms that saturates these forces is bound together far more strongly than any pair of already saturated aggregates that may happen to be adjacent. The deformation or melting of a molecular solid, or the flow or vaporizing of a molecular liquid, separates adjoining molecules without destroying them as entities.

The molecules of all substances, to the extent that they behave as independent, rigid masses, make equal contributions to the pressure in the gaseous phase and have equal effects on the well-known colligative properties of the liquid phase. From these properties the total mass of a single molecule can be established. The number of atoms of each type in a molecule is, by definition, an integer. Therefore the proportions in the formula of the molecular compound must be definite and integral. Those molecules which are easily studied in the gaseous phase have formulas that are also comparatively simple. The study of the simpler molecules has revealed the principles of bonding by which we understand the far larger molecules, whose proportions are by no means simple and whose study in the vapor phase may be impossible.

As molecules become larger the possibilities increase for relatively slight differences in molecular structure and concomitantly in energy. In crystallization, one type of molecule may be capable of replacing another without great differences in energy; solid solutions may form. Moreover, as molecular size increases the energy required for vaporization may become so large that many molecules decompose under the impacts of their neighbors rather than passing unchanged into the vapor. Ultimately, even for molecular compounds, the definition of the compound may depend on an aggregate of atoms that is stable only in condensed phases—perhaps only in the solid.

The smallest formula unit of an ionic structure may consist of a very few atoms in a simple ratio, such as CaO in calcium oxide. On the other hand the unit cell may contain a large number of atoms with complex ratios such as $Ca_2Mg_5Si_8O_{22}(OH)_2$ in tremolite [Zussman, 1959]. Such complexity often results from comparatively stable and specific bonding within certain groups of atoms, termed complex ions.

In discussing the formula of an ionic compound we rely implicitly on the idealized crystal structure, whose unit cell and space group must always be considered provisional. The size of the unit cell established by research correctly done in the past may be increased by more sensitive observations in the future, but never decreased; and the space group symmetry may be reduced, but never raised. In the case of many compounds in the perovskite family, for instance, the originally accepted cubic unit cell containing the formula unit ABX_3 is only an approximation to the presently accepted larger unit cells of lower symmetry [Wood, 1951]. Even $CaTiO_3$, after which the "perovskite structure" was named, does not actually have that simple a structure [Náray-Szabó, 1943].

The ideal crystal is described as a static array of atoms in assigned positions, but even the determination of the ideal structure has usually required the abandonment of that picture. Almost invariably the calculation of theoretical intensities in X-ray crystal structure analysis applies a "temperature factor" to the scattering power of each atom, to correct approximately for the thermal vibrations that distort the structure and smear out the time-averaged electron density distribution. The departures from ideal structures are even more important in many phenomena that concern us. We must base any quantitative interpretations of polymorphism, phase transitions, and solid solution in a clinker mineral, for instance, on the structure of the real crystal.

Thus the simplicity, definiteness, and permanence of composition decreases as the state of union or independence between each individual atom and its neighbors becomes less distinct, even in molecular compounds. In the materials that concern us, many of the interactions between atoms are not covalent at all, but ionic. Ionic and metallic bonding form stable structures in which a given atom is surrounded by a proper number of others of suitable type, the exact identity of the surrounding atoms being secondary to their size and electric charge. The numbers of positive and negative ions must of course be such as to yield zero net charge in the macroscopic crystal.

The tendency to form a complete coordination shell around each atom leads geometrically to aggregates that are indefinitely large in all three dimensions, rigid, and periodic in structure. Such an aggregate is not a molecule, but a crystal. Furthermore, the nonspecificity of the interactions between atoms permits the displacement, removal, or replacement of a small fraction of the atoms of a given element, with correspondingly small fractional change in the energy of the aggregate. Such a process changes the "pure" crystal to a solid solution.

Crystal Structures

A compound that is not defined by a molecular structure is in fact rather poorly defined. The preceding sketch of the transition from small covalent molecules to large ionic aggregates suggests that the formulas of ionic compounds, to represent properly the corresponding aggregates of atoms, should contain extremely large numbers. The simple formulas we actually use are justified by an idealization of the crystal structure.

The ideal crystal is conceived as a repetition, through the translations of a three-dimensional lattice, of a single aggregate of atoms. Whether this aggregate is a molecule, or simply the contents of a geometrical unit cell in a purely ionic structure, its formula is the formula of the substance. Moreover, this ideal structure may have a space group whose symmetry elements prescribe certain equivalences between groups of atoms within the unit cell. The asymmetric unit, from which the space-group symmetry generates the entire structure, may be an even smaller aggregate of atoms whose formula represents the substance. This smallest aggregate must contain equal positive and negative ionic charges, but may be only conceptual. The mistake of assuming it to be a physical entity is well expressed by Sir Lawrence Bragg [1960]: "Having found that the numbers of ladies and gentlemen at dinner parties is generally equal, we had falsely concluded they were all necessarily married couples, instead of realizing that it was because each lady liked to have a gentleman on either side, and vice versa."

Real Crystals

In real crystals there are many types of departures from the ideal infinite structure of atoms, related by the exact translations of the lattice and other symmetry elements of the space group. One of the most evident departures from the ideal is finiteness of size, which affects the Fourier transform representing the diffraction properties of the crystal [Hosemann and Bagchi, 1953]. Other departures, such as mosaic structure and thermal vibration, are usually considered in crystal structure analysis because of their effects on the diffracted intensity [James, 1954]. The discussions of these effects treat the structure itself as a continuum, and may apply to any crystal. We are more interested, however, in the interactions of particular atoms in specific structures that affect the phase equilibria, transition rates, growth, and thermal, mechanical, and electrical properties of the crystals so powerfully. The success of solid-state physics with the study of certain materials, in which these properties are crucial, indicates that our understanding of the behavior of cement clinker minerals will be greatly enhanced by future research, as our understanding of their composition has already been strengthened by structure investigations in the past.

Dislocations

Of the various types of imperfections in crystals, the most ubiquitous are dislocations. These are loci at which the arrangement of atoms is different from that in the ideal structure because two parts of the structure separated by a half-plane (a plane that slices into, but not through the crystal) are displaced relative to one another.

Screw Dislocations

When the displacement is parallel to the boundary of the half-plane, as in figure 5, a screw dislocation results. Such screw dislocations have been shown to exist in a great many crystals [Verma, 1953] and probably form the mechanism of most crystal growth from fluid phases. Estimates of the relative energies of deposition on a perfect crystal face and on a stepped face [Stranski, 1949; Frank, 1949; Verma, 1953], indicate that the former process cannot lead to a significant rate of growth under most ordinary conditions, but the latter can. If the step is due to a screw dislocation, as in figure 5, further deposition perpetuates it as growth proceeds around the screw, through any number of successive layers. Experimental evidence seems to favor this mechanism for many instances of crystal growth [e.g., Albon and Dunning, 1960].

If the displacement that forms the step height is only one layer of atoms, or one unit cell of the ideal structure, then we may expect the crystal to resemble the ideal structure except for the minute fraction of the atoms lying at the locus of the screw dislocation. On the other hand, if the displacement is more than one unit of the structure, the structural relationship within the layer of atoms deposited at the step may be different from that between the new layer and its predecessor. There may be, for instance, a difference in the manner in which planes of atoms are stacked on one another—a stacking fault—between successively deposited layers. Being regularly repeated, this difference constitutes a change in the repetitive pattern of the ideal crystal. Depending on the importance we attach to the new arrangement as an individual structure, we might call it a superlattice, a polytype, or a polymorph.

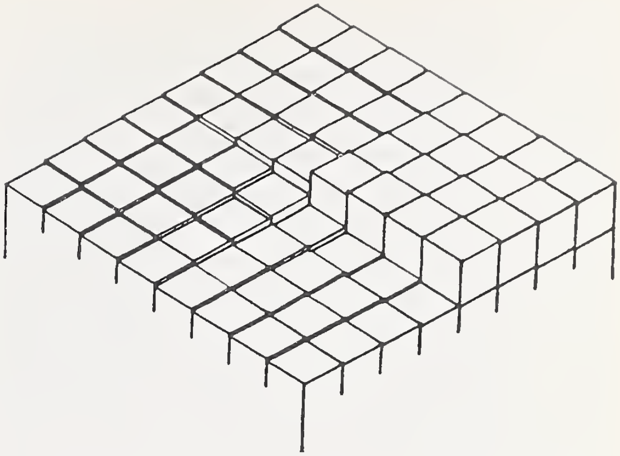

Figure 5. *A screw dislocation with a step height of one unit cell (Frank, 1949).*

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Structures that develop by the stacking of close-packed layers of atoms [Pauling, 1942] are affected comparatively little in energy by an error in the placement of one layer relative to its predecessors, as the relations between nearest neighbors are unchanged. Many structures which are geometrically related to close packing, such as those of zinc sulfide, silica, ice, and silicon carbide, can accommodate random or regular changes in the stacking pattern. In the case of silicon carbide [Ramsdell and Kohn, 1952] more than sixteen different polymorphs have been identified, and in a number of these the lattice period has been correlated with the measured step height of screw dislocations in the crystals [Verma, 1951; Frank, 1951]. Bernal [1954] mentioned in the preceding Symposium the possibility that the large unit cells of certain clinker minerals may originate as the step height in a screw dislocation through which growth of the crystal takes place.

Edge Dislocations

If the relative displacement of the two parts of the structure is perpendicular to the edge of the half-plane separating them, rather than parallel as for a screw dislocation, the result is called an edge dislocation. A section through such a structure is beautifully represented in photographs of bubble models by Bragg and Nye [1947]. A simple diagram representing a series of edge dislocations is shown in figure 6. This figure suggests the manner in which an array of dislocations may represent a grain boundary in a mosaic crystal or a polycrystalline single-phase specimen. The geometry and properties of such boundaries in comparatively simple structures have been thoroughly reviewed by Amelinckx and Dekeyser [1959]. Dislocations at grain boundaries and within nearly perfect crystals are strikingly displayed by the elegant X-ray diffraction technique of Lang [1959], which even yields stereoscopic "photographs" of their distribution.

Observation of the bubble models suggests that an edge dislocation in a ductile material should move through the crystal rather easily. The theory of the energies and motions of dislocations [Fisher et al., 1957; Atwater, 1959; Amelinckx and Dekeyser, 1959] appears indispensable for understanding such phenomena as creep, recrystallization, and diffusion in metals.

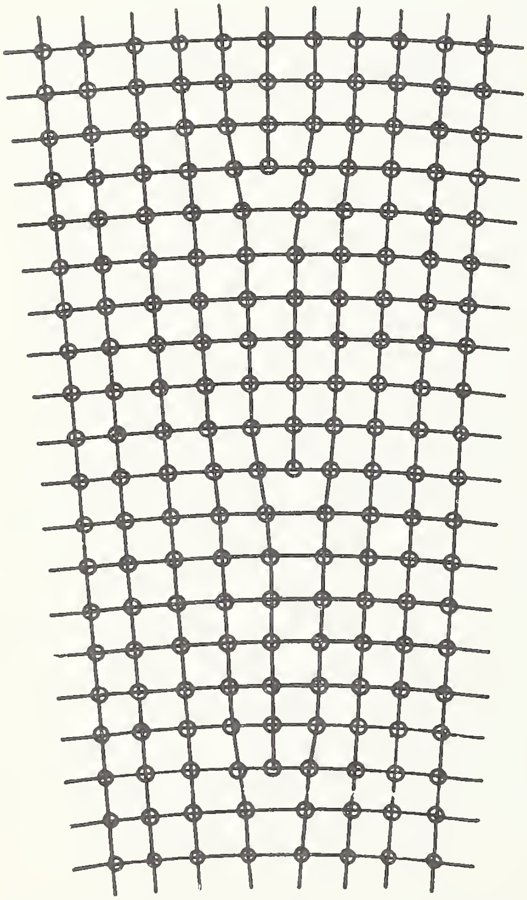

Figure 6. *A series of edge dislocations forming the grain boundary between two single crystals of slightly different orientation (Amelinckx and Dekeyser, 1959).*

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The more complex, rigid, and brittle structures of the cement clinker minerals permit comparatively little movement of dislocations at room temperature, but at elevated temperatures such processes may occur rather freely. Certainly many ordinarily brittle materials raised to high temperatures, such as sapphire above 1,000 °C [Wachtman and Lam, 1959], readily undergo plastic deformation.

Point Defects

The presence of dislocations in the crystal structure implies a departure from the ideal arrangement of atoms but not any particular departure from the ideal composition of the crystal. Departures from the ideal composition may exist, however, and in three possible ways: (1) by the substitution of an atom of a different element for one that is present in the ideal structure; (2) by the removal of an atom from the ideal structure to leave a vacancy; (3) by the incorporation of an interstitial atom in the space between atoms of the ideal structure. In each case, the unit involved can also be more than one atom—a complex ion or a molecule.

There is bound to be a finite equilibrium concentration of each possible type of defect in any crystal [Frenkel, 1946]. We discuss the behavior of individual impurity atoms or vacancies, and their interactions, treating their concentration as a continuous variable. If all possible sites are saturated, or a definite fraction in an ordered manner, the result is a new ideal structure. Thus the equilibrium concentration of randomly distributed defects would represent the equilibrium solid solution in the terms of the discussion of "Solid Solutions," and an ordered array of identical defects would constitute a definite compound in the terms indicated under "Crystal structures."

We might expect our clinker "compounds" to be Daltonides—fixed in composition—if their crystallization and subsequent passage through all phase transitions has been very slow. We expect that they may be Berthollides—variable in composition—if held above the temperature at which ordering of defects occurs, or if cooled too rapidly for the ordering process.

When a phase change requires diffusion of atoms to new sites (as in a transition between order and disorder of point defects) or realignment of unit cells (as in the formation or removal of stacking faults) it may not take place rapidly or completely. Such effects are well known in cement clinker (see, for example, the discussion of dicalcium silicate by Nurse [1954] in the previous Symposium), and have been even more intensively studied in some other silicates. Megaw [1959] has described the structural relations among the felspars, in which the distribution of silicon and aluminum atoms among their sites is ordered at low temperatures and becomes disordered on heating through the transition to a high temperature form, but cannot be reordered by cooling or further treatment. Other cases of sluggish transformation are discussed by Buerger [1951]. Clearly we may expect the crystals in clinker to have equilibria that are inaccessible under some conditions.

Thus a clinker constituent may vary in composition at the high temperatures of burning, and may vary in structure as well after cooling. The precise determination of these variations in all details is beyond the power of our present physical and chemical methods, except perhaps for sizable single crystals. The X-ray diffraction pattern of a microcrystalline sample leaves in doubt not only its surface chemistry but also much about its internal structure that has chemical significance.

Oscillation and Rotation

The ordering of defects may constitute a phase change as discussed under "Continuity With External Conditions," even though the energy involved is very small. This kind of process has been intensively studied in metallic structures such as the copper-gold alloy Cu_3Au and β-brass CuZn [Siegel, 1951].

There are, however, other kinds of disorder that may also be responsible for phase changes. Whenever certain atoms in the unit cell may rest in one of two or more positions of approximately equal energy separated by a potential barrier, there is a possibility of disorder without change in the unit cell contents.

The possibility of rotatory oscillation of certain groups such as NH_4 [Marshall, Staveley, and Hart, 1956] or SiO_4 [Bredig, 1943; see Nurse, 1954, and Douglas, 1954] or the oscillation of an ion [Megaw, 1954], may provide a mechanism for an order-disorder transition. In ferroelectric and ferromagnetic substances the spontaneous electric or magnetic polarization results from ordering of dipoles; it disappears at the Curie temperature, above which the dipole orientations are disordered. Some iron-containing phases of interest to the clinker chemist may well show transitions of this kind.

Clinker Structures

The models that have developed in the vigorous growth of solid-state physics are already helpful for understanding in general certain aspects of the behavior of clinker mixtures, but many detailed interpretations will require further study or experimental data. We shall review only the knowledge of clinker structure revealed by the literature since the previous Symposium.

A general result of considerable interest from recent X-ray powder work on clinker is the conclusion, which Nurse has already mentioned, that the glass content is vanishingly small. This must be not only reasonable, but self-evident to anyone who has watched the rapid final crystallization of clinker melts under the microscope, as investigators have often done at the Building Research Station and the Portland Cement Association Fellowship, and probably in other laboratories as well. The presence of glass as an explanation for abnormal heats of solution may be freely replaced by the existence of disorder, dislocations, and other regions of imperfection in an aggregate of submicroscopic crystals, the difference between the two pictures being more in degree than in kind. If the X-ray and electron diffraction properties and other characteristics of the "glass" alone are measured, however, we may be led to a more detailed description that eliminates one of the alternatives. Until there is an operational distinction between them [Bridgman, 1927] economy of hypotheses dictates that we make no distinction. These two opposing views, like the crystallization and colloid theories of setting [reviewed by Bogue, 1955] and many others through the history of science, may be resolved by a more detailed description of the phenomenon, which replaces both earlier descriptions without confirming either.

The major clinker constituents appear in several cases to be superstructures, in which the true unit cell is extremely large but can be approximated by the repetition of a considerably simpler pseudostructure. Such a relationship is to be expected when the X-ray diffraction patterns of a crystal show a great many absent reflections distributed with noticeable regularity. The expectation was mentioned in the previous Symposium, for instance by Jeffery, and in fact much of the discussion at that time dealt with pseudostructures rather than the actual structures themselves.

The full unit cells of the complex clinker structures are still at the outer limits of the crystallographer's mastery, but considerable progress has been made in the interpretation of pseudostructure relationships in crystals. Reference has been made to the possible role of screw dislocations in producing layer superstructures. There are more complicated ways in which slightly unsymmetrical small units may arrange themselves so that the true large unit cell approximates a repetition of symmetrical small units. The relationship may be thought of as twinning in which the domains are only one or a few unit cells in size, rather than macroscopic. The effect of periodic structural distortion on the diffraction pattern has been discussed by Jeffery [1951]. More recently there have been notable successes in the unraveling of unit-cell twinning in a number of mineral families, such as the sulfide solid solutions whose end members are bornite Cu_5FeS_4 and digenite Cu_9S_5 [Donnay, Donnay, and Kullerud, 1958; Morimoto and Kullerud, 1959]. These minerals show transformations from twinned to simple structures at a few hundred degrees very similar to the transformations of tricalcium silicate at higher temperatures. A recent determination of a felspar structure [Newnham and Megaw, 1960] was actually carried out in two steps: first, the determination of the "average structure" and, second, of the "difference structure." It is the second step that remains, in the case of some clinker minerals.

The crystal chemistry of clinker constituents is generally surveyed through the eyes of a mineralogist, and may therefore often be interpreted in the light of well-established generalizations about the structural configurations found in minerals. To avoid being misled by extensive knowledge of stable mineral structures, we must remember that the important clinker constituents are highly unstable configurations by geological standards. They have a lower average cation charge than many minerals, and may have lower or less regular coordinations for large cations and smaller or unusually constituted complex anions. Although the cementitious properties of these substances suggest a quantitatively different environment for the reactive atoms, it is not certain that a qualitatively different picture, such as the "one-sided" coordination of calcium proposed by Büssem [1939] for tricalcium aluminate, would be justified by the energy of reaction.

The general structural relationships among the clinker constituents and other minerals have been ably reviewed by Büssem [1939] and O'Daniel [1957]. The latter concludes with a sentiment to which we heartily subscribe: "Wir müssen noch viel arbeiten!"

Calcium Silicates

Tricalcium Silicate

The pre-eminent authority on the structure of tricalcium silicate is still the work of Jeffery [1950, 1952], which was reported in the previous Symposium [Jeffery, 1954]. The alternative structure proposed by O'Daniel and Hellner [1950] has been abandoned because it disagrees with Patterson-Harker syntheses calculated from single-crystal X-ray diffraction intensities [O'Daniel, Hahn, and Müller, 1953].

The pseudostructure has been described, and shown in stereoscopic photographs [Jeffery, 1954]. It has a rhombohedral cell containing three formula units $3CaO{\cdot}SiO_2$ but is usually referred to the corresponding hexagonal cell containing nine formula units, with approximate dimensions $a=7.0$ A, $c=25.0$ A. The structure was confirmed by comparing observed and calculated intensities for 189 X-ray reflections.

Jeffery [1950, 1952] derived for alite a C-centered monoclinic lattice. In vector notation [see Buerger, 1942] this is defined in terms of the hexagonal unit-cell vectors $\mathbf{a}_H$, $\mathbf{b}_H$, $\mathbf{c}_H$ ($\gamma_H=120°$) by the equations

$$\mathbf{a}_M=\frac{1}{3}\,(14\mathbf{a}_H+7\mathbf{b}_H+2\mathbf{c}_H)$$

$$\mathbf{b}_M=\mathbf{b}_H$$

$$\mathbf{c}_M=\frac{2}{3}\,(2\mathbf{a}_H+\mathbf{b}_H-\mathbf{c}_H)$$

The expressions with fractional coefficients correspond to integral lattice translations because the hexagonal cell is triply primitive, being related to the vectors of the primitive rhombohedral cell by the usual equations [International Tables, 1952]:

$$\mathbf{a}_R=\frac{1}{3}\,(\mathbf{a}_H-\mathbf{b}_H+\mathbf{c}_H)$$

$$\mathbf{b}_R=\frac{1}{3}\,(\mathbf{a}_H+2\mathbf{b}_H+\mathbf{c}_H)$$

$$\mathbf{c}_R=\frac{1}{3}\,(-2\mathbf{a}_H-\mathbf{b}_H+\mathbf{c}_H)$$

This use of the subscript R for the rhombohedral cell should not be confused with Jeffery's [1950, 1952] notation, in which certain vectors corresponding to the hexagonal cell have that subscript. Jeffery [1952] gave the monoclinic lattice parameters as $a=33.08$ A, $b=7.07$ A, $c=18.56$ A, $\beta=94°10'$. His monoclinic cell departs from convention [Donnay and Nowacki, 1954] in having a left-handed set of axes, but this does not affect the relationships that have been discussed.

The monoclinic cell has twelve times the volume of the rhombohedral cell, and thus contains 36 formula units $3CaO{\cdot}SiO_2$, $108CaO{\cdot}36SiO_2$, or a total of 324 atoms. This large a number represents considerable difficulty to the structure analyst. It is noteworthy, however, that one axis of the large cell is simply a doubling of an elementary rhombohedral lattice translation [Jeffery, 1952]. Jeffery [1950] tentatively proposed a structure corresponding to the formula $108CaO{\cdot}32SiO_2{\cdot}2[(Al_2O_3)_x,(Fe_2O_3)_{1-x}]{\cdot}2[(MgO)_y,(FeO)_{1-y}]$, in which the two added divalent cations and the four trivalent cations substituted for silicon per unit cell play an essential structural role. He mentioned the availability of further data requiring a large-scale computer for analysis, and we hope that this work has been, or will be, carried through. The chemical uniqueness of the suggested composition for $x=y=1$ (i.e., that it is a compound rather than a solid solution) would require very careful phase-equilibrium studies or critical examination of many "natural" samples for complete confirmation, but is not essential for usefulness of the formula. Copeland et al., [1959] report that the specified composition formed two phases, and similar results have been obtained at the Portland Cement Association Fellowship [unpublished work, 1957]; but compositions only slightly different produced one phase under the same conditions, and the extent in composition of the solitary existence region may vary significantly with temperature.

The work reported by Jeffery [1950] on tricalcium silicate crystals produced by evaporating a calcium chloride flux (the procedure of Nurse, 1948, described also by Lea and Nurse, 1949) indicates that their unknown triclinic unit cell is another slightly distorted multiple of the primitive rhombohedral pseudocell. The fact that the true repetitive unit of the structure is a multiple of the pseudocell leads to "satellite" reflections in the single-crystal diffraction patterns in the following manner.

The true structure corresponds to a modulation of the pseudostructure by a three-dimensionally periodic function of comparatively long wavelength. In the diffraction patterns the Fourier transforms of the electron density distributions become visible, the pattern of the true structure being a convolution [vide Lipson and Taylor, 1958] of the transform of the pseudostructure with that of the modulating function. Distances in the transform are proportional to the frequencies of periodicities in the structure, and thus the transform of the low frequency modulating function has closely-spaced maxima.

To obtain the convolution, the widely spaced peaks in the transform of the pseudostructure (corresponding to the diffraction pattern of the rhombohedral structure) are repeatedly superimposed. Each of the superimposed repetitions of the array of widely-spaced pseudostructure peaks corresponds in position and weighting to one of the closely-spaced maximums in the transform of the modulating function. The total (corresponding to the diffraction pattern of the monoclinic structure) has strong, widely-spaced peaks like the pseudostructure, with closely-spaced peaks nearby whose intensity declines rapidly with distance from the main peaks.

A departure of the true structure from the simpler pseudostructure of rhombohedral symmetry may produce satellite reflections in this way, and may also displace the original pseudostructure reflections. The former effect is most vivid in single-crystal diffraction patterns but tends to be obscured by the powder method, which is relatively insensitive to weak reflections. The latter effect, which Jeffery [1950] detected in the single-crystal patterns by careful examination for splitting of certain spots, is detectable in well-resolved powder patterns.

The splitting of certain lines in the powder pattern has been interpreted in terms of specific distortions of the rhombohedral lattice by Yamaguchi and Miyabe [1960]. They have assumed that the unit cells for both monoclinic alite and triclinic tricalcium silicate may be approximated by the orthogonal cell whose defining vectors are

$$\mathbf{a}_Y=-\mathbf{a}_H+\mathbf{b}_H$$
$$\mathbf{b}_Y=\mathbf{a}_H+\mathbf{b}_H$$
$$\mathbf{c}_Y=\mathbf{c}_H$$

They have confirmed by high-temperature X-ray powder diffraction that the splitting of the lines changes with temperature in a manner that corresponds to the expected transitions to higher symmetry on heating: monoclinic→rhombohedral at 830 °C for alite; triclinic→monoclinic at 920° and monoclinic→rhombohedral at 970° for tricalcium silicate.

They measured the positions of peaks in the powder patterns of the low-temperature forms precisely by the internal standard method. They assigned indices to the components of the split powder lines by comparing their relative intensities with the multiplicities of the components theoretically produced by slightly distorting the orthohexagonal unit cell $\mathbf{a}_Y\mathbf{b}_Y\mathbf{c}_Y$ to monoclinic and triclinic symmetry.

Their unit-cell calculations were based on the interplanar spacings (*d* values) between 3.06 and 1.45 A, but in both of the patterns there were some parts of this region that could not be clearly indexed. The monoclinic unit cell was based on 24 indexed lines in the ranges 3.04–2.30 A, 1.83–1.53 A, and 1.487–1.459 A, and the triclinic unit cell was based on 25 indexed lines in the ranges 3.06–3.02 A, 2.79–2.31 A, 1.78–1.54 A, and 1.48–1.45 A. They found the dimensions of the monoclinic unit cell to be $a=12.246$ A, $b=7.045$ A, $c=24.985$ A, $\beta=90°04'$, and those of the triclinic cell, $a=12.195$ A, $b=7.104$ A, $c=25.096$ A, $\alpha=90°$, $\beta=89°44'$, $\gamma=89°44'$.

A calculation by the writer, using a least-squares program for the IBM 704 computer which minimizes the quantity $\Sigma(1/d^2)^2$, gave for the monoclinic cell $a=12.248$ A, $b=7.045$ A, $c=24.972$ A, $\beta=90°06'$, and for the triclinic cell $a=12.196$ A, $b=7.103$ A, $c=25.094$ A, $\alpha=89°57'$, $\beta=89°43'$, $\gamma=89°44'$. Either of the two sets of lattice parameters gives agreement between observed and calculated spacings within 0.003 A. (average discrepancy less than 0.0009 A) for the monoclinic pattern and within 0.004 A (average discrepancy less than 0.0007 A) for the triclinic pattern.

The relations between the various unit-cell vectors are indicated in figure 7. Yamaguchi and Miyabe [1960] state that their monoclinic cell corresponds to the following dimensions for Jeffery's monoclinic cell: $a=33.091$ A, $b=7.045$ A, $c=18.546$ A, $\beta=94°08'$. Their unit cells are justified by utility for indexing of the powder patterns, but do not have structural significance. A structural unit cannot properly be defined, with our present information, for the triclinic crystals, nor any but that of Jeffery for the monoclinic crystals.

The powder data of Yamaguchi and Miyabe [1960] are probably the most precise available within the range they have covered, although the tabulation by Heller and Taylor [1956] indicates

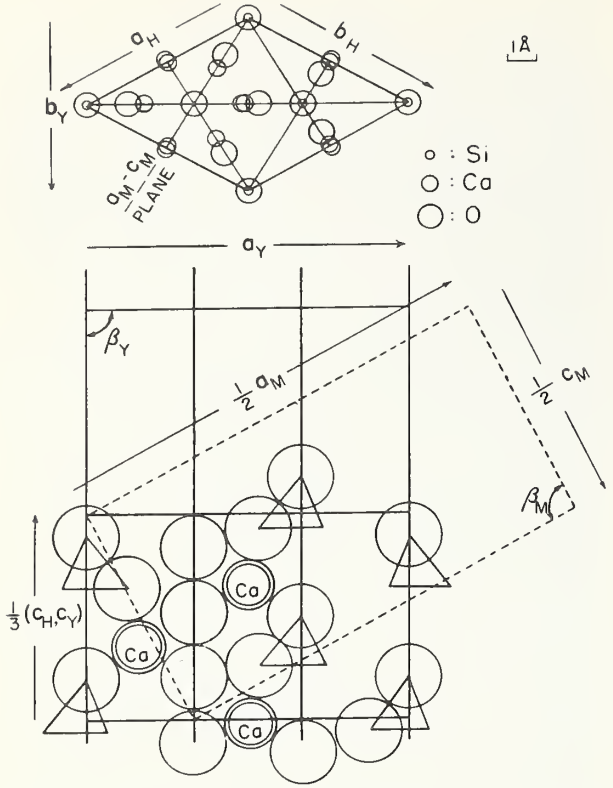

FIGURE 7. *Diagram of unit-cell relationships for tricalcium silicate.*

Subscripts indicate the definer of each set of vectors: H and M, the hexagonal and monoclinic cells of Jeffery (1950, 1952); Y, the monoclinic and triclinic cells of Yamaguchi and Miyabe (1960), from whom the diagram is adapted. (Used by permission, Am. Ceram. Soc.)

additional lines at larger and smaller interplanar spacings.

Dicalcium Silicate

No extensive structure investigations of pure dicalcium silicate or belite have appeared in the literature since the review in the previous Symposium by Nurse [1954]. His paper quotes in detail the X-ray powder data, lists the available unit-cell data from single-crystal measurements, and shows the structure found for β–dicalcium silicate by Midgley [1952a]. Extensive data on the powder patterns have been given by Yannaquis [1955]. A later review of the powder data, with indexing where possible, has been given by Heller and Taylor [1956].

The α Form

Mrs. Douglas [1952] detected a trigonal phase in crystals of bredigite from vugs in a slag, which was identified with α–dicalcium silicate. Mrs. Midgley [1952b] studied nagelschmidtite, a slag mineral containing $3CaO{\cdot}P_2O_5$ and $2CaO{\cdot}SiO_2$ in the ratio of 1:2 or 1:3, and found that its unit cell is a multiple of that determined by Mrs Douglas. These results were discussed by Nurse [1954] in the previous Symposium.

The α' Form

Mrs. Douglas [1952] has reported preliminary studies of bredigite, a naturally occurring calcium orthosilicate of the composition $(Ca_{1.59}Ba_{0.08}Mg_{0.31}Mn_{0.09})SiO_4$. This material gives a significantly different powder pattern from pure α'–Ca_2SiO_4, but probably is closely related in structure. The analogy with β–K_2SO_4 [Bredig, 1950] may be approximately but not exactly true.

The β Form

The determination of the structure of β-dicalcium silicate (B_2O_3-stabilized) by Mrs. Midgley [1952a] makes this the most carefully investigated of the several polymorphs. The determination was based on 200 measured X-ray diffraction intensities—73 *h0l*, 100 *0kl*, and 27 *hk0*. The structure amplitudes calculated from the final atomic coordinates agree with observed values to an average discrepancy of 19 percent. This is reasonable confirmation of the basic structure, although the use of additional data on *hkl* reflections in more elaborate calculations might permit refinement of the atomic positions to higher precision.

The γ Form

Nurse [1954] reported that there were no single-crystal data on γ-dicalcium silicate. The reason for this lack is the fact that the crystals are obtainable only by dusting of the β form, and these are extremely small. Recently D. K. Smith of the Portland Cement Association Fellowship has been able to isolate usable single crystals of the γ form, however. He has been able to collect complete X-ray intensity data on this polymorph, confirm that it has the olivine structure as proposed by O'Daniel and Tscheischwili [1942], and determine the atomic positions with good precision. This work will be reported separately.

Calcium Aluminates

Tricalcium Aluminate

The paper on this phase in the previous Symposium [Ordway, 1954] was mainly a discussion of the pseudostructure proposed still earlier by Professor Büssem [1938]. The unit cell and space group (T_h^6—$Pa3$) of the true structure were given, but not a complete structure determination. Other activities have prevented us from applying the large-scale computation facilities now available to the X-ray intensity data on tricalcium aluminate, which were gathered some time ago, but it is hoped that this work can be carried through in the near future.

The X-ray powder pattern of tricalcium aluminate was given in detail in the previous Symposium by Yannaquis [1954], and even more high-angle lines were reported by Swanson, Gilfrich, and Ugrinic [1955]. The latter authors report the lattice constant as $a=15.262$A at 25 °C.

$12CaO\cdot 7Al_2O_3$ and $5CaO\cdot 3Al_2O_3$

The literature on "12:7" or "5:3" calcium aluminates is a striking example of the uncertainties in ascribing formulas to ionic compounds that form at high temperatures. Shepherd, Rankin, and Wright [1909] reported stable and unstable 5:3 compounds. Koyanagi [1931] thought there might also be a 3:2 compound. Büssem and Eitel [1936] found a crystal structure for the stable cubic compound corresponding to the 12:7 ratio. Lagerquist, Wallmark, and Westgren [1937] proposed a 9:5 formula. Aruja [1957] determined the unit cell and space group for orthorhombic crystals grown with a hot wire device by J. H. Welch. These apparently correspond to the "unstable 5:3" phase originally reported, and actually do have the 5:3 ratio.

At this stage, the formula must derive from a knowledge of the chemical composition, the unit cell, and the density. It is necessarily assumed that there are no defects in the structure. The manner in which these data determine the formula is best shown in a graph such as figure 8. Its coordinates are the numbers of formula units (CaO and Al_2O_3 respectively) in the unit cell. For any calcium aluminate of given unit-cell volume V and density ρ the possible compositions are represented by a line of negative slope, whose intercepts are ($NV\rho\div$formula weight of CaO) and ($NV\rho\div$formula weight of Al_2O_3) where N is Avagadro's number, or 0.01074 $V\rho$ formula units of CaO and 0.00591 $V\rho$ formula units of Al_2O_3 where V is in A^3 and ρ is in g/cm^3. Results of a chemical analysis are indicated by a line through the origin with a slope that corresponds to the molar ratio found. The line from the crystal data and that from the analytical data should intersect at a point whose coordinates are the integers x and y in the formula $x CaO\cdot y Al_2O_3$ for the unit-cell contents.

Inspection of the figure shows that the intersections are indeed closer to the points $24CaO\cdot 14Al_2O_3$ and $20CaO\cdot 12Al_2O_3$ than to the other possible points nearby. It also shows how slight an error in chemical composition, unit-cell size, or density would be required to change the indicated formula.

The structure proposed for $12CaO\cdot 7Al_2O_3$ by Büssem and Eitel [1936] is based on 51 estimated X-ray intensities. It does not account for two of the oxygen atoms, which were taken to be statistically distributed over a number of possible positions in the unit cell. Definite positions for these atoms were felt to be unlikely because the unit cells of lower symmetry that were tried did not give satisfactory calculated intensities, and no superlattice lines were seen in the powder pattern. This structure seems worthy of further study with the more powerful experimental and computational techniques now available to crystallographers, but the validity of the 12:7 formula is independent of the structure determination, as figure 8 shows.

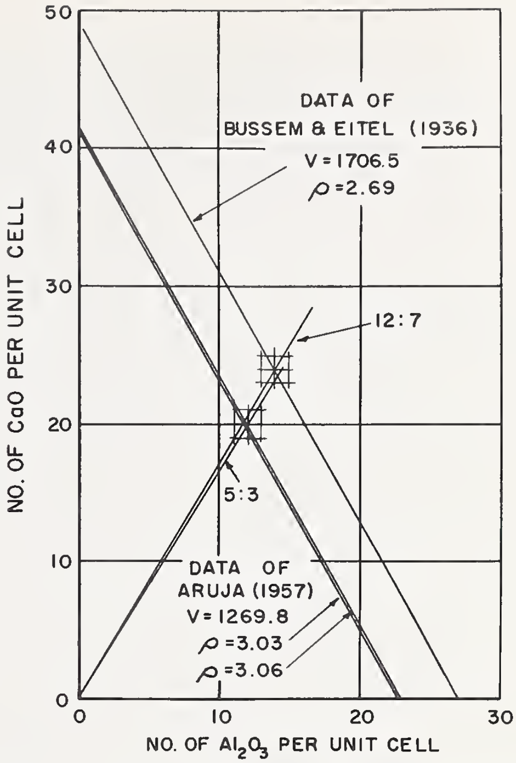

FIGURE 8. *Unit-cell contents of calcium aluminates based on unit-cell volume V (A^3), density $\rho(g/cm^3)$, and molar ratio* $CaO:Al_2O_3$.

Aruja [1957] has noted an analogy between $5CaO\cdot 3Al_2O_3$ and gehlenite, $2CaO\cdot Al_2O_3\cdot SiO_2$, which may be a useful starting point in determining the 5:3 structure.

Ferrites

Nurse's paper in this Symposium reviews the phase-equilibrium studies on the ferrite solid-solution series. The continuous variation in positions of the X-ray powder lines with the parameter p ($0\leq p\leq 0.69$) in the general formula $2CaO\cdot(Fe_{1-p}Al_p)_2O_3$ was used by Midgley (1958) for characterizing the ferrite phases in clinker samples, and by Newkirk and Thwaite [1958] for determining the tie lines representing equilibria, in the ternary system C–A–F at various temperatures, between ferrite, liquid, and either lime, C_3A, or $C_{12}A_7$. The apparent tendency of the solid solution toward lower lime content with increasing p, reported by Newkirk and Thwaite [1958,] might be taken to suggest replacement of some lime by FeO, but the phase-equilibrium study of Phillips and Muan [1958] argues against such an explanation. Studies of the structure have concentrated on the variation of p and ignored any possibility of other departures from the formula mentioned above.

It was Büssem [1937, 1939] who found for $2CaO\cdot(Al_{0.5}Fe_{0.5})_2O_3$ the probable space group *Imma*—D_{2h}^{28} [International Tables, 1952] and proposed the structure of layers of RO_6 octahedra separated by calcium ions from alternating layers of RO_4 tetrahedra. He took the cations *R* to be aluminum in the octahedra and iron in the tetrahedra. Cirilli and Burdese [1951] and Malquori and Cirilli [1954] accepted the space group *Imma* for the entire solid-solution series, but believed the aluminum to be distributed randomly over both tetrahedral and octahedral sites. Bertaut, Blum, and Sagnières [1957a, 1957b, 1959] investigated $2CaO{\cdot}Fe_2O_3$ and found the space group to be $Pnma$–D_{2h}^{16}. (Their unit cell has the *a* and *c* axes interchanged from the choice of Büssem. Thus their paper states the space group as $Pcmn$—D_{2h}^{16}, and the *h* and *l* indices of X-ray reflections in their tables must be interchanged for comparison of tabulated intensities.) The determination of the atomic positions for $2CaO{\cdot}Fe_2O_3$ [Bertaut, Blum, and Sagnières, 1959] has been done with considerable precision, although the rather large corrections for absorption applied to the measured X-ray intensities were estimated empirically. The final average relative discrepancy between measured and calculated structure amplitudes of the 252 reflections they observed was 14.7 percent.

The series has been further investigated by D. K. Smith [1960]. He obtained X-ray precession patterns from carefully annealed single crystals with seven different values of *p* covering the possible range, and found that there is actually a definite change of symmetry. As *p* increases from zero to 0.33, certain X-ray reflections of considerable intensity permitted by the space group *Pnma* decrease steadily to zero. The added extinctions correspond to the higher symmetry of the space group *Imma*.

Smith's interpretation of this symmetry change is shown by stereoscopic drawings in figure 9, superimposed on the structure found by Bertaut, Blum, and Sagnières [1959]. As the figure shows, the increased symmetry corresponds to a slight rotation of the tetrahedral groups.

In conjunction with the change of symmetry there is a change in the slopes of certain interplanar spacing curves as a function of composition. This nonlinearity was noted by Newkirk and Thwaite [1958], and is visible in the curves published by Malquori and Cirilli [1954] and Midgley [1954, 1958]. Like the change in symmetry, it suggests that the substitution of aluminum for iron atoms with increasing *p* does not take place in the same manner throughout the composition range.

Smith studied the ionic packing affecting the symmetry change, and compared the intensity variations of the sensitive X-ray reflections with those calculated for various distributions of the aluminum atoms. He concluded that the aluminum substitutes only for iron in the tetrahedral positions at first, but when *p* reaches 0.25–0.3 the substitution in octahedral positions appears to become equally probable. The phase change is a so-called "higher-order" transition. Further details on these changes will be available at the completion of a full three-dimensional structure refinement based on integrating Weissenberg data, which is being carried out.

It is interesting to note that none of Smith's single crystals, grown from the melt by lowering the furnace temperature 1 °C per day, showed detectable elongation of diffraction spots which would be expected if compositional zoning caused variations of *p* by 0.05 or more within the crystal. Swayze [1946] has repeatedly emphasized the likelihood of zoning as a persistent phenomenon because of nonequilibrium crystallization around a protected phase. Midgley [1958], in surveying the powder patterns of numerous cements, found

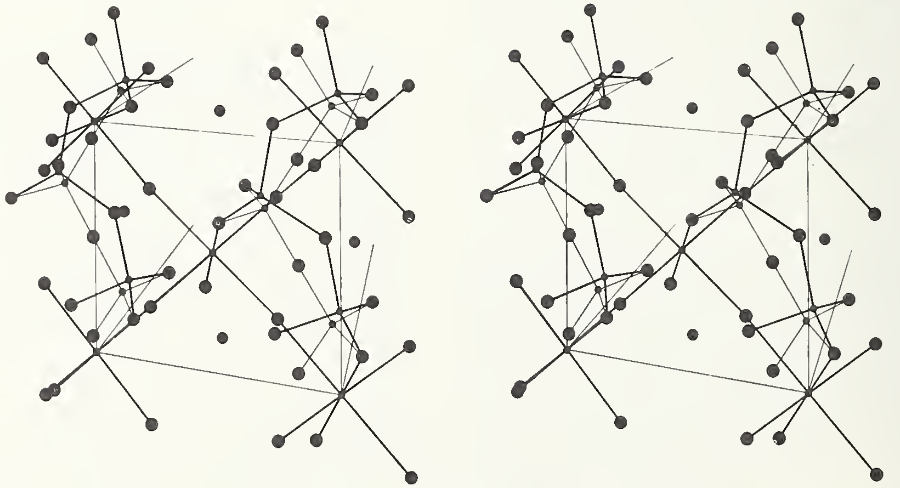

FIGURE 9. *Stereoscopic pair showing half of the unit cell of* $2CaO{\cdot}Fe_2O_3$. (*Smith, 1960.*)

The full unit cell contains four formula units. The *a* axis is vertical, the *b* axis points away from the observer, and the *c* axis is approximately horizontal and parallel to the page. The atoms connected by lighter lines indicate the proposed structure of higher symmetry corresponding to $p \geq 0.03$.

(To view in three dimensions, hold the figure about 10 cm from the eyes and rotate slowly until the blurred images merge. Then move it away without rotation until the merged images focus. A stereoscope can be used instead, if desired.)

in many cases a considerable line broadening ascribed to zoning. The aluminum and iron atoms apparently have a sufficiently high diffusion coefficient at the higher temperature to approach equilibrium in some clinkers but not in others. The dependence of this diffusion rate on temperature and composition should be studied quantitatively for better understanding of clinker. Even if the dependence is simple, however, its use by the chemical engineer to predict the results of given processing conditions will be a far more difficult statistical problem.

Techniques

The long-range goal of structure studies for clinker chemistry may be to determine atomic configurations that will guide the refinement of statistical models, in the theoretical approach mentioned at the start of the section on "Fundamental Concepts". The more immediately visible short-range goal, however, is the characterization of phases and transitions. For this purpose the crystallographer has continuously striven to examine real equilibrium structures, rather than "quenched" or metastable ones. The development of high-temperature microscopy, mentioned in Nurse's paper in this Symposium, is one result of this tendency.

For structure investigations, the most important developments are naturally improvements in high-temperature X-ray diffraction techniques. Powder diffraction cameras for high-temperature work have long been available, and much of the progress in studies of high-temperature polymorphism has come from their use. High-temperature microscopy has been reviewed by Brenden, Newkirk, and Bates [1960]. The hot-wire technique developed years ago for high-temperature microscopy has been used with the X-ray powder camera at the Building Research Station [Aruja, Welch, and Gutt, 1959], and we have tried similar experiments at the Portland Cement Association Fellowship. The apparatus has the advantage of being easily set up, adjusting quickly to a desired temperature, and requiring only small samples, but for our purposes these were not major considerations and many of the published designs for conventional high-temperature powder cameras seemed to have more important advantages. Since the counter diffractometer appears to promise better sensitivity for detecting weak powder lines and resolving complex patterns, we have been rather more interested in high-temperature diffractometer equipment. Several papers have described furnace attachments for use with the diffractometer [Chiotti, 1954; Mauer and Bolz, 1955; Perri, Banks, and Post, 1957], but they have either required a vacuum or special atmosphere or been incapable of routine operation over the entire temperature range (to 1,650 °C) in which we are interested. Further development of such apparatus will be extremely helpful to clinker chemists.

For the structure worker, an even more potent tool is the technique of high-temperature single-crystal X-ray diffraction. Development of that technique was the prime object of the improved version of the original hot-wire apparatus [Ordway, 1954], constructed at the Portland Cement Association Fellowship about the time of the previous Symposium [Ordway, 1955]. This unit, having automatic temperature control (fig. 10) and a suitable physical design, is intended for growing crystals under the misroscope and then transferring them, without further cooling, to the precession camera for X-ray diffraction. Similar use could undoubtedly be made of the apparatus developed by Aruja, Welch, and Gutt [1959]. Other devices for single-crystal X-ray work at elevated temperatures [Dent and Taylor, 1956; McKeown, 1956; Katz and Kay, 1957; Smith and Brown, 1959] either do not approach the highest temperatures we require or do not provide conveniently for microscopy, although some may give better uniformity of temperature across the sample.

Even the hot-wire apparatus, seemingly best for the intended manipulations, has shown certain remaining difficulties in our few preliminary tests. The removal of superfluous liquid from the crystal, and its firm attachment to the wire in order to maintain fixed orientation, are now extremely painstaking operations. The technique will have to be improved for routine use, but such a development seems inescapable. To obtain full structural information the original high-temperature clinker constituents must be examined, since they undergo so many changes when cooled.

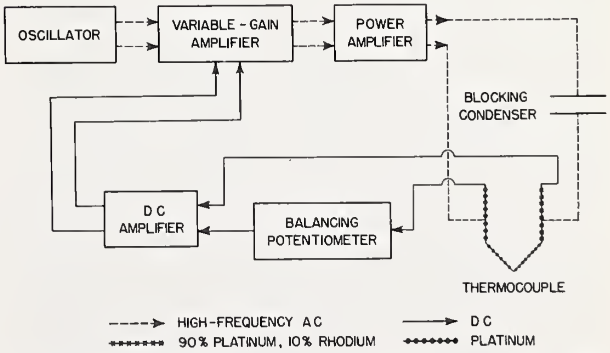

FIGURE 10. *Basic circuit of hot-wire apparatus with automatic temperature control.*

Conclusion

Further development of specialized high-temperature techniques and of the more generally used methods of structure analysis, and more intensive use of the methods already available, will undoubtedly reveal much about the structures of clinker minerals. The full benefit of this knowledge cannot be obtained, however, unless we apply it widely. The phenomena observed qualitatively in phase-equilibrium studies on clinker, or quantitatively in thermodynamic measurements, must be fundamentally interpreted in terms of structure. The results of our engineering processes of clinker burning and cooling must be interpreted in terms of microstructure and the reaction kinetics within small particles, which must be further interpreted in terms of the arrangements and motions of atoms. Regardless of the possible economic benefits, I am confident that our understanding of these processes will grow. It is sure to progress as long as it can enlist the talents of as many practitioners of insatiable human curiosity's highest development—modern science—as the present Symposium represents.

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Paper II–S1. The Effect of Minor Components on the Hydraulicity of the Calcium Silicates *

J. H. Welch and W. Gutt

Synopsis

Early studies on the constitution of cement clinker sought to interpret cement properties in terms of potential compound formation, because an overall chemical analysis of cement clinker was not in itself sufficiently indicative of the behaviour of the material.

Model phase equilibrium studies are necessarily restrictive in relation to the number of components studied, and we have become accustomed to interpreting cement performance in terms of the potential calcium silicate, aluminate, and aluminoferrite formation from the available CaO, SiO_2, Al_2O_3, and Fe_2O_3. As these oxides comprise the bulk of the clinker, the minor components have tended to assume a correspondingly minor significance.

This paper emphasises the importance of minor components in modifying the properties of the major clinker phases, a role in which their influence is far greater than their quantitative representation in the clinker might suggest. The separate effects of phosphate and fluorine additions to C_2S and C_3S have been studied in relation to the formation, polymorphic stabilization, decomposition, and hydraulicity of the calcium silicates. The effect of fluorine additions to a phosphatic clinker has also been investigated, and the results obtained underline the importance of not relying too much on subjective estimates of cement quality, based on microscopic examination of the phases present in the clinker.

It is concluded that a knowledge of the chemical composition of the major phases is insufficient to define their qualities, and that atomic arrangement as influenced by minor components plays an extremely important part in determining their potential hydraulicity.

Résumé

Les premières études sur la constitution du clinker de ciment cherchaient à interpréter les propriétés du ciment en fonction de formation potentielle des composées, parce qu'une analyse chimique complète du clinker de ciment n'était pas en soi une indication suffisante du comportement du matériau.

Les études modèles sur l'équilibre des phases sont nécessairement restrictives par rapport au nombre de composants étudiés, et nous avons pris l'habitude d'interpréter le comportement du ciment en fonction de la formation potentielle du silicate, aluminate, et de l'aluminoferrite de calcium à partir des CaO, SiO_2, Al_2O_3, et Fe_2O_3 disponibles. Comme ces oxydes comprennent la plupart du clinker, on a eu tendance à accorder aux composants mineurs une importance également mineure.

Cet exposé souligne l'importance des composants mineurs en ce qu'ils modifient les propriétés des phases majeures du clinker, et dans ce rôle leur influence est bien plus forte que ne le suggère leur représentation quantitative dans le clinker. Les effets séparés des additions de phosphate et de fluor aux C_2S et C_3S ont été étudiés par rapport à la formation, la stabilisation polymorphique, la décomposition, et l'hydraulicité des silicates de calcium. L'influence d'additions de fluor à un clinker phosphaté a également été examiné, et les résultats obtenus soulignent le fait qu'il est important de ne pas se fier trop aux évaluations subjectives de la qualité du ciment, basées sur l'examen au microscope des phases présentes dans le clinker.

On en conclut que la connaissance de la composition chimique des phases majeures ne suffit pas pour déterminer leurs qualités, et que la disposition atomique, en tant qu'elle est influencée par des composants mineurs, joue un rôle extrêmement important dans la détermination de leur hydraulicité potentielle.

Zusammenfassung

Die früheren Untersuchungen betreffend der Konstitution der Zementklinker haben immer versucht, die Zementeigenschaften als verursacht durch die Bildung dieser oder jener Verbindung auszudrücken, weil doch die quantitative chemische Analyse der Zementklinker keine genügende Aufschlüsse über das Verhalten des Materials gibt.

Modelle Phasengleichgewichtsstudien sind in ihrer Natur beschränkt, da man nie eine genügende Zahl der Komponenten studieren kann, und daher hat man sich angewöhnt, das Verhalten eines Zements in der Form der möglichen Kalziumsilikat-, Aluminat- und Aluminoferritbildung aus den vorhandenen CaO, SiO_2, Al_2O_3 und Fe_2O_3 zu erklären. Da diese Oxyde die Hauptbestandteile des Klinkers sind, hat man immer angenommen, daß alle anderen Bestandteile die nur in kleiner Menge vorhanden sind, auch nur die Eigenschaften in untergeordneter Weise beeinflussen.

Die Untersuchung zeigt, daß man großen Nachdruck auf die Bedeutung der Komponenten, die nur in kleinen Mengen vorkommen, legen muß, daß diese die Eigenschaften der Hauptphasen der Klinker sehr beeinflussen, daß sie dort wirklich eine Rolle, die in keinem Verhältnis zu dem Mengenverhältnis in dem sie vorkommen, spielen. Die Einzeleffekte der Phosphat- und Fluoridzugaben wurden für C_2S und C_3S in ihrer Beziehung zur Bildung,

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zur polymorphen Stabilisierung, Zersetzung und hydraulischen Eigenschaften des Kalziumsilikats studiert. Auch der Einfluß einer Fluoridzugabe in einem phosphathaltigen Klinker wurde untersucht, und die Ergebnisse zeigen, daß es falsch ist, sich zu sehr auf die subjektive Abschätzung der Zementqualität, wie sie auf der mikroskopischen Betrachtung der im Klinker existierenden Phasen aufgebaut ist, zu verlassen.

Es ist daher so, daß die Kenntnis der chemischen Zusammensetzung der Hauptphasen für die Qualitätsbestimmung ungenügend ist, and daß der Atomaufbau, der sehr durch Spurenelemente beeinflußt wird, eine große Rolle in der Bestimmung des voraussichtlichen hydraulischen Verhaltens spielt.

Introduction

It has long been asserted that the presence of phosphate in cement is detrimental to its quality, and for this reason phosphatic limestone has normally been avoided in cement manufacture. In Uganda no other limestone is readily available, and a cement industry was established there using phosphatic limestone as the basic raw material. In connection with this project, Nurse [1][1] studied the phosphate problem and his work formed the basis for the manufacturing process used. Nurse found that the presence of phosphate hindered the formation of C_3S, and that the phosphate combined to form a particular solid solution with C_2S. He recommended a limit for the phosphate content which would permit the attainment of satisfactory strength in the cement, and he devised a process of ignition, hydration, and elutriation for the limestone which would separate in the elutriation stage the phosphate exceeding this limit. As experience was gained it became known that the effect of P_2O_5 was less deleterious than had been forecast from the original laboratory work. This fact, combined with a fluorspar addition to the raw meal, has ensured the production of a cement of excellent quality.

Since the inception of the cement industry in Uganda, its material and products have been regularly examined at the Building Research Station. The present research program includes also the examination of laboratory-prepared clinkers containing phosphate alone, or phosphate and fluorine, by chemical and X-ray analysis, and by microscopy. Considerable evidence has been obtained in the course of this work that subjective estimates of cement quality, based on microscopic examination of the phases present in the clinker, can be wholly unreliable. This observation applies particularly to the presence of phosphate and fluorine, which are capable of causing profound structural modification of C_2S and C_3S, but it could clearly apply to certain other minor components as well. It appears essential to establish the precise properties of the phases present, and in particular their latent hydraulicity. Several recent papers [2–4] on the effect of minor components on cement quality contain no reference to actual strength determinations, and the conclusions drawn solely from mineralogical examination may well be misleading. In order to understand the phosphatic cement process more clearly, high-temperature phase equilibria in the system $CaO\text{-}SiO_2\text{-}P_2O_5$ have been studied, together with the separate effects of phosphate and fluorine on C_2S and C_3S. The results of these studies will now be discussed because although seemingly related to one manufacturing problem they appear to have a much wider implication.

Dicalcium Silicate

Effect of Phosphate

The dicalcium silicate phase was fully discussed by Nurse [5] in the previous Symposium. Since then, new techniques of high-temperature microscopy and X-ray analysis [6–8] have been developed which enabled Nurse, Welch, and Gutt [9] to examine the phase equilibria in the system $C_2S\text{-}C_3P$. This work revealed that not only $\beta\text{-}C_2S$ but also the α' and α polymorphs could be stabilized by appropriate additions of phosphate. The hydraulicity of these polymorphs and also of $\gamma\text{-}C_2S$ has now been determined.

Experimental Procedure

The mixes were prepared from crushed quartz (99.95% pure), $CaCO_3$ (99.9% pure), and C_2P ($\nless$99.9% pure) prepared from AnalaR phosphoric acid and $CaCO_3$. The powdered materials, which had been screened through a 100-mesh sieve, were mixed dry and ignited in platinum trays at 1,000° and subsequently at 1,550° in an electric furnace for 20 hr. The phases present were identified by means of a Guinier-type focusing camera, 114 mm. diam., with CuKα radiation. After grinding to a fineness of 4,000 cm^2/gm. with 4 percent of added gypsum, hydraulicity was determined by compressive-strength tests on half-inch 1:3 mortar cubes, which had been cured in moist air for one day and in water thereafter. The composition of the mixes and the strength results are shown in figure 1.

The quantities of material available for test necessitated the adoption of small-scale specimens. Although the strength results obtained on half-inch cubes enable a direct comparison to be made of different materials, the absolute strength figures cannot be directly compared with those obtained by the B.S. test on 2.78-in. mortar cubes. A number of portland cements were tested using the two different specimen sizes, and in this instance an approximate correlation was obtained from the expression:

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[1] Figures in brackets indicate the literature references at the end of this paper.

$$\text{Strength (2.78-in. cube)} = 2.2 \times \text{strength } (\tfrac{1}{2}\text{-in. cube}) + 1{,}200 \text{ lb/in.}^2$$

Discussion

It is clear that only β-C_2S is substantially hydraulic under the conditions of the test. In view of this, the assessment of the effect of any minor component on the quality of portland cement must take into account the possible stabilizing action on C_2S, and in this respect Nurse [5] has drawn attention to the enhanced hydraulicity of P_2O_5-stabilized β-C_2S. However, the detrimental action of P_2O_5 on cement quality, attributed by Nurse [1] to the elimination of C_3S, may additionally be due in some circumstances to the stabilization of α'-C_2S. A laboratory-produced clinker, made from a plant cement raw meal containing 1.97 percent P_2O_5 and 2.0 percent K_2O (ignition loss 30.5 percent), contained α'-C_2S as the main phase provided the clinker was cooled rapidly after ignition. The compressive strength of this cement was found to be correspondingly low. α'-C_2S has also been identified in a plant-produced cement of recent manufacture. It is possible that one of the beneficial effects of fluorspar addition to phosphatic cement raw meal as practiced in Uganda consists in reducing the content of "active" phosphate below the limit for α'-C_2S stabilization. The situation is of course complicated in practice by the simultaneous presence of several minor components.

Effect of Fluorine

The addition of fluorine as fluorspar to C_2S was ineffective in stabilizing α' or α-C_2S, the products in presence of 0.81 percent or 1.7 percent fluorine being a mixture of β and γ-C_2S. This was in contrast to the behavior of C_2S in the presence of C_3S and fluorine together, as described subsequently.

Supplementary Studies

Attempts to prepare α'-C_2S by addition of K_2O, aiming at the composition $KC_{23}S_{12}$, were unsuccessful. Only β-C_2S was obtained in these experiments in contrast to the results obtained by Suzukawa [10].

Toropov, Volkonsky, and Sadkov [11] have claimed that a β' form of C_2S exists in addition to the established γ, β, α' and α forms, and this has also been investigated. Heating for 65 days at 600° failed to produce any change in γ-C_2S. X-ray analysis at ascending temperatures as shown in table 1 gave no indication of a new polymorph.

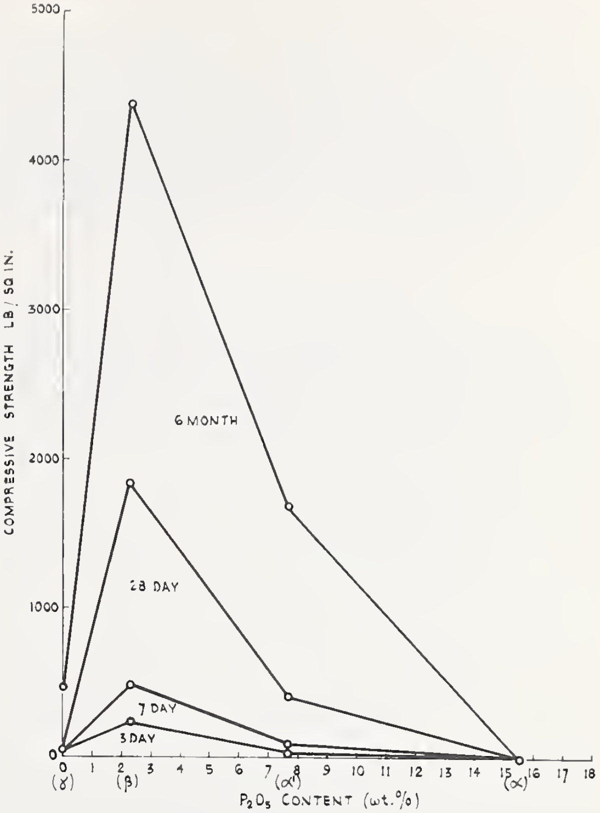

FIGURE 1. *Compressive strength (on 1/2'' 1:3 mortar cubes) of preparations on the join* C_2S–C_3P, *showing effect of* C_2S *polymorphism.*

TABLE 1. *Results of high-temperature X-ray analysis of* C_2S

Temperature	X-ray identification
Room temp.	γ
°C	
800	γ
900	γ+trace α'
1000	α'
1100	α'
1200	α'
1300	α'
1400	α'
1500	α

Tricalcium Silicate

Effect of Phosphate

Phase equilibria in the system CaO-SiO_2-P_2O_5 are being studied by Gutt [12], and this work provided compositions for the experiment. The compositions chosen lie on a hypothetical join C_3S—($24.1C_3P$–$75.9C_2S$), the latter being the composition (wt percent) at the maximum on the liquidus curve in the system C_2S-C_3P [9].

Experimental Procedure

The preparation of the mixes followed the description given earlier for the phosphatic C_2S preparations, except that the ignition time was extended to 60 hr and samples were pelleted and steamed during the heat treatment. The samples were then submitted to strength tests as described for phosphatic C_2S, to free lime analysis, and to X-ray examination.

Results and Discussion

The composition, free lime content, and phases identified in the X-ray diffraction patterns of the mixes are given in table 2, and the compressive strengths in figure 2. The X-ray diffraction pattern in mixes with 2, 3, and 4 percent of P_2O_5 was characterized by an overall increase in the line spacings, denoting a decrease in the unit cell volume as compared with C_3S. The line shift was observable at 1 percent P_2O_5 and was at a maximum at 2 percent P_2O_5, no further shift being detectable in mixes of higher P_2O_5 content. At 1 percent P_2O_5, α'-C_2S was also present and it grew in quantity as the proportion of P_2O_5 increased. Figure 6 gives the X-ray diffraction pattern of the composition containing 2 percent P_2O_5 side by side with the pattern given by a mixture of 85 percent pure C_3S and 15 percent (wt) α'-C_2S. The α'-C_2S, stabilized by P_2O_5, was added to serve as a quantitative standard for this phase in the experimental mixes. The fixed position of the α' pattern in the two films also emphasizes the relative shift in the C_3S lines.

As phosphate is added to pure C_3S, compressive strength at first falls, but as the addition continues it again rises at the composition 71.7 CaO, 26.3 SiO_2, 2 P_2O_5 (weight percent), giving by a small margin the highest strength in the series at 3, 7, and 28 days. Further addition of up to 4 percent P_2O_5 is detrimental to strength.

Table 2. *Effect of phosphate on* C_3S: *composition of mixes studied and phases present: (duplicated preparation enclosed in brackets)*

Composition			X-ray identification	Analytical [a] free CaO
P_2O_5	CaO	SiO_2		
	wt. %	*wt. %*		*wt. %*
1	72.7	26.3	$C_3S+\alpha'$ C_2S	nil
[1	72.7	26.3]	$C_3S+\alpha'$ C_2S	nil
2	71.7	26.3	$C_3S+\alpha'$ C_2S	0.1
[2	71.7	26.3]	$C_3S+\alpha'$ C_2S	.1
3	70.6	26.4	$C_3S+\alpha'$ C_2S	not det'd
4	69.6	26.4	C_3S+much-α'-C_2S	not det'd

[a] Glycerol alcohol method, W. Lerch and R. H. Bogue, Ind. Eng. Chem. Anal. Ed. 2, 296–8 (1930).

In interpreting these results, allowance must be made for the increasing amount of α'-C_2S occurring in mixes of increasing P_2O_5 content. In the 2 percent P_2O_5 mix, for example, the α'-C_2S content can be estimated to be about 30 percent by weight of the total. So far it has not proved possible to isolate the individual P_2O_5-containing C_3S phase (or phases) for study, and it has therefore been necessary to use mixes containing one additional phase and draw deductions accordingly. Since the α'-C_2S is comparatively inert hydraulically, the fall in strength in the mixes progressing from 2 to 4 percent P_2O_5 can be accounted for by the increasing dilution of the C_3S phase with almost nonhydraulic material. The 2 percent P_2O_5 mix, although diluted with some 30 percent of α'-C_2S, gives strengths comparable to pure C_3S, so that the form of C_3S present in this mix can be considered to possess enhanced hydraulic value. Between this form of C_3S and pure C_3S, however, an intermediate state occurs in the 1 percent P_2O_5 mix resulting in decreased hydraulicity.

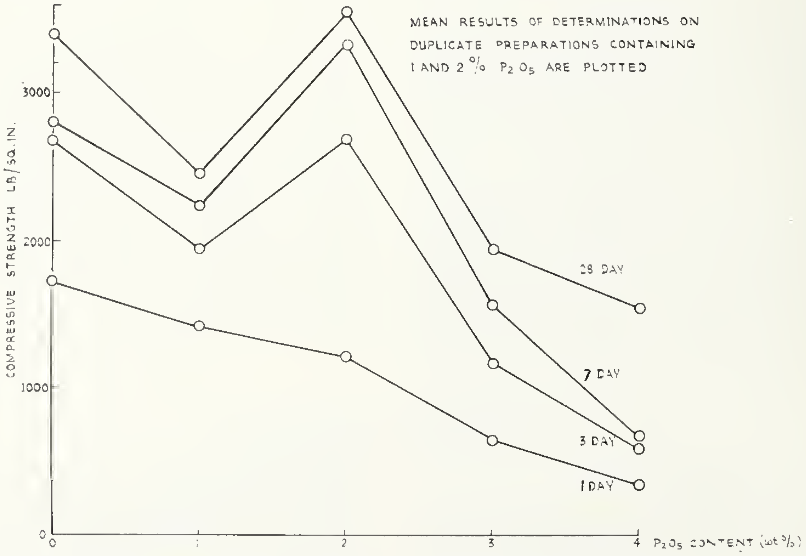

Figure 2. *Compressive strength (on 1/2″ 1:3 mortar cubes) of preparations on the join* C_3S–(24.1 C_3P, 75.9 C_2S wt %) *in the system* CaO-SiO_2-P_2O_5.

From the experimental work conducted to date it seems most probable that C_3S can take up a maximum of about 1 percent P_2O_5 in solid solution, but the results could also be interpreted on the basis of a 3 to 4 percent solubility of CaO in C_3S. The strength results may be explainable when further mixes in this region of composition have been examined. In this instance it seems that the increased reactivity of C_3S may be due to lattice distortion rather than true polymorphism.

Effect of Fluorine

Experimental Procedure

As in the preparation of phosphatic C_2S, the finely ground components, $CaCO_3$, crushed quartz, and fluorspar (99 percent pure), were mixed and pelleted, the components being proportioned to give a weight percentage composition between C_3S and fluorine. The heat treatment, however, was conducted in a closed tubular furnace designed to minimise the loss of volatile components. As expected from earlier work, a proportion of fluorine was lost during ignition, as indicated in table 3. The ignited products were analysed for free lime and fluorine content, and submitted to X-ray examination. Strength tests were determined as for the phosphatic C_2S preparations.

Table 3. *Effect of fluorine on* C_3S: *analytical fluorine and free lime in mixes studied*

Nominal composition		Actual fluorine content [a] (±0.02)	Free CaO
C_3S	F		
wt %	*wt %*	*wt %*	*wt %*
99.75	0.25	0.22	1.8
99.5	.5	.38	Nil
99.4	.6	.51	0.3
99.25	0.75	.74	.5
99.0	1.0	.88	Nil
98.0	2.0	1.73	0.1

[a] Method based on those of H. H. Willard and O. B. Winter. Ind. Eng. Chem. Anal. Ed. **5**, 7 (1933), and W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, 2d Ed., 744, Chapman and Hall, London, (1953).

Results and Discussion

The analytical results are given in table 3, and the strength results in figure 3. It was found that fluorine greatly accelerates the formation of C_3S. Whereas for complete reaction pure C_3S requires heating at 1,550 °C for about 60 hours, a fluorine content of 0.2 percent reduces the heating period to 2 hours or less. As fluorine content increases there is a progressive change in the X-ray diffraction pattern from that of C_3S towards that of alite. Triplets and doublets in the characteristic triclinic C_3S pattern tend towards single lines associated with the alite pattern. The greatest change from a pure C_3S-type to an alite-type pattern occurred in the interval between 0.38–0.51 percent fluorine, and the pattern at 0.74 percent fluorine is the nearest to that of alite found in this series (fig. 7). With still higher fluorine content, α'-C_2S and α-C_2S patterns appeared. Stabilisation of α'- and α-C_2S by fluorine alone has not been previously reported, and attempts to stabilise these forms with fluorine in the absence of C_3S were unsuccessful, resulting only in the formation of a mixture of γ and β-C_2S. It has been suggested [5] that C_2S is stabilised by CaO, and if the C_3S is regarded as a source of excess CaO the fluorspar may well be acting as a flux to aid the incorporation of excess CaO in the C_2S lattice. The composition given for the alite of normal portland cement by Jeffery [13] is $(CaO)_{54}(SiO_2)_{16}Al_2O_3MgO$, and the production of a material containing neither Al_2O_3 or MgO which gives an X-ray diffraction pattern somewhat similar to that of alite is therefore noteworthy.

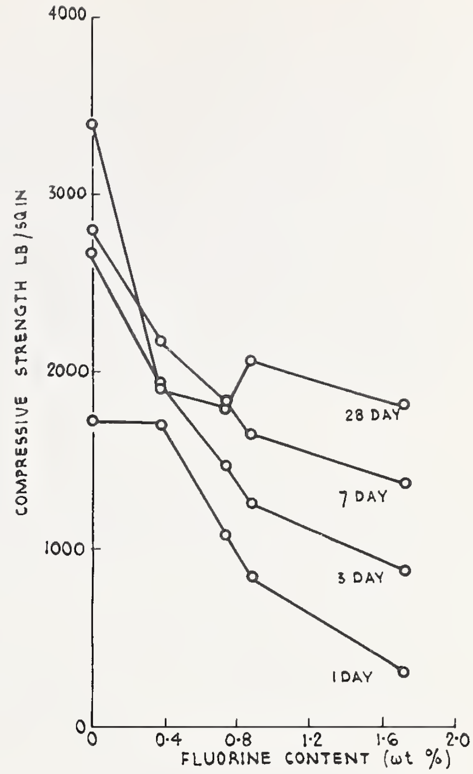

Figure 3. *Compressive strength (on 1/2'' 1:3 mortar cubes) of* C_3S *preparations with different fluorine content.*

Apart from some anomalies in the 28-day results which have so far not been accounted for, the compressive strength results given in figure 3 show that as fluorine content increases the compressive strength of C_3S decreases. Although some α'- and possibly α-C_2S, as detected in mixes of fluorine content above 0.74 percent, must contribute to the overall fall in strength, the major effects are thought to be associated with the polymorphism of C_3S. The present results indicate that the effect of fluorine is not merely that of a flux, but that structural changes are produced which have considerable influence on hydraulicity.

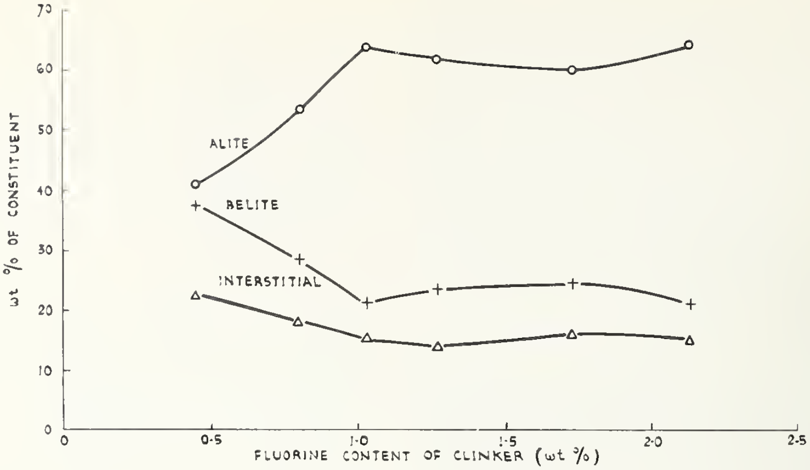

FIGURE 4. *Mineral composition of clinkers containing fluorine as determined by microscopic point counts.*

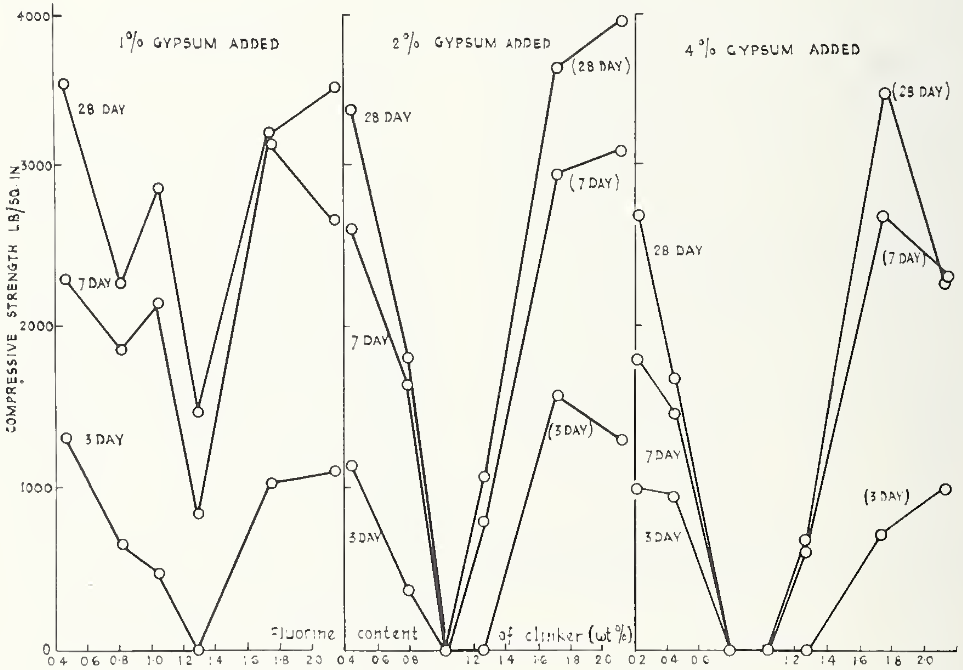

FIGURE 5. *Compressive strength (on 1/2″ 1:3 mortar cubes) of cements with different fluorine content.*

It had been previously observed in laboratory experiments on the addition of fluorspar to phosphatic clinkers that compressive strength did not rise proportionately to "C_3S" content. This is illustrated by figures 4 and 5. Figure 4 shows the mineralogical composition of the clinkers as determined by microscopic point counting, and figure 5 gives the corresponding strength results with various gypsum additions. The raw meal analysis from which this series of fluorinated clinkers was prepared is given in table 4. The lack of correlation between "C_3S" content and strength finds a partial explanation in the experimental results of fluorine addition to pure C_3S. Thus fluorine facilitates the formation of C_3S, but the fluorinated phase becomes less hydraulic, and the net effect of fluorine addition to clinker is beneficial only if the advantage of greater quantity outweighs the loss in quality.

In figure 5 two features are remarkable. First, the strength of the cement falls to a minimum in the region of 0.8–1.27 percent fluorine content, and then rises again at higher fluorine levels. This behaviour suggests that optimum performance of the cement could be achieved, at least under laboratory conditions, by careful control of the phosphate and fluorine content, and equally that considerable falls in strength might occur through unsuitable proportioning of these components. The second feature in figure 5 is the marked effect that the gypsum addition has on strength development. It can be seen that the minimum strength region referred to above is particularly accentuated by increased gypsum addition, although the reasons for this are obscure. The results do, however, emphasise the importance of the minor components in modifying the behaviour of an actual cement composition through their effect on the principal constituents.

TABLE 4. *Fluorinated clinker series: analysis of cement raw meal*

	%
SiO_2	12. 52
Fe_2O_3	4. 03
Al_2O_3	2. 79
TiO_2	0. 22
Mn_2O_3	. 23
CaO	42. 94
MgO	0. 89
Na_2O	. 65
K_2O	1. 72
P_2O_5	1. 62
F	0. 27
Total S	. 49
Sulfate (SO_3)	. 34
Sulfide (S)	. 07
Loss on ignition	31. 31
CO_2	28. 88
Loss at 110 °C	0. 70

Decomposition of C_3S

Until recently C_3S occupied a unique position in silicate chemistry. Early investigators claimed that the pure compound is formed only in a solid-state reaction between CaO and C_2S at temperatures above 1,250 and below 1,900 °C, at which temperature it again dissociates in the solid state into CaO and C_2S. It has since been established by Welch and Gutt [7] that C_3S does not decompose at 1,900°, but that it melts incongruently at 2,070° to form CaO and liquid. In fact the C_3S primary phase field in the system CaO–SiO_2 extends from the eutectic with C_2S at 2,050 °C, 69.5 wt percent CaO, to the incongruent boundary with CaO at 2,070 °C, 71.5 wt percent CaO. These results are supported by new work on the system CaO-C_2S-C_3P, in the course of which Gutt [12] has explored the liquidus surface and found that the primary crystallization field of C_3S extends to about 13 percent P_2O_5.

The lower temperature limit of C_3S stability has been regarded [14] as 1,250°, but this has been questioned by Yannaquis [15] and by Yamaguchi and Miyabe [16]. The former author maintains that only impure C_3S is decomposed at low temperature, and the latter authors state that they were able to cool C_3S slowly from 1,550 to 1,000 °C without decomposition. It must be remembered, however, that the actual rate of decomposition is very slow, and can only be detected by analysing the small quantities of free lime liberated over a period of many hours. In the present work the separate effects of phosphate and fluorine on the stability of C_3S in the region of 1,250 °C have been studied, and in both instances decomposition has been observed.

Effect of Phosphate

The composition 71.1CaO,26.9SiO_2,2P_2O_5 (wt percent) was heated for about 100 hr in turn at descending and then at ascending temperatures, free lime determinations being made between ignitions. Decomposition occurred between 1,160 (no free lime) and 1,050 °C (appearance of 1.4 percent free lime). On reheating, a reduction of 0.2 percent free lime occurred between 1,160 and 1,210 °C, thereby locating the decomposition temperature at approximately 1,160 °C. The stability range of C_3S therefore would appear to be slightly prolonged by the incorporation of phosphate.

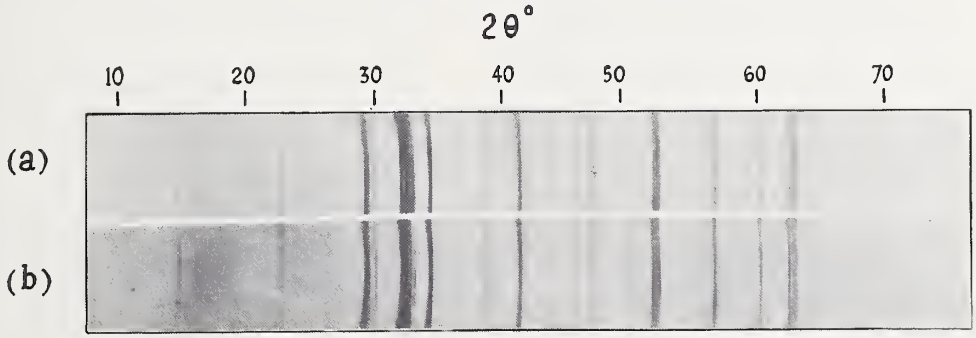

FIGURE 6. *X-ray photographs obtained in Guinier type focusing camera,* CuKα *radiation, showing shift in* C_3S *pattern due to phosphate.*

(a) Composition $2P_2O_5$, 71.7 CaO, 26.3 SiO_2, Wt. %.
(b) Mixture of pure C_3S (85%) and α'-C_2S (15%).

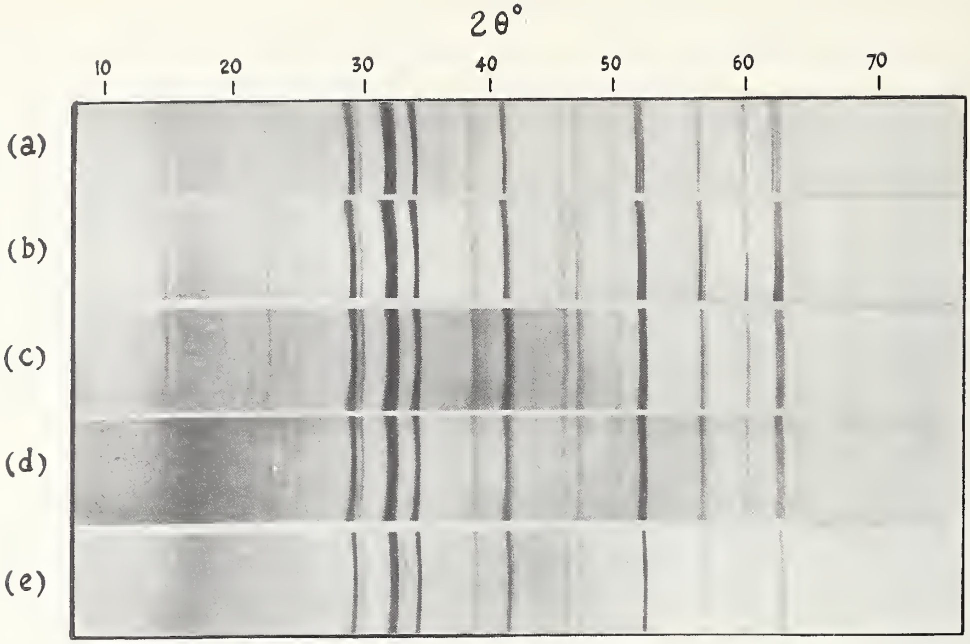

FIGURE 7. *X-ray photographs obtained in Guinier type focusing camera,* CuKα *radiation, showing change towards alite in* (C_3S+*fluorine*) *Wt% compositions.*

(a) C_3S (Pure).
(b) C_3S (0.38 F content).
(c) C_3S (0.51 F content).
(d) C_3S (0.74 F content).
(e) Alite ($C_{54}S_{16}AM$).

Effect of Fluorine

For C_3S containing 0.75 percent fluorine, decomposition was first observed at 1,230 °C and occurred readily at 1,170 °C. At the latter temperature 3.9 percent free lime was liberated after 1 hr during which the fluorine content had become reduced to 0.64 percent. The free lime had risen to 16 percent and the fluorine level dropped to only 0.06 percent after a period of 16 hr at 1,170 °C. Clearly fluorine greatly accelerates the rate of decomposition below the stability limit just as it promotes rapid combination above, and this point should be considered as one of practical importance in relation to slowly cooled fluorinated clinkers.

Conclusions

Early studies of cement constitution emphasised that gross chemical composition could only be related to cement performance by discovering the actual cement compounds produced in the clinker, and then evaluating their separate contributions to the overall behaviour. Of necessity the complexity of phase equilibrium studies has concentrated attention on the four basic components CaO, Al_2O_3, SiO_2, Fe_2O_3, and the four major phases produced by their combination in clinker compositions. In this way perhaps there has grown up a tendency to regard the four major phases as possessing rather rigid characteristics, only influenced to a minor degree by the presence of the lessor components in the raw material.

We have now progressed to the stage where we can recognise that a knowledge of the chemical composition of the major phases is not sufficient to define their qualities, and that atomic arrangement plays an extremely important part in determining the way in which water will enter into the crystal lattice and develop hydraulicity. It is in this role of modifying the crystal lattice that the minor components play such an important part, one which is quite out of proportion to their quantitative representation in the clinker.

If the significance of the minor components in cement clinker has been underestimated in the past, it is hoped that this contribution will help to underline their importance. It may also disabuse us of any idea that the constitution of clinker in terms of four major compounds gives us anything like a complete picture of predictable cement behaviour. Rather does it provide a working sketch from which we have still to fill in much of the detail.

The investigations which have been described were undertaken with the cooperation and financial support of Uganda Cement Industry Ltd.

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Discussion

C. A. White

This paper draws attention to a particular field of great importance on which there has been little previous published work. The authors have stated a very special case largely connected with the combination of the effects of both phosphate and fluoride. Ershov [1][1] has already published some unusual results on the additions of phosphate to cement raw materials. So far no mechanism for the increased hydraulicity has been proposed. The two main possibilities would appear to be, increased free surface energy of the mineral crystal faces due to the deformation of the crystal lattice by interstitial emplacement of the minor components, alternatively an effect whereby nucleation or crystal growth is controlled to give smaller crystals [2]. It would be of interest to know if the authors have noted any effect on the crystal size during their microscopic examinations.

Graphs are given showing the influence of fluorine on phosphate-containing clinkers in relation to gypsum addition and compressive strength. No evidence is given for any effects on setting times of these cements. The use of fluorine as an additive to raw meal has been variously recommended and condemned, and included in certain patents for many years. Its use in shaft kilns has been studied over the past six years and it has been found that 0.2 to 0.3 percent of fluorine results in twenty to twenty-five percent higher compressive strengths for cement compositions from sulfate resistant to 13 percent alumina content. However, it has been noted that fluorinated clinkers of this composition show different setting times when ground hot or cold, in direct relationship to the compressive strengths. Laboratory cold ground clinkers having a final setting time of 1½ hr will give 25 percent more compressive strength and yield a final setting time of approximately 5 hr when milled under normal production conditions. Heating of the cold ground cement produces a similar change. Temperature studies indicate that this is connected with formation of hemihydrate, but in the presence of fluorine no false setting or change of consistency is noted. This connection of fluorine and setting suggests that apart from effects reported by Toropov et al., [3] the fluoride ion may be complexing with aluminum and acting as a carrier in its aqueous reactions.

The general effects of such small amounts of certain minor components, there being evidence for others than phosphate and fluorine, and their influence on compressive strengths, heats of hydration and other properties are of extreme interest when it is considered that such quantities freely occur in many cement raw materials at present in use. Much further work on these lines is obviously required.

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Closure

J. H. Welch

We would like to take this opportunity of replying to the comments made by Mr. White on this paper. Our object in presenting the strength results obtained on fluorinated clinkers was principally to emphasise the danger of assessing cement quality solely by mineralogical examination without also checking on the actual strengths obtained. We realised that in so doing we were presenting data which to say the least appeared unusual, and for which we have not so far been able to find a satisfactory explanation. We felt, however, that the results were so interesting that they should be presented with the object of stimulating interest and discussion. On the points specifically mentioned by Mr. White we can give little help because no observations on setting time were made, except that it was observed that no set appeared to take place in the samples for which zero strength at all ages was reported. The mineralogical point counts revealed no outstanding differences in crystal development within the series as a whole, and this in turn appeared quite normal when compared with the appearance of typical factory produced clinkers.

Mr. White's observations on strength and setting time relationships, and in turn their relation to grinding temperature, must lead us to a more careful examination of these factors. It is somewhat disconcerting to find that an apparently well-burnt clinker might be very largely influenced in its cementing behaviour by the manner of the gypsum addition. Our view is that the gypsum addition during the grinding of cement clinker tends to be made somewhat empirically in normal circumstances, and that for fluorinated clinkers the optimum performance of the cement requires a much more rigorous appraisal of the problem than has hitherto been attempted.

Paper II–S2. X-Ray Diffraction Examination of Portland Cement Clinker*

H. G. Midgley, D. Rosaman, and K. E. Fletcher

Synopsis

Two methods of determining the mineral composition of portland cement clinker are discussed, both of which depend on X-ray diffraction analysis. The first is a modified method of compound calculation from the oxide chemical analysis, knowing the composition of the ferrite phase from an X-ray diffraction analysis. The second is compound analysis by direct X-ray powder diffraction using a counter spectrometer.

A comparison between the modified calculation, direct diffractometry and the more usual Bogue method shows that there is a better agreement between the first two than between the latter and either of the first two.

The greatest errors in the Bogue method appear in those cements with the lowest C_3A. In these cements the ferrite appears to be richest in C_2F which makes the Bogue estimate of C_3A too low. In these cases the direct diffractometry is not yet entirely satisfactory, owing to interference.

Résumé

Cet exposé présente la discussion de deux méthodes pour déterminer la composition minérale du clinker de ciment Portland; toutes deux dépendent de l'analyse à l'aide de la diffraction des rayons X. La première est une méthode modifiée du calcul des composés à partir de l'analyse chimique des oxydes lorsque la composition de la phase ferrite est connue grâce à une analyse à l'aide de la diffraction des rayons X. La seconde, qui utilise un spectromètre à compteur Geiger, est une analyse des composés par diffraction directe des rayons X par la méthode à poudre.

Une comparaison entre le calcul modifié, la diffractométrie directe et la méthode de Bogue plus habituelle, montre qu'il y a du meilleur accord entre les deux premières qu'entre cette dernière et l'une ou l'autre des deux premières.

Dans la méthode de Bogue les plus grandes erreurs se montrent avec les ciments de moindre teneur en C_3A. C'est dans ces ciments que le ferrite semble être le plus riche en C_2F, ce qui rend trop basse l'évaluation de Bogue. Dans ces cas-ci la diffractométrie directe n'est pas encore complètement satisfaisante à cause d'interférence.

Zusammenfassung

Zwei Methoden für die Bestimmung der Mineralzusammensetzung der Portlandzementklinker, die beide auf einer Analyse der Röntgenstrahlenbeugung beruhen, werden erörtert. Die erste Methode ist eine Spezialberechnungsmethode, die man anwenden kann, wenn man die chemische Oxydanalyse und die Zusammensetzung der Ferritphase von einem Röntgenstrahlenbeugungsdiagramm kennt. Die zweite Methode ist eine Verbindungsanalyse durch eine direkte Herstellung eines Röntgenpulverdiagramms, in der man ein Spektrometer mit Zähler benutzt.

Ein Vergleich zwischen der modifizierten Berechnung, der direkten Beugungsmessung und der gewöhnlich angewandten Bogue Methode zeigt, daß die ersten beiden Methoden besser miteinander übereinstimmen, als mit der Bogue Methode.

Die größten Fehler treten in der Bogue Methode bei Zementen mit kleinsten C_3A-Gehalten auf. In diesen Zementen ist der Ferrit augenscheinlich im C_2F angereichert, und das bringt hervor, daß die Bogue Abschätzung zu klein ausfällt. In diesen Fällen ist die direkte Beugungsmessung noch nicht ganz zufriedenstellend, da Interferenz auftritt.

Introduction

The normal Bogue [1][1] method of calculating the compound content of a cement assumes that there is complete combination between raw materials at maximum temperature in the kiln, and that the clinker formed is cooled slowly so that chemical equilibrium is maintained. The formulae for the Bogue system show the four constituents to be linear mathematical functions of the chemical analysis. As a result, if some property such as strength is to be related statistically to composition, it follows from the mathematics that an analysis in terms of the Bogue constitution is no more informative than one in terms of the simple oxide analysis but it gives a more enlightened picture of the function of chemical composition in cement technology.

As a result of the study of the quaternary system $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$ by Lea and Parker [2] it became possible to correct the Bogue treatment for possible deviations from equilibrium which might result from rapid cooling or separate crystallisation of that part of the clinker which had been liquid at the burning temperature.

In drawing up formulae for calculating compound composition it is assumed that the minerals

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Building Research Station, Department of Scientific and Industrial Research, Watford, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

identified in cement clinker are exactly the same as those found in phase rule studies using pure chemicals. This leads to two sources of error. Firstly, in real cement there are present the so-called minor constituents such as alkalis, FeO, MnO, and SO_3; these alter the relationship between the main cement compounds and, by entering into solid solutions with them, alter their nature as well as the amount present. Secondly, even in pure mixtures the cement compounds dissolve in each other to some extent.

Examples of the first kind are given by Welch and Gutt [3]. The best known example of the second is shown by the fact that the iron compound is not necessarily C_4AF, but a member of a solid solution series of variable composition [4–7].

To overcome these difficulties, either the composition of the ferrite must be determined before calculation, or a direct method of estimating the cement minerals must be employed. The only suitable way available for either ferrite composition determination or direct compound determination is X-ray powder diffraction. Midgley [8, 9] has shown that the ferrite composition may be determined by reference to the parameters of the ferrite solid solutions; Von Euw [10] and Copeland et al., [11] have shown that X-ray diffraction methods may be used to determine the phase composition. When the ferrite composition is known the oxide chemical analysis may be used to calculate the phase composition in the modified Bogue method as follows. First the composition of the ferrite phase is determined from powder X-ray data; all the Fe_2O_3 in the chemical analysis is assigned to $2CaO{\cdot}Fe_2O_3$ with which the appropriate amount of CaO and Al_2O_3 are then combined to give the ferrite composition determined. The remaining Al_2O_3 is assigned to C_3A; then the remaining CaO and SiO_2 are combined in the normal Bogue manner to form $3CaO{\cdot}SiO_2$ and $2CaO{\cdot}SiO_2$.

This paper will present investigations by X-ray methods into the two important questions, determination of ferrite composition and direct measurement of phase composition by X-ray powder diffractometry.

Measurement of Ferrite Composition

It is usually accepted that the ferrite phase in portland cement lies in the solid solution range C_6AF_2-C_6A_2F. The determination of the composition of this phase is not possible by chemical analysis for it is impossible to separate the ferrite from the other cement phases. It is therefore necessary to use an indirect physical measurement as an indication of the composition. Three possible physical properties that might be used are refractive index, magnetic susceptibility and X-ray diffraction. Parker and Ryder [12] used the refractive index method to determine the composition of ferrites in high-alumina cement clinkers, but unpublished data of Midgley and Ryder [13] did not give reliable results for portland cement clinker. Magnetic susceptibility measurements have not been used on portland cement clinker, for although Malquori and Cirilli [6] showed that there was a direct relationship between ferrite composition and magnetic susceptibility, the measurement of susceptibility of a cement would not give a measure of composition without knowing how much of the constituent was present. In the case of portland cement clinker both composition and quantity are equally unknown. There remains the X-ray diffraction method. It was shown by Midgley [8] that the composition of the ferrite phase could be determined from the lattice parameters measured in the powder X-ray diffraction pattern.

Three methods of measuring these parameters have been suggested: firstly on a magnetically separated fraction [8, 9] by measuring the 202 reflection at 1.94 A; secondly on the normal cement clinker by measuring the 141 reflection at 2.63 A [11, 14]; or thirdly, on a chemically separated fraction [15].

Nothing more need be said about the first two methods but the third method due to Fratini and Turriziani has been further investigated and the results are given below.

Fratini and Turriziani described a reagent consisting of 25 cm^3 water, 65 cm^3 ammonia, and 10 g ammonium citrate which preferentially dissolves the silicates from portland cement, leaving a residue consisting mainly of C_3A and ferrite. They used the method in order to obtain better X-ray powder diffraction patterns of the ferrite phase than was possible from the original cement.

The treatment they describe consists of shaking 1 g of the sample of cement with 100 cm^3 of the reagent for 12 hr. The solution is decanted from the residue and the residue shaken with a further 100 cm^3 of reagent for a further 12 hr. The residue is filtered off on a sintered glass crucible, washed rapidly with ammonia and dried at 110 °C. Their residue varied between 34 and 38.7 percent.

Keil and Gille [16] have pointed out that the aluminates are more sensitive to attack than the aluminoferrites, while Fratini and Turriziani [15] indicate that the aluminoferrites become less sensitive to attack with increasing iron content. The latter authors found that brownmillerite, ground just to pass a 178 mesh sieve, dissolved up to a maximum of 6 percent in 12 hr and that the X-ray pattern of the residue was similar to that of the original sample.

Data for the solubility of three ferrites, C_6AF_2, C_4AF and C_6A_2F, have been redetermined and the results are given in figure 1. The rate of solubility for C_3A is even greater than for C_6A_2F. Despite this, the method does give a concentration of the ferrite and C_3A phases in portland cements. Fratini and Turriziani suggest that the ferrites in

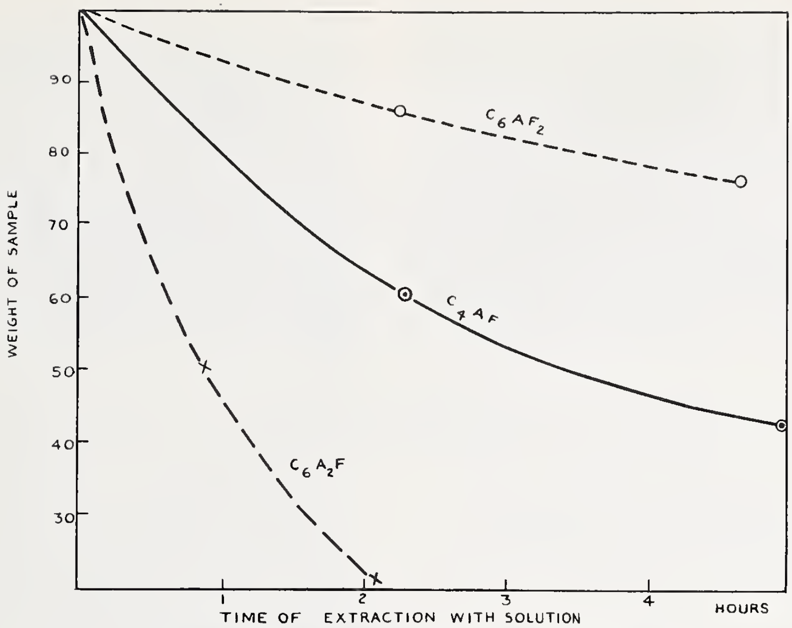
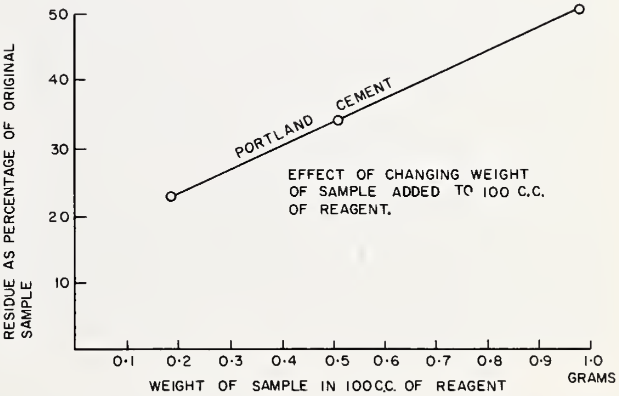


Figure 1. *Comparative rates of solution of ferrites* (*1g solid/100 cm*^{3}).

Table 1. *Weight percent of* C_2F *in 15 clinkers, determined by three methods*

Clinker	Camera; magnetic fraction (1958)	Direct X-ray diffraction	X-ray diffraction after Fratini and Turriziani extraction	
	202 reflection	141 reflection	141 reflection	202 reflection [a]
A. 9	56	54	52	48
A. 10	65 39 (52)	56 47 (51)	60 54 (57)	50 42 (46)
A. 20	66	60 48 (54)	61 51 (56)	No distinct peak.
A. 35	71 39 (55)	57	58 53 (55)	50
A. 36	74 39 (57)	56 48 (52)	50	48
A. 37	66	63 47 (55)	56	46 35 (40)
A. 39	66	50	54 50 (52)	49 41 (45)
A. 40	66	63 52 (57)	56	46
A. 143	65 39 (52)	59 50 (55)	56 48 (52)	48 42 (45)
A. F	56	73 59 (66)	64	62
A. 141	65 39 (52)	62 50 (56)	63 55 (59)	45
A. 7	54 39 (47)	64 46 (55)	62 52 (57)	No distinct peak.
A. 5	54 39 (47)	62 54 (58)	54	48
A. 33	71 39 (55)	68 51 (59)	63 57 (60)	37 33 (35)
A. 113	----------------	70 54 (62)	70 46 (58)	66 46 (56)

[a] The use of the 202 reflection is not very satisfactory for the diffractometric techniques of using KBr or Si as an internal standard. Both KBr and Si give peaks close to the ferrite 202 region; i.e., ferrites (46.6–47.5)° 2*θ*; KBr 45.60°2*θ*, 47.74°2*θ*; Si 47.30°2*θ*.



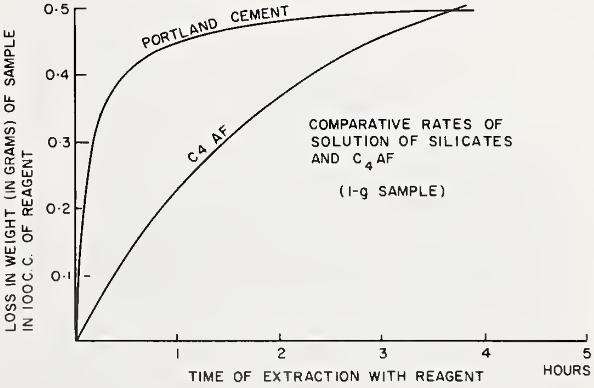


Figure 2. *Comparative rates of solution of silicates and* C_4AF.

portland cement are protected from attack by the silicate phases. We would suggest the much more rapid dissolution of the silicate phase can effectively deactivate the reagent before solution of the other phases has proceeded to any extent.

Further work on the chemical method has been carried out, and we have found that a single extraction carried on for about three hours can leave a residue of about 22 percent whose X-ray diffraction pattern indicates the complete removal of crystalline silicate phases. This is effected by reducing the initial concentration of the sample in 100 cm³ of reagent to about 0.2 g (fig. 2).

The three methods outlined above have been tried on 15 of the cements originally investigated by Midgley [8] and the results are given in table 1. The experimental error in the composition is about ±3 percent C_2F.

The results given by magnetic separation, by direct diffractometry, and those given by the 141 reflection after chemical separation agree reasonably, but the results given by measurement of the 141 and 202 reflection on the same sample disagree badly. This discrepancy may be due to solid solution with some other component such as MgO.

Direct Determination of Cement Composition by X-ray Diffractometry

The method used for the quantitative estimation of cement compounds is based on the fact that the integrated intensity of a reflection produced by X-ray powder diffraction is directly proportional to the amount of the substance producing it [17, 18].

In the method reported here the integrated intensity of the diffracted beam is recorded by a ratemeter using a Geiger-Müller tube. The different diffracted beams are recorded on a ratemeter recorder plotting intensity against 2θ; thus the integrated intensity can be measured as the area under the peak produced. The apparatus used is the commercial Dutch Philips Diffractometer. To obtain a reasonably small standard deviation of the integrated intensity the powder sample for the diffractometer must be ground to less than 5μ. Various methods are available to carry out the grinding; agate pestle and mortar, ball mills, or vibratory mills, but experience has shown that all these methods either take too long or require too large a sample. To overcome these difficulties a miniature vibratory rod mill (fig. 3) has been designed and built at the Building Research Station, which will grind 0.3 g of sample in isopropyl alcohol to less than 5μ in 2 hr.

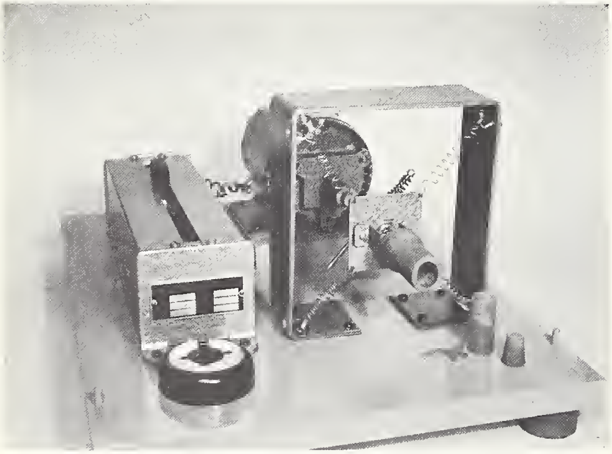


Figure 3. *Vibratory micro-rod mill.*

It is usual to compare all intensities with that produced by a fixed proportion of a suitable internal standard. This eliminates differences which might arise from sample to sample due to the method of preparation. It was found that a 12 to 1 weight ratio of sample to potassium bromide was satisfactory. In only one case has potassium bromide proved unsatisfactory as an internal standard, namely, for a cement containing calcium chloride. It is for such cases that silicon as an internal standard would be preferable. Silicon is much more difficult to grind than potassium bromide and if the sample is not equally ground, segregation may occur and there will be discrepancies in the diffraction intensities produced. The micro rod mill will adequately handle silicon mixes.

The samples were prepared by a loose packing method in a standard sample holder to avoid preferred orientation.

Mechanical mixtures of the four main cement minerals, alite, β-dicalcium silicate, tricalcium aluminate, and ferrite were made. After repeated diffractometer traces, the average integrated intensity of the compound (I_C) divided by the integrated intensity of the potassium bromide peak (I_{KBr}) was plotted against the percentage of the compound present; these were the calibration graphs.

In preparing the calibration graphs sixteen mixtures were used, eight containing alite, C_2S, C_3A, and C_4AF, four containing C_3A and C_3S, one containing alite, β-C_2S, and C_3A and three containing alite and C_3A. The standardization was complicated by the presence of C_3A in the alite used. In work on the ferrite phase it was found that, as a first approximation, the calibration for C_4AF could be used for ferrites of slightly different composition. The calibration was extended to the range C_6AF_2–C_6A_2F. The calibration constant for a composition within the range can be found by interpolation.

The peaks used for the particular compounds were as follows:

$CuK\alpha$ radiation,

Alite 29.4° $2\theta = 3.04$ A
Alite 30.0° $2\theta = 2.98$ A
β-C_2S 31.1° $2\theta = 2.87$ A
C_3A 33.2° $2\theta = 2.699$ A
C_4AF 33.5°–33.85° $2\theta = 2.67$A.

The calibration graphs obtained were all straight line plots passing through the origin.

Any interference due to adjacent peaks was allowed for in the graphical interpretation of the resulting pattern. In interpreting the patterns produced by cements, frequent reference is made to the original standard patterns, and also to superimposed patterns of the four main cement compounds.

The peak due to C_2S at 31.1° 2θ is weak and we have attempted a different treatment for estimating C_2S. At 32.6° 2θ and 34.4° 2θ peaks occur which are due to C_2S and alite. The total intensity is the sum of the individual intensities. Standard graphs were prepared relating I/I_{KBr} and percent alite for these two peaks in the absence of C_2S, and standard graphs relating I/I_{KBr} and percent C_2S for these two peaks in the absence of alite. The latter was checked by examining standard patterns in which both alite and C_2S were present and subtracting the contribution due to alite alone.

The method used for cements would be to estimate alite from the peaks at 29.4° 2θ, and 30.1° 2θ, and to subtract the intensity due to alite alone from the total intensity at 32.6° 2θ and 34.4° 2θ. The amount of C_2S is determined from the residual intensity. We do not always get good agreement between the three results obtained for C_2S and at the moment our data for the peak at 34.4° 2θ are suspect. Two simultaneous equations can be written for the interfering peaks and solved for alite and C_2S. These results are not always in good agreement with results obtained on the other peaks, and have only been used in interpreting patterns obtained from set portland cement mortars when the line due to alite at 29.4° 2θ can be obscured by calcite whose main peak occurs at the same position.

At the moment there is some difficulty in determining low C_3A contents in the presence of high ferrite content since severe ferrite and β-C_2S interference means that no definite C_3A peak need be apparent, and at the time of writing this has not been solved to our complete satisfaction.

Using the methods outlined in this note and scanning each sample three times the following coefficients of variation of the mean were obtained:

Alite, 5 percent
β-C_2S, 11 percent
C_3A, 3 percent
Ferrite, 6 percent

The methods outlined have been used on two series of cements, one of old cements (some more than 25 years old) used by Midgley [8] in his work on ferrites, and a second series of modern British portland cements of various kinds.

Result of X-Ray Examination of Cements

The results given by the three methods of compound determination are given in tables 2 and 3.

Table 2. *Compound composition of old cement clinkers*

Compounds \ Cement No.		A.40	P. 893	A.5	539 S. R. P. C.	540 S. R. P. C.	520	512	Dg
Alite	Diff [a]	65	58	59	56	39	59	53	50
	Mod		68		52	31			
	Bogue	70	66	61	56	34.5	46	53	36
β-C_2S	Diff	13	16	11	17	32	16	21	30
	Mod		7		20	41			
	Bogue	7	8	9.1	17	38.3	29	22	37
C_3A	Diff	11.5	3.7	13.5	4.8	4.5	11	12.1	14
	Mod		5.8		3.0	4.7			
	Bogue	9.5	2.5	15.4	0.7	0.9	9.6	10.7	15
Ferrite	Diff	8.5	17.5	10.5	17.5	16.5	6.4	8.8	9
	Mod		15.2		17	16.6			
	Bogue	9.2	18	10.2	19	19.3	6.2	6.3	10
Ferrite comp., wt % C_2F by diffractometer 141 reflection		57	66	54	62	67	56	56	56

(N.B. Where the C_2F content is nearly equal to C_4AF no modified calculation is shown as it would be the same as by the Bogue calculation.)

[a] Diff =by Diffractometer
Mod =by Modified Bogue calculation
Bogue=by Bogue calculation

TABLE 3. *Compound composition of modern British cement clinkers*

Cement No. Compounds		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
		572 O.P.C.[a]	625 O.P.C.	580 R.H.P.C.	615 O.P.C.	561 O.P.C.	569 O.P.C.	597 L.H.P.C.	592 O.P.C.	A. S. R. S.R.P.C.
Alite	Diff	53	54	49	53	43	60	35	53	55
	Mod		42.5			42.5			56	50
	Bogue	47	42	44	48	42	48	26	55	53
β-C_2S	Diff	24	24	27	23	30	27	45	23	17
	Mod		25			29			21.5	20
	Bogue	28	26	32	23	30	29	49	22	18
C_3A	Diff	9.3	12.8	8.3	14.5	9.8	9.7	8.8	9.7	3.6
	Mod		12.1			10.0			9.1	4.0
	Bogue	8.4	12.9	8.8	13.1	10.9	9.5	9.2	9.7	0.9
Ferrite	Diff	9.5	11.0	6.2	9.0	12.5	7.6	6.9	7.5	17.5
	Mod		9.9			9.7			6.1	17.1
	Bogue	9.2	9.2	6.6	7.3	9.0	6.3	6.6	5.6	19.6
Ferrite comp., wt % C_2F		56	52	56	56	52	56	56	51	64

[a] O.P.C. = Ordinary portland cement
R.H.P.C. = Rapid hardening portland cement
L.H.P.C. = Low heat portland cement
S.R.P.C. = Sulfate resisting portland cement

Conclusions

Although all three methods of estimating the compound composition of portland cement clinker are still subject to errors, there appears to be a better agreement between the modified method of calculation from chemical analysis and direct diffractometry, than between the Bogue method and either of the other two.

The great errors in the Bogue method appear in those cements with the lowest C_3A. In these cements the ferrite appears to be rich in C_2F, making the Bogue estimate of C_3A too low.

The diffractometry measurement of C_3A in these cases (539, 540, A.S.R.) is not yet satisfactory but the modified calculation shows agreement with the diffractometer estimate.

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Discussion[*]

D. L. Kantro, L. E. Copeland, and Stephen Brunauer

Quantative Analysis of Portland Cements by X-rays

Over the past few years, experimental work has been performed at a number of laboratories throughout the world in an effort to apply the method of X-ray quantitative analysis to portland cement. Much of this work has already been discussed by Dr. Nurse. However, at the time of his writing, Dr. Nurse did not have at his disposal our paper on an extension of our previously published quantitative method combining X-ray and chemical data [1][1] to the pure X-ray method [2]. We should like to discuss the results of this latter work, including data heretofore unpublished, on a recently analyzed group of cements. In addition, we should like to present a few sidelights arising from our investigations in this field.

Experimental Problems in X-ray Cement Analysis

The X-ray diffraction pattern of a portland cement involves many complexities. A portion of a pattern of a normal portland cement is reproduced in figure 1. A number of strong lines are evident, one of which, at 2.71 A (33°2θ) represents tricalcium aluminate, and one, in the vicinity of 2.67 A (33.7°2θ) represents the calcium alumino-ferrite solid solution phase.[2] The ferrite and aluminate lines overlap, so that the area designated as "tricalcium aluminate peak" in figure 1 contains a considerable contribution from the ferrite phase. In spite of this serious overlap problem, we had to use these lines, because we were unable to find other lines of either of these materials sufficiently strong and sufficiently unhampered as to be useful for quantitative analysis.

The ferrite-aluminate overlap problem is complicated by the fact that the amount of overlap depends upon the composition of the ferrite solid solution phase. This composition can be expressed in terms of the A/F ratio of the phase. The *d*-spacings of the ferrite phase lines are dependent on the A/F ratio, and may be used for the evaluation of this quantity. For the whole cement, only the line at 2.67 A may be used, but if the cement is fractionated, either chemically [3,4] or magnetically [3], other lines may be used. However, there is always the possibility of a disproportionation in a separation procedure, if the ferrite phase is not homogeneous. The A/F ratio may also be evaluated from combined X-ray intensity and chemical data [1]. In a pure X-ray method, however, a *d*-spacing determination must be used.

The other strong lines in the pattern shown in figure 1, besides the silicon line, are due to the calcium silicates. Actually, each of these strong lines contains a contribution from each of the silicates: only a weak line, at 31°2θ, is due to but one of the silicates, β-dicalcium silicate. Thus, a serious overlap problem exists for the silicates as well. However, because of the relatively numerous strong lines of these constituents of portland cement, some selection of lines is possible.

Thus, there are three basic experimental problems associated with the X-ray quantitative analysis of portland cement. These are: (1) resolution of the C_3A and ferrite phase lines, (2) precise determination of the *d*-spacing of a ferrite line, and (3) selection of suitable silicate lines. It would seem that the differences in results reported by various investigators are based on the different attacks on these three basic problems.

There is a fourth problem, though not as serious as those enumerated above, the selection of a suitable internal standard. Von Euw [5] used the 2.81 A line of NaCl; Midgley, Rosaman, and Fletcher [3] used the 3.30 A line of KBr. During the first year of our investigations we also used the latter as the internal standard, but we discarded it later in favor of the 3.14 A line of silicon. Because of the height of the KBr peak relative to the heights of the cement compound peaks, a weight ratio of 0.05 g of KBr/g of cement was used; when we substituted silicon, we could use twice as much internal standard. This has resulted in a larger area for the silicon line, and

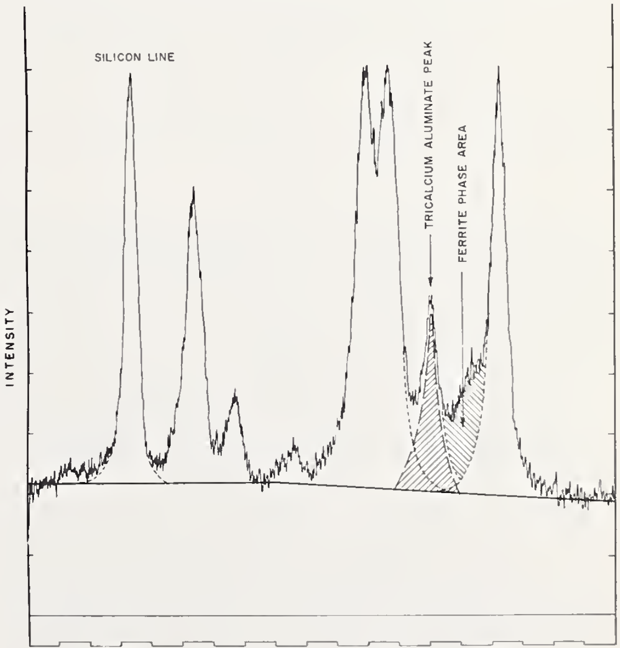

FIGURE 1. *X-ray diffraction pattern of a portland cement.*

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[*] This discussion discusses papers II-1, "Phase Equilibria and Constitution of Portland Cement Clinker" by R. W. Nurse, and II-S2, "X-Ray Diffraction Pattern of Portland Cement Clinker" by H. G. Midgley, D. Rosaman, and K. E. Fletcher.

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] All angles refer to locations of reflections obtained with CuKα radiation.

in an improved precision of the data. In addition, it was not infrequent that we obtained anomalously high peaks with KBr, perhaps because of concentration of KBr in the surface layer of the mixture. Whatever the cause, this difficulty has not bothered us since we use silicon with the technique described earlier [2].

Calibration With the Internal Standard

In general, the calibration procedure is to observe intensity ratios for known weight ratios of cement compound to standard. However, it is equally important that the characteristics of the patterns from which the calibration data are obtained are as nearly like those of cement patterns as is possible. This is necessary not only because of the overlap between ferrite and C_3A lines, but also, as will be seen later, because we could not obtain linear relationships between relative intensities of lines and weight ratios of the silicates. Thus, one cannot simply make binary mixtures of each cement compound with internal standard and get usable data. Von Euw [5], Midgley and his coworkers [3] and ourselves [1] have all calibrated from mixtures of the cement compounds in proportions such as occur in portland cement.

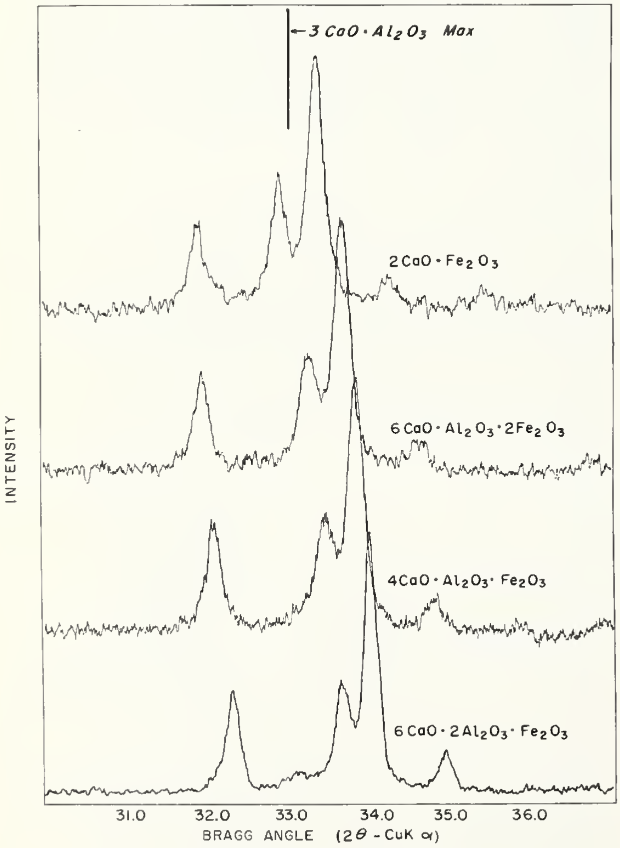

FIGURE 2. *X-ray diffraction patterns of calcium aluminoferrites.*

1. The calibration of the ferrites and aluminates requires, as was pointed out above, a consideration of the complex overlap situation that exists. As a first approximation, one may consider that the overlap correction may be obtained by a simple graphical procedure such as is illustrated in figure 1. Such a graphical procedure was used by Midgley, Rosaman, and Fletcher [3]. If this is the case, the calibration equations would take the form

$$\frac{P_F}{P_0}=\mu\frac{I_F}{I_0}=\mu R_F \qquad (1)$$

where P_F/P_0 is the weight ratio of ferrite to internal standard, μ is a proportionality constant, and R_F is the intensity ratio of the ferrite line to the standard line.

On the other hand, the fact of the matter is that the ferrite region, actually composed of two ferrite lines, may strongly overlap the C_3A line and extend to even lower angles than that at which the C_3A peak occurs, as can be seen from figure 2. Thus, there may be an intensity contribution to the apparent C_3A peak which cannot easily be corrected graphically. As a second approximation, then, some equation may be set up to account for this phenomenon. We have adopted an empirical form

$$\frac{P_F}{P_0}=\mu[R_F+g(\nu)R_A] \qquad (2)$$

where $g(\nu)$ is a function of ν, the molar A/F ratio, and R_A is the intensity ratio of the C_3A line to standard line.

Midgley, Rosaman, and Fletcher [3] found it expedient in their calibration to use C_4AF to represent all of the ferrites. As a first approximation, over a narrow molar A/F ratio range about unity, this is a simple and straightforward approximation, represented by eq (1) with μ independent of A/F ratio. Over the entire range of A/F values from 0 to 2, however, μ is not independent of A/F. Smith [6] has shown that there are A/F-ratio dependent intensity variations in ferrite diffraction lines, these variations being the results of crystallographic changes in symmetry caused by the substitution of aluminum for iron in C_2F. The dependence of μ on A/F ratio is of course a result of this phenomenon, and is illustrated in figure 3, the data for which were obtained from binary mixtures of C_2F, C_6AF_2, C_4AF and C_6A_2F with silicon. With the dependence of μ on A/F ratio taken into consideration, eq (2) becomes

$$\frac{P_F}{P_0}=g_1(\nu)[R_F+g_2(\nu)R_A] \qquad (3)$$

where $g_1(\nu)$ and $g_2(\nu)$ are both empirical functions of ν, the A/F ratio. The use of such an equation avoids introduction of a systematic error proportional to the deviation of the A/F ratio from unity, which would result from the assumption of a μ value independent of the A/F ratio.

A similar expression may be set up for C_3A, wherein, however, the quantity μ' is independent of A/F ratio. Thus

$$\frac{P_A}{P_0}=\mu'[R_A-f(\nu)R_F] \tag{4}$$

where P_A/P_0 is the weight ratio of C_3A to internal standard and $f(\nu)$ is some empirical function of the A/F ratio. In this equation R_A is corrected for the overlapping ferrite line in such a way that systematically high C_3A results are avoided in low overall A/F ratio cements.

2. The calibration of the silicates presents a different problem. As was stated before, all of the strong lines of either silicate coincide with lines of the other.

There is a reasonably strong line at 29°2θ, which is predominantly a C_3S line, though C_2S also makes a contribution to it. For equal weights of C_3S and C_2S, the contribution of C_3S to the intensity of the line is about 8 times that of C_2S. Midgley, Rosaman, and Fletcher [3], as well as Von Euw [5], have used this line for their determinations of C_3S. Neglect of the β-C_2S contribution to this line by Von Euw introduces only a small error for cements high in C_3S, but somewhat more significant errors for low C_3S cements (type IV).

At the beginning of our investigations we also used the same line, though we always considered the contributions of both C_3S and C_2S to the line. We discarded the line later because we found that calcium sulfate hemihydrate and gypsum, with strong lines at 2.98 A and 3.06 A, respectively, made significant contributions to the intensity of the line [7]. At the suggestion of Katharine Mather, we adopted the line at 51°2θ, instead.

There is a rather weak line at 31°2θ, which is a pure C_2S line. Midgley, Rosaman, and Fletcher, as well as Von Euw, have used this line for their determination of C_2S. We also tried this line, but found it unsatisfactory. Von Euw found it so unsatisfactory that he did not report any C_2S results in his paper. Midgley and his coworkers used the 32 and 34°2θ C_3S-C_2S lines, in addition to the 31°2θ line, to evaluate C_2S. The three results did not always agree well, and they especially suspected the 34°2θ results. In our early work, we tried both the 32 and 34°2θ lines, and we did not find either line satisfactory.

In our final work, we have adopted the 41°2θ C_3S-C_2S line and the already mentioned 51°2θ line for the quantitative determination of C_3S and C_2S. The use of two lines permits the simultaneous solution of two equations of the type

$$\frac{I_1}{I_0}=\alpha_1\frac{w_1}{w_0}+\alpha_2\frac{w_2}{w_0} \tag{5}$$

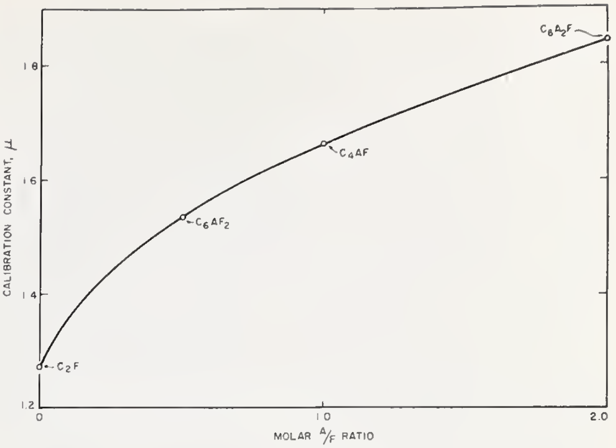

FIGURE 3. *Dependence of ferrite calibration constant on molar A/F ratio.*

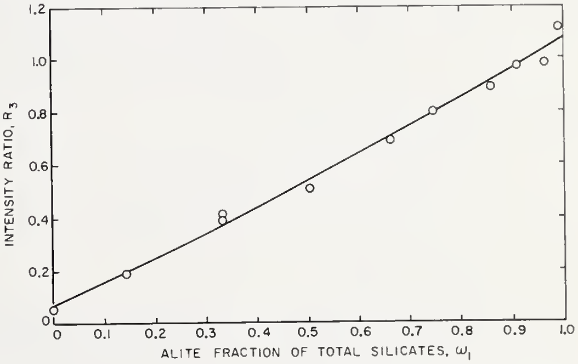

FIGURE 4. *Dependence of ratio of intensities of 51° 2θ line to 41° 2θ line on relative amounts of alite and belite in silicate calibration mixtures.*

$$\frac{I_2}{I_0}=\beta_1\frac{w_1}{w_0}+\beta_2\frac{w_2}{w_0} \tag{6}$$

where I_1, I_2 and I_0 are the intensities of the two selected lines and the standard line, respectively. α_1, α_2, β_1, and β_2 are proportionality constants, and w_1/w_0 and w_2/w_0 are the weight ratios of C_3S and C_2S to standard, respectively. In our work. I_1 is the intensity of the line at 51.6°2θ, and I_2 that of the line at 41.1°2θ. I_0 is the intensity of the (111) silicon line (28.4°2θ).

Even though suitable lines are found from which interpretable X-ray data can be obtained, certain calibration problems still exist. It is not certain that the alite form of C_3S found in one cement is identical with that found in another cement; the same is true of the belite (C_2S) phase. That differences do exist is clearly shown by the results obtained when the calibration is carried out on preparations designed to give certain alite/belite ratios upon burning. These preparations were described previously [1]. On the basis of eqs (5) and (6) it can be shown that I_1/I_2, the ratio of the 52°2θ line to the 41°2θ line should be a linear function of w_1, the alite fraction of the total silicates. A plot of I_1/I_2 $(=R_3)$ against w_1 is shown in figure 4. It can be seen that a curvilinear plot is obtained. This deviation from expectation indicates that there is a structural variation of either alite or belite or both as a function of composition. This was accounted for by the modification of eq (5) which we described in detail in an earlier publication [1]. Experimental evidence shows that the curvature of R_3 is caused by a curvature in I_1. Within experimental error, I_2 varies with composition in a linear manner.

The alite used for this work had the approximate composition $52C_3S{\cdot}C_6AM$, as contrasted to the composition $16C_3S{\cdot}C_6AM$ reported by Jeffery at the last symposium [8]. However, his results, and the results of other investigators, including ourselves, who have attempted to make alite of this composition indicated the presence of a significant amount of C_3A. We have prepared materials with overall A/S ratios of 1/52 $(52C_3S{\cdot}C_6AM)$ which, while still demonstrating the alite diffraction pattern, contain negligible amounts of C_3A. These results are in quantitative agreement with those reported by Von Euw [5].

We have prepared alite using ferric oxide and magnesia instead of alumina and magnesia. The F/S ratio was 1/52. So far we have not investigated the iron stabilized alite, but it is clear that the presence of ferric oxide in alite may cause further complications.

Because of the possible variations in alite and belite structures due to the solution of different impurities, the calibration curves obtained for the silicates are not strictly applicable to the determination of alite and belite in portland cements. A somewhat better approximation is described in our second paper [2], in which the alite-belite results obtained for 20 portland cements by the combined X-ray and chemical analysis method were used for calibration purposes.

Analysis of Cements

Composition of the Ferrite Phase

The X-ray quantitative analysis of a cement is carried out in two steps: (1) determination of the composition of the ferrite phase and (2) determination of the amounts of the four major phases.

The results of the determinations of A/F ratio for 36 cements are given in table 1. The results are expressed in this table as molar A/F ratio, designated ν (columns 2, 3, and 4) and as mole percent C_2F, designated n (columns 5, 6, and 7). Values were obtained in two ways: (1) by determination of the *d*-spacing of the (141) ferrite line (ν_d and n_d, columns 2 and 5, respectively), and (2) by calculation from the intensity of this line and the total iron in the cement, as was described previously [1] (ν_1 and n_1, columns 3 and 6, respectively). The average values from these two methods, ν_{avg} and n_{avg} are given in columns 4 and 7, respectively. The determination of ν_1 involves the solution of a quadratic equation. In a few cases, a real solution could not be obtained because of the occurrence of a negative discriminant. In such cases, no value for ν_1 is given.

Table 1. *Ferrite phase compositions in portland cements*

1 *Cement*	2 ν_d	3 ν_1	4 ν_{avg}	5 n_d %	6 n_1 %	7 n_{avg} %
LTS-11	0.733	1.362	1.047	57.7	42.3	48.9
LTS-12	1.000	1.000	1.000	50.0	50.0	50.0
LTS-13	1.212	----------	1.212	45.2	--------	45.2
LTS-14	0.980	----------	0.980	50.5	--------	50.5
LTS-15	1.150	0.738	.944	46.5	57.5	51.4
LTS-16	0.949	1.180	1.064	51.3	45.9	48.4
LTS-17	.764	0.928	0.846	56.7	51.9	54.2
LTS-18	1.445	1.129	1.287	40.9	47.0	43.7
LTS-19C	0.862	0.983	0.922	53.7	50.4	52.0
LTS-21	1.096	1.058	1.077	47.7	48.6	48.1
LTS-22	0.815	1.178	0.997	55.1	45.9	50.1
LTS-23	.740	0.641	.690	57.5	60.9	59.2
LTS-24	.984	.966	.975	50.4	50.9	50.6
LTS-25	.805	.765	.785	55.4	56.7	56.0
LTS-31	1.170	1.014	1.092	46.1	49.7	47.8
LTS-33	0.920	1.254	1.087	52.1	44.4	47.9
LTS-34	.838	1.214	1.026	54.4	45.2	49.4
LTS-41	.865	0.939	0.902	53.6	51.6	52.6
LTS-42	1.150	----------	1.150	46.5	--------	46.5
LTS-43	0.815	.979	0.897	55.1	50.5	52.7
LTS-43A	.923	1.122	1.023	52.0	47.1	49.4
LTS-51	.764	0.923	0.844	56.7	52.0	54.2
SBR-15754	1.440	----------	1.440	41.0	--------	41.0
SBR-15698	0.742	.450	0.596	57.4	69.0	62.7
SBR-15622	.709	.920	.814	58.5	52.1	55.1
SBR-15497	.897	.842	.869	52.7	54.3	53.5
SBR-15669	1.217	.974	1.096	45.1	50.7	47.7
LS-1	0.300	.452	0.376	76.9	68.9	72.7
LS-2	.300	.442	.371	76.9	69.3	72.9
B-H	.835	.651	.743	54.5	60.6	57.4
B-L	1.070	.830	.950	48.3	54.6	51.3
BR-A	0.880	1.156	1.018	53.2	46.4	49.6
BR-B	.894	1.050	0.972	52.8	48.8	50.7
BR-C	1.008	0.970	.990	49.8	50.8	50.3
BR-D	0.613	.659	.636	62.0	60.3	61.1
BR-E	.783	----------	.783	56.1	--------	56.1

The median value of ν_d for the first 27 cements listed in table 1 is 0.96; that for ν_1 (23 of the first 27 cements) is 0.98. The median of the average values for the first 27 cements is 1.00, while the average of the average values is 0.99. In terms of mole percent, the average values of n_d, n_1 and n_{avg} are 51.4, 51.1, and 50.7 percent. These n values correspond to ν values of 0.95, 0.96, and 0.97, respectively. The mean deviation from the average is 2.7 percent.

Because there is only one ferrite diffraction line in the cement pattern amenable to *d*-spacing determination, and because even this determination can become quite uncertain when only a small amount of ferrite phase is present, other investigators have developed methods for separating a cement fraction containing a high percentage of ferrite. Thus, there is the chemical separation method of Fratini and Turriziani [4] and the magnetic separation method of Midgley [9]. These methods permit unencumbered observation of weaker diffraction lines.

Midgley, Rosaman, and Fletcher [3] have employed the chemical separation method, the magnetic separation method, and observations on the whole cement to determine the ferrite compositions for a group of 15 cements. They considered that their results by the magnetic separation method contained a bias on the C_2F side compared with results by the other techniques. This would indicate an inhomogeneous ferrite phase. Certainly a few cements are of this type as can be ascertained from the lack of sharpness of the (141) peak, as was pointed out by both Midgley [9] and ourselves [1]. Midgley, Rosaman, and Fletcher also observe, however, that their chemical separation results are in good agreement with the results from observation of the whole cement. At the same time they point out that the rate of solution of ferrite phase in the chemical medium used to dissolve away the silicates depends on the A/F ratio of the ferrite. On the basis of these two facts it would appear that the ferrite phase is homogeneous. Thus one may draw two conflicting conclusions from the results.

In spite of the claim of the C_2F bias of the results by the magnetic separation technique, only 7 of the 14 values reported indicate higher C_2F contents than the corresponding direct observation values, and 7 indicate lower C_2F contents. The molar A/F ratios corresponding to the mean weight percentages of C_2F for the 14 cements, obtained by magnetic separation, chemical separation and direct observation are 0.97, 1.00 and 1.00, respectively. These values are in excellent agreement with each other and are also in excellent agreement with our results.

One may, therefore, conclude that at least in the great majority of portland cements the ferrite phase is homogeneous. Because, however, there may be some cements in which the ferrite phase is not uniform [1, 9], it is safest to use the method of direct observation on the whole cement.

The constancy of A/F ratio after chemical extraction of the silicates, during which time a part of the ferrite phase is also dissolved, is consistent with the evidence presented by Copeland, Kantro, and Verbeck [10], showing that the A/F ratios of unhydrated residues of partly hydrated cement pastes are the same as those of the original cements.

The Quantities of the Four Major Phases

Analyses of 36 cements have been obtained by the combined chemical and X-ray method (CCX) [1] and by the method utilizing only X-ray data [2]. The primary calibration was that published by us originally [1], and the secondary calibration was that based on 20 of the 36 cements and published by us recently [2]. The results are given in table 2.

The conclusions based on the results from 36 cements are unchanged from those previously published. The CCX silicate data, given in columns 6 and 8 are those obtained by the total silica calculation described previously [1]. A comparison of the X-ray with the CCX results shows that the systematic errors of the pure X-ray ferrite, C_3A, C_3S, and C_2S values relative to the CCX values are +0.5, +0.1, +0.3, and +0.5 percent, respectively. The mean deviations are 0.9, 0.3, 2.5, and 1.4 percent, respectively, and the root mean square deviations (standard deviations) are 1.1, 0.4, 3.3, and 1.9 percent, respectively. Because of the nature of the calculations, the ratio of C_3S error to C_2S error is the same as the C_3S/C_2S ratio.

TABLE 2. *Compositions of portland cements*

1	2	3	4	5	6	7	8	9
Cement	Ferrite, percent		C_3A, percent		C_3S, percent		C_2S, percent	
	CCX	X-ray	CCX	X-ray	CCX	X-ray	CCX	X-ray
LTS-11	7.5	9.2	8.4	7.6	57.3	60.0	19.0	19.9
LTS-12	7.3	7.3	7.9	7.9	51.0	48.3	27.4	26.0
LTS-13	7.0	8.3	6.8	6.8	50.2	53.8	27.6	29.7
LTS-14	9.0	11.1	3.2	3.2	57.1	55.2	26.0	25.1
LTS-15	7.4	6.0	9.9	10.4	60.9	63.5	12.5	13.0
LTS-16	11.0	11.7	4.3	3.9	54.5	58.7	22.8	24.5
LTS-17	8.8	9.6	7.6	7.3	58.6	53.4	20.2	18.5
LTS-18	7.9	7.6	7.4	7.6	52.5	53.2	26.5	26.9
LTS-19C	8.5	9.0	6.2	6.0	57.7	54.1	20.8	19.6
LTS-21	10.1	10.0	3.6	3.6	45.7	49.6	35.6	38.6
LTS-22	11.8	13.4	3.1	2.3	49.4	50.2	29.9	30.4
LTS-23	14.2	13.3	2.2	2.6	55.6	55.5	23.2	23.2
LTS-24	14.4	14.4	2.1	2.2	48.8	50.3	26.4	27.2
LTS-25	13.5	13.2	0.2	0.3	38.7	37.6	43.0	41.8
LTS-31	6.6	6.3	7.6	7.7	57.7	56.7	17.1	16.8
LTS-33	7.9	8.7	7.4	7.0	55.8	58.7	17.6	18.5
LTS-34	10.2	11.4	3.6	3.0	61.3	62.8	13.6	13.9
LTS-41	14.6	15.0	0.2	0.0	25.4	25.6	52.4	52.8
LTS-42	8.8	10.0	1.3	1.3	31.6	33.2	52.4	55.0
LTS-43	13.1	14.1	3.0	2.5	30.2	33.9	47.9	53.7
LTS-43A	9.5	10.1	1.6	1.2	29.9	30.2	53.6	54.1
LTS-51	9.4	10.1	0.6	0.2	49.7	48.2	36.4	35.2
SBR-15754	8.0	10.0	7.1	7.1	52.0	52.3	25.2	25.3
SBR-15698	6.2	5.0	8.3	8.7	65.0	54.2	16.4	13.6
SBR-15622	11.7	13.1	0.0	0.0	52.6	51.9	30.6	30.3
SBR-15497	7.5	7.2	8.9	9.0	55.6	59.2	16.2	17.3
SBR-15669	6.0	5.7	0.7	0.9	29.7	30.4	57.8	59.1
LS-1	11.5	13.1	.0	.0	65.3	66.8	17.9	18.3
LS-2	10.8	12.2	.0	.0	70.0	63.9	12.3	11.2
B-H	13.2	11.8	6.4	7.0	56.6	55.2	23.8	23.3
B-L	8.6	7.7	9.0	9.3	51.8	56.4	28.6	31.2
BR-A	6.8	7.6	11.8	11.5	44.1	42.9	26.8	26.2
BR-B	6.3	6.8	9.3	9.2	41.5	46.6	32.0	36.0
BR-C	8.5	8.4	7.1	7.2	39.5	43.8	35.9	39.8
BR-D	15.3	15.6	0.0	0.0	43.4	42.8	34.6	34.0
BR-E	0.8	2.3	6.4	6.4	59.0	56.8	31.1	29.9

The C_3A contents determined for these cements are in every case lower than the values obtained by the Bogue potential compound calculation. Midgley, Rosaman, and Fletcher [3] reported C_3A values higher than the potential values for cements with low overall A/F ratios. However, one would expect that the C_3A would be the lowest in these very cements because of the tendency of low A/F ratio ferrites to take up additional alumina. As was stated before, the ferrite line may overlap the C_3A line in such a way as to be unresolvable graphically. As can be seen from figure 2, this would be the case all the more if the ferrite has a low A/F ratio. Hence, the Midgley, Rosaman, and Fletcher result appears to be a manifestation of an increasing high systematic error in C_3A content with decreasing ferrite A/F ratio.

TABLE 3. *Sums of oxides and major phases in portland cements*

Cement	Oxide sum	CCX sum	X-ray sum
	Percent	*Percent*	*Percent*
LTS-11	92.3	92.2	96.7
LTS-12	93.6	93.6	89.6
LTS-13	93.0	91.6	98.5
LTS-14	94.0	95.4	94.6
LTS-15	94.5	90.8	92.9
LTS-16	93.3	92.5	98.8
LTS-17	94.9	95.2	88.7
LTS-18	93.6	94.3	95.3
LTS-19C	92.2	93.3	88.7
LTS-21	95.5	95.0	101.8
LTS-22	93.9	94.3	96.2
LTS-23	95.7	95.3	94.6
LTS-24	91.8	91.8	94.0
LTS-25	94.2	95.4	92.9
LTS-31	90.3	89.0	87.6
LTS-33	91.5	88.7	92.9
LTS-34	90.9	88.6	91.1
LTS-41	92.6	92.5	93.4
LTS-42	94.4	94.1	99.4
LTS-43	94.1	94.2	104.3
LTS-43A	95.0	94.5	95.6
LTS-51	94.8	96.0	93.7
SBR-15754	92.0	92.2	94.7
SBR-15698	93.1	95.9	81.6
SBR-15622	94.6	95.0	95.3
SBR-15497	90.9	88.2	92.8
SBR-15669	94.4	94.3	96.1

The combined chemical and X-ray method has the advantage of restricting the error in the system somewhat by the limitations imposed by the oxide analysis. There are, however, a number of minor oxides in portland cement which may be dissolved in one or more of the four major phases. The CCX method does not take these into account. On the other hand, the X-ray method, not limited by the oxide analysis, measures the total amount of each of the major phases, regardless of the presence of minor oxides. Thus, a comparison of the sum of the major and minor oxides, corrected for substances known not to occur in the major phases [2], with the sums of the major phases obtained by the CCX and X-ray methods is useful in illustrating the overall accuracy of the methods. These sums are given in table 3. The CCX sums are on the average 0.3 percent smaller than the oxide sums, while the X-ray sums are on the average 0.8 percent greater. This implies that at least some of the minor oxides in the cement are dissolved in the four major phases. The mean deviations of the CCX and X-ray sums from the oxide sums are 1.0 and 2.6 percent, respectively, and the root mean square deviations (standard deviations) are 1.5 and 4.4 percent, respectively. It is to be expected that the CCX deviations would be smaller than the X-ray deviations because of the restrictions imposed on the system by the method.

Finally, the oxide results indicate that there is no significant amount of amorphous material in cement. The material designated as glass or glassy phase is actually microcrystalline, and hence detectable by X-rays.

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Discussion

H.-G. Smolczyk

Methods of X-ray investigation were the subject of several discussions at the Symposium. Although I discussed the matter several times with different gentlemen I shall try to combine some of these different discussions about preparation methods in one contribution. I should like to offer this discussion as a supplement to the very interesting paper of the Building Research Station.

At the Forschungsinstitut für Hochofenschlacke at Rheinhausen we fully agree to the opinion that the technique of preparing the samples is one of the most important parts of a quantitative X-ray diffraction analysis, and that wet grinding has important advantages.

Therefore, I want to report about the good experience we have had—for about 4 years—with a very simple wet grinding method for X-ray powder samples.

We use an ordinary small closed agate ball mill with a volume of 100 ml. In it, 1 cm^3 of the coarsely ground material together with 30 cm^3 of benzene (C_6H_6) are ground for 40 min. Then the benzene is removed and the very fine powder (2–6μ) dried quickly in a flow of dry air or in a vacuum. Afterwards the powder is placed in an ordinary sample holder with a rectangular window and is densely compacted. Careful precautions are taken to obtain an entirely even surface.

Some smaller advantages of this method are the short grinding time, the easy separation of the powder, with its higher density, from the lower density benzene, and the chemical inactivity of the benzene which excludes any reaction with the cements or with their hydration products.

The two main advantages will be described in detail:

(1) By carefully using this preparation technique a high degree of reproducibility is obtained. Moreover, the preferred orientations of some hydrates—e.g., calcium hydroxide or ettringite—are reproducible, too, and diagrams obtained with these substances can be used even for quantitative analysis. Care must be taken, however, that the X-ray pattern of the mineral used for comparison shows the same degree of preferred orientation.

To give an impression of the accuracy that can be obtained by this method, two examples from our practice are given. Each sample was prepared four times, and the intensity of the $Ca(OH)_2$ peak at $2\theta=18°$ (CuKα) of each of the 8 specimens obtained was measured. The results were as follows (in percent of $Ca(OH)_2$):

Sample A: 21.8; 20.1; 18.8; 19.4; average, 20.0 ±0.7

Sample B: 0.9; 1.3; 1.5; 1.2; average, 1.2 ±0.2

$$\left(\text{Error calculated by } E=\pm\sqrt{\frac{\Sigma\Delta^2}{n(n-1)}}\right).$$

It must be mentioned here that the 18° peaks showed intensities which were approximately five times higher than normal, due to the effect of preferred orientation. The determination of 1.2 percent of $Ca(OH)_2$ was possible, however, only by using this orientation effect. Otherwise the low peak would have been disturbed too much by the high statistical background.

(2) In spite of the material being ground to an extremely fine powder, this method is nondestructive, and even the hydrates are not destroyed. Ettringite ($32H_2O$), which was nearly destroyed by 1 hr of dry grinding, did not change its intensities after having been ground in benzene for 10 hr (fig. 1a, 1b, and 1c). In order to detect a possible change of the diagram with time of exposure, the intense X-ray beam (CuKα; 30 kv) was directed on the surface of the sample for 12 hr. Even then, however, the X-ray diagram did not change at all.

It should be added that after the Symposium it was learned that for the last two years, a similar method of wet grinding has been used in the laboratories of the Portland Cement Association at Skokie, Illinois (cf. L. E. Copeland, and R. H. Bragg, ASTM Bull. No. 228, Feb. 1958, pp. 56–60).

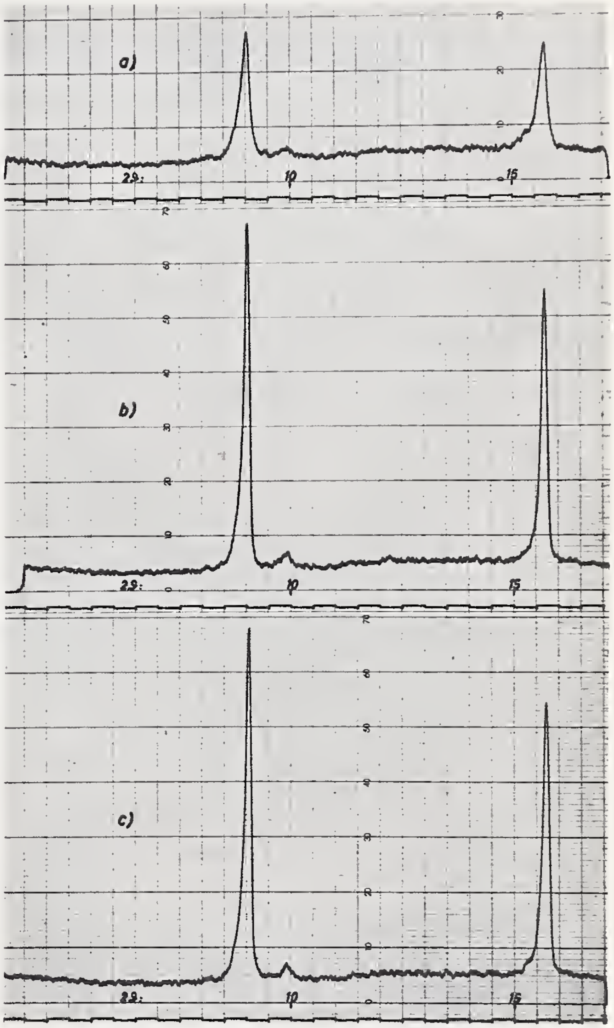

FIGURE 1. *Ettringite* (*X-ray diagrams*).

(a) 1 hr dry grinding
(b) 40 min grinding in benzene
(c) 10 hr grinding in benzene

Paper II–S3. Influence of Reducing Atmosphere on the Constitution of Clinker*

Y. Suzukawa and T. Sasaki

Synopsis

The influence of FeO on the β-γ inversion of C_2S stabilized with various kinds and amounts of agents and on the dusting of synthetic clinkers of the system C—A—F—S—M—N was studied.

It was found that the β-γ inversion due to the presence of FeO is related to the ionic radius of stabilizers and that the amount of FeO required for dusting the clinker decreases with the increase in the content of Na_2O.

Furthermore, commercial shaft kiln clinker, which is partially reduced, was studied, and the presence of $C_{12}A_7$ (or unstable C_5A_3) was shown.

Based on the results obtained, it is clear that C_2S forms solid solutions with FeO more predominantly than with alkalis.

Résumé

Cet exposé étudie l'influence de FeO sur l'inversion β—γ de C_2S stabilisée par différentes sortes et quantités d'agents, et sur la pulvérisation spontanée de clinkers synthétiques du système C—A—F—S—M—N.

L'étude révèle que l'inversion β—γ due à la présence de FeO est en relation avec le rayon ionique des stabiliseurs, et que la quantité de FeO requise pour pulvériser spontanément le clinker décroît avec l'augmentation de la teneur en Na_2O.

On étudie également le clinker commercial de four à cuve, qui est partiellement réduit, et la présence de $C_{12}A_7$ (ou C_5A_3 instable) est indiquée.

Les résultats obtenus montrent nettement que C_2S forme des solutions solides avec FeO d'une façon plus prédominante qu'avec les alcalis.

Zusammenfassung

Der Einfluß des FeO auf die β—γ-Inversion des C_2S, nachdem es mit verschiedenen Verbindungen und durch verschiedene Mengen dieser Verbindungen stabilisiert wurde, wurde für synthetische Klinker des C—A—F—S—M—N Systems studiert, und die Staubentwicklung der Klinker wurde unter den gleichen Bedingungen untersucht.

Es wurde gefunden, daß die durch FeO hervorgebrachte β—γ-Inversion zu dem Ionenradius der Stabilisatoren in einem gewissen Verhältnis steht, und daß die Menge des FeO, welche nötig ist, einen zerrieselnden Klinker hervorzubringen, nimmt ab, wenn der Gehalt an Na_2O zunimmt.

Auch Klinker, welche in einem Drehrohrofen einer Fabrik erzeugt wurden, wo sie teilweise reduziert werden, wurden untersucht, und es wurde gefunden, daß $C_{12}A_7$ (oder unstabiler C_5A_3) anwesend ist.

Die Ergebnisse zeigen, daß C_2S vorzugsweise mit dem FeO feste Lösungen bildet; dieses wird den Alkalien vorgezogen.

Inversion of C_2S

There has been little information on the influence of FeO on the β-γ inversion of C_2S except for reports of Bowen, Schairer, and Posnjak [1–4].[1]

The β-C_2S stabilized with various kinds and amounts of agents, such as B_2O_3, P_2O_5, Na_2O, K_2O, BaO, Cr_2O_3, MnO_2, or their combinations, was prepared from pure γ-C_2S, and mixtures of the system β-C_2S-$2FeO{\cdot}SiO_2$ were heated in a pure N_2 atmosphere at 1,220 °C for 20 min by the same method as reported by Bowen and Schairer [1].

Chemical and X-ray analysis of the preparations showed that in the β-C_2S stabilized with Na_2O, K_2O, BaO, Cr_2O_3, or MnO_2 (substituting groups for Si^{4+}), the β-γ inversion occured when 0.4–0.5 percent FeO was added, but in the β-C_2S stabilized with B_2O_3 or P_2O_5, no β-γ inversion occurred when 4 percent FeO was added [5, 6]. As has already been reported by Dietzel and Tscheischwili [7] and Glasser and Osborn [8], the β—γ inversion of the preparations containing Cr_2O_3 or MnO_2 is due to the reduction of stabilizers during heat-treatment. The β-C_2S stabilized with both B_2O_3 and Na_2O showed similar behavior to that stabilized with B_2O_3.

As an example, X-ray diffraction results on β-C_2S stabilized with 0.28 percent Na_2O are shown in figure 1.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Central Research Institute, Ube Industries, Ltd., Ube-Shi, Yamaguchi-Ken, Japan. (A summary of this paper was read at the Symposium by R. H. Bogue.)

[1] Figures in brackets indicate the literature references at the end of this paper.

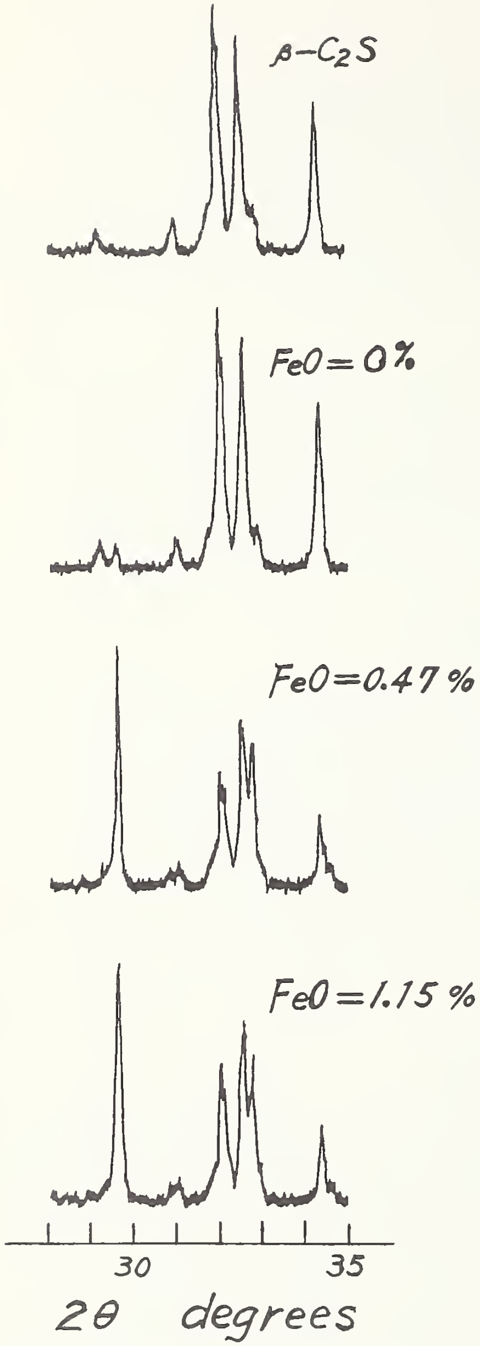

FIGURE 1. *Geiger-counter diffractometer tracings.*

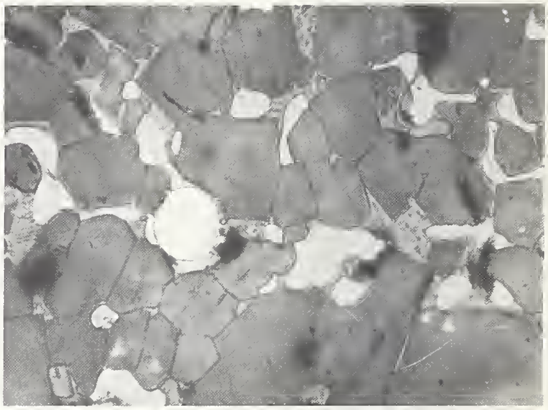

FIGURE 2. *Partially reduced shaft-kiln clinker etched with 0.5 percent alcoholic solution of* HNO_3. × *250.*

Dusting of Clinker

A series of clinkers of the system C–A–F–S–M–N having constant major oxide components except for Na_2O were prepared from pure chemical reagents. Chemical compositions of the original clinker of the system C–A–F–S–M are: S=25.0, A=6.4, F=3.0, C=64.6, and M=1.2 percent.

After pulverizing, the clinkers were mixed with various amounts of ferrous oxalate and reheated in a pure N_2 atmosphere at 1,350 °C, and then cooled slowly or quickly near the bottom of the furnace. The amount of FeO required for dusting the clinker, which was determined by the method of trial and error, is shown in table 1 [5].

The decrease in the amount of FeO with the increase in the content of Na_2O is due perhaps to the lowering of the inversion temperature of C_2S as reported by Newman and Wells [9] and to the change in the chemical compositions of clinker as reported by Suzukawa [10].

Similar experiments were also made on the synthetic clinkers of the system C–A–F–S–M–K, but owing to the volatilization of K_2O, no apparent results were obtained on the relation between the amount of K_2O and that of FeO.

TABLE 1. *Amount of* FeO *required for dusting*

Sample No.	Method of cooling	Na_2O (Residual)	FeO
		Percent	*Percent*
A	Cooled slowly from 1,350 to 1,200 °C for 30 min	0.00	2.36
B		.13	1.71
C		.40	1.10
A′	Cooled quickly at 1,350 °C	.00	2.81
B′		.14	2.69
C′		.36	2.48

A comparative test was made on the strength of mortar (1×1×6 cm; water : cement : sand =0.65 : 1 : 2) containing synthetic normal and dusted clinkers of the system C–A–F–S–M–N. It was found that the dusting due to the presence of FeO (1.76 percent) decreased the strength by 20 to 30 percent.

Shaft-Kiln Clinker

In shaft kilns, partially reduced clinker is sometimes produced, and the Fe_2O_3 is reduced to FeO or on rare occasions to metallic iron. A typical microscopic photograph is shown in figure 2. No ferrite phase is observed, and the presence of $C_{12}A_7$ (or unstable C_5A_3) and metallic iron is shown. X-ray analysis of the clinker showed patterns ($d=4.90$; 2.975 A) corresponding to those of ($C_{12}A_7$ [11].

Furthermore, partially dusted clinkers were sieved into two fractions. Chemical analysis of each fraction showed that in the fraction <1.2 mm, the content of SiO_2 and FeO was greater and that of Al_2O_3, CaO, and MgO smaller, respectively, than in the fraction >1.2 mm.

On the basis of the preceding discussions, the dusting of shaft-kiln clinker is partially ascribed to the formation of solid solution of C_2S with FeO

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Paper II–S4. Reactions of Coal Ash With Portland Cement Clinker During the Burning Process*

T. Heilmann

Synopsis

When using fuel of high ash content for burning portland cement clinker in a rotary kiln, a certain part of the ash will be precipitated onto the raw materials during their passage through the kiln, forming an integral component of the clinker produced.

The various components of the raw mix are introduced into the kiln as a more or less homogeneous mixture; however, the ash from the fuel, or at least part of it, is precipitated onto the surface of the nodules or clinker during their heating, calcination, and sintering in the burning zone, thereby causing a degree of heterogeneity. The nature and the extent of the reaction between ash and clinker is, naturally, of great importance to the operation of the kiln as well as to the general quality of the clinker.

Results are given of laboratory test burnings made in order to investigate the way in which the ash reacts with the clinker minerals and the components resulting from these reactions. The molten ash has a very pronounced "wetting action" in relation to the surface of the clinker minerals. Therefore, only a small part of the ash will remain on the outer surface, the rest penetrating very quickly into pores and cracks to initiate reactions with the clinker minerals.

The speed of the reactions has been investigated together with its dependence on the burning temperature as well as on the composition of the clinker. In particular, the important part which the movement of CaO plays in the formation of the clinker minerals has been demonstrated. The results are illustrated by a number of photographs of polished clinker sections.

Résumé

Lorsqu'un combustible de forte teneur en cendres est utilisé pour la cuisson de clinkers de ciment Portland dans un four rotatif, une certaine partie des cendres se dépose sur les matières premières pendant leur passage à travers le four, formant un composant intégral des clinkers produits.

Les différents composants du mélange cru sont introduits dans le four sous forme d'un mélange plus ou moins homogène; cependant, les cendres provenant du combustible, ou au moins une partie de celles-ci, se déposent sur la surface des nodules ou des clinkers pendant la chauffe, la calcination et le frittage de ceux-ci dans la zone de cuisson, provoquant ainsi un degré d'héterogénéité. La nature de la réaction des cendres sur les clinkers et la mesure dans laquelle s'opère cette réaction sont, bien entendu, de grande importance pour le fonctionnement du four aussi bien que, d'une façon générale, pour la qualité des clinkers.

L'exposé contient des résultats de cuissons d'essai faites aux laboratoires en vue d'une étude de la façon dont réagissent les cendres avec les minéreaux des clinkers et les composants résultant de ces réactions. Les cendres fondues ont un "effet humidificateur" très prononcé sur la surface des minéraux des clinkers. En conséquence, seule une faible partie des cendres reste à la surface tandis que la partie restante pénètre très rapidement dans les pores et les fissures en amorçant des réactions avec les minéraux des clinkers.

La vitesse des réactions a été étudiée en fonction de la température de cuisson ainsi que de la composition des clinkers. Tout particulièrement, on a relevé le rôle important que joue le mouvement du CaO pour la formation de minéraux de clinkers. Les résultats sont illustrés au moyen de photos de sections polies des clinkers.

Zusammenfassung

Bei Benutzung von Brennstoff mit großem Aschengehalt zum Brennen von Portlandzementklinker in einem Drehofen wird ein Teil der Asche sich beim Durchgang der Rohmaterialien durch den Ofen auf denselben niederschlagen und einen integrierenden Bestandteil des erzeugten Klinkers bilden.

Die verschiedenen Bestandteile der Rohmischung werden dem Ofen als eine mehr oder weniger homogene Mischung zugeführt; die Asche des Brennstoffes, oder wenigstens ein Teil davon, schlägt sich indessen auf der Oberfläche der Granalien oder Klinker nieder, während diese im Ofen erhitzt, kalziniert und gesintert werden, und verursacht dadurch eine gewisse Heterogenität. Beschaffenheit und Umfang der Reaktion der Asche mit dem Klinker sind natürlich für den Betrieb des Ofens als auch für die allgemeine Qualität des Klinkers von großer Bedeutung.

Es liegen Resultate von Laborbrennversuchen vor, die unternommen wurden, um die Weise, in der die Asche mit den Klinkermineralen reagiert, und die durch diese Reaktionen entstehenden Bestandteile zu untersuchen. Die geschmolzene Asche hat eine sehr ausgesprochene "benetzende Wirkung" auf die Oberfläche der Klinkerminerale. Daher wird nur ein geringer Teil der Asche an der äußeren Oberfläche verbleiben, während der Rest sehr schnell in Poren und Risse eindringen wird, um Reaktionen mit den Klinkermineralen einzuleiten.

Man hat die Reaktionsgeschwindigkeit und auch ihre Abhängigkeit von der Brenntemperatur und der Zusammensetzung des Klinkers untersucht. Besonders ist nachgewiesen worden, welch bedeutende Rolle die CaO-Wanderung bei der Bildung der Klinkerminerale spielt. Die Ergebnisse sind durch einige Fotos von Klinkerschliffen veranschaulicht.

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Introduction

During the burning of portland cement clinker with coal in a rotary kiln, the ash, introduced as part of the fuel, will for the greater part react with and become an integral part of the clinker.

The amount of ash in relation to clinker may vary within a wide range and in the first instance will naturally depend on the ash content of the fuel, as well as on the heat economy of the kiln. Furthermore the type of heat-transmitting elements used will influence the amount of ash which is absorbed by the raw materials during the contact with the smoke gas.

The possible dust-absorbing elements installed and the extent to which the dust is recycled to the rotary kiln will also be of influence. In the case where a highly effective filter is installed, the total dust which is absorbed being returned to the kiln, the ash enters completely into the clinker as an integral component.

In general the coal ash will have a chemical composition which differs widely from that of the desired clinker and from the composition of the raw mix which is introduced into the kiln.

By suitable fine grinding and homogenization of the raw mix it is possible to insure that complete reaction between the individual components of the raw mix takes place during the burning process. The coal ash, however, will on account of its deviating composition and the way in which it is absorbed by the material in the kiln cause a certain amount of inhomogeneity in the clinker produced. Consequently the clinker will be a heterogeneous mixture of:

a. Clinker minerals formed by the original components of the raw mix, and,

b. Products resulting from the reaction between the ash and the clinker minerals.

The nature and the extent of this reaction, which is naturally of great importance to the general quality of the clinker, have been examined by a number of laboratory test burnings. The speed has also been investigated to discover its dependence on the burning temperature as well as the composition of the clinker.

General Remarks on the Absorption of Ash in a Rotary Kiln

Generally a coal ash will have a composition varying within the following limits:

	Average	Usual limits of variation
	Percent	*Percent*
SiO_2	46	35–60
Al_2O_3	26	15–35
Fe_2O_3	13	5–20
CaO	5	0–10

MgO, sulfur, and alkalies will also be present in varying amounts. In special cases a coal ash may have a composition outside the above-mentioned limits.

The melting range of coal ash will generally be within 1,050 to 1,250 °C; thus the ash in the coal flame will be in a completely molten state. However, during the further passage of the smoke gas through the kiln, the molten particles of ash will be cooled and thus gradually solidify.

In most kilns about half of the ash will be absorbed by the raw materials in the calcining and the burning zones, where the greater part of the raw materials is usually present in the form of nodules. In this part of the kiln the ash will be precipitated onto the surface of the nodules to initiate the reaction with the clinker minerals.

In the wet process the ash absorbed in the chain system part of the kiln will for the greater part be mixed homogeneously with the raw mix and behave as any of the other components.

The amount of ash which is introduced into a kiln will, as already mentioned, depend both on the ash content of the fuel and on the kiln's heat economy. In table 1 some figures are given, showing the amount of ash in relation to clinker calculated for different ash contents, (15 to 35 percent), and different heat economies, (800 to 1,600 kcal/kg clinker).

Table 1. *Ash content of clinker, in percent. Heat value of ash-free fuel, 7,800 cal/g*

% Ash in coal	Calories per kilogram clinker				
	800	1000	1200	1400	1600
15	1.8	2.2	2.6	3.1	3.5
20	2.6	3.2	3.8	4.5	5.1
25	3.5	4.3	5.2	6.0	6.9
30	4.4	5.5	6.6	7.7	8.8
35	5.5	6.9	8.3	9.6	11.0

From the table it can be seen that in the case of, for instance, a wet kiln with an average heat economy of 1,400 kcal/kg clinker and fired with coal containing 20 percent of ash, 4.5 percent of ash in relation to the clinker will be introduced into the kiln. If the ash is completely absorbed by the raw materials, the ash will lower the lime saturation of the clinker by about 10 percent. If for instance a lime saturation in the clinker of about 95 percent is desired, then the raw mix should have a composition corresponding to a lime saturation of 105 percent. Thus the raw mix will contain an amount of CaO which is a surplus when compared with the amount which could normally react with the SiO_2, Al_2O_3, and Fe_2O_3 of the raw mix.

If portland cement clinker, burnt with a fuel of moderately high ash content, is examined microscopically, a certain inhomogeneity in the clinker is usually found. Sometimes an outer shell of comparatively low lime content is seen, clearly originating from the ash precipitated onto the surface of the clinker or nodules. Often, however, the clinker surface will show to a limited extent only signs which could be traced to the precipitation of coal ash. Thus the ash must have a pronounced tendency to react effectively with the ordinary components of the raw mix, even if a considerable amount of the ash is precipitated onto the surface of nodules or clinker during their passage through the kiln.

Before describing in detail the method of testing, it would be of interest to estimate the amount of ash which would, under conditions normally prevailing in a coal-fired rotary kiln, be available per unit contact area between ash and clinker.

The amount of ash per unit area expressed in grams per square centimeter (a) will depend on:

a. The amount of ash in relation to clinker (A percent), and

b. The specific surface of the clinker (o cm^2/g) as expressed by the following equation:

$$a=\frac{A}{100\ o}. \tag{1}$$

If the size of the clinker nodules is measured by the diameter d cm, and the apparent specific gravity of the clinker is s g/cm^3, the specific surface would be given by

$$o=\frac{6}{ds},$$

and the amount of ash per unit area could also be expressed as

$$a=\frac{Ads}{600}. \tag{2}$$

Table 2 shows the variation of ash per unit area (mg/cm^2) with the total amount of ash in relation to the clinker weight and the average size or the specific surface of the clinker. An apparent clinker specific gravity (s) of 2.8 g/cm^3 is assumed, which corresponds to about 10 percent by volume of pores.

Table 2. *Average amount of ash per unit area (mg/cm^2) of the clinker surface, calculated for an apparent specific gravity of the clinker, s=2.8 g/cm^3*

Average diameter of clinker .... mm	1	2	5	10	20
Specific surface of clinker .... cm^2/g	21	9.3	4.3	2.1	1.1
Ash in relation to clinker weight:					
2 .... %	0.9	1.9	4.7	9.4	19
5 .... %	2.3	4.7	12	23	47
10 .... %	4.7	9.4	23	47	94
20 .... %	9.4	19	47	94	190

Character and Extent of the Reactions Between Ash and Clinker

The tests have shown that two factors influence the character and the extent of the ash absorption:

a. The tendency of the molten ash to spread out over the surface of the clinker substance, and

b. the direct reactions, where the layer of ash is in contact with the clinker substance.

The molten ash has a very pronounced "wetting action" in relation to the clinker minerals, giving rise to a very small angle of contact between them. This means that the ash will be able to penetrate very quickly from the outer surface into cracks and openings in the clinker substance, thereby greatly increasing the area for reaction.

By the direct reactions through the contact areas, lime is gradually (although initially very rapidly) transferred from the clinker into the ash This leads to the formation of C_2S crystals in the original layer of ash and a corresponding transformation of C_3S into C_2S in the clinker. Furthermore, free CaO is also transferred from the clinker to the ash.

The above-mentioned two factors were investigated separately by two series of tests (A and B).

Test Series A

The Spreading of the Molten Ash Over the Clinker Surface

The tendency of the molten ash to spread out over the surface of the clinker minerals is shown quite clearly by some of the tests in series B, in particular in cases where small amounts of ash per unit area have been used. Furthermore, this tendency was also investigated by some special tests carried out in the following way:

The raw mix to be used for the tests was first calcined for one hour at 1,000 °C and then compressed into a briquet 1.5 cm diam with a pressure of about 5 tons, corresponding to 2.8 t/cm^2. The surface was then drilled to form a spherical depression having a total surface of about 1 cm^2, for receiving the ash. In the bottom of the depression a small hole of 1 mm diam was drilled and filled with *uncalcined* raw mix. The briquet was then burnt for 30 min at 1,500 °C.

During this burning the sintering of the uncalcined raw mix would cause one or more cracks, whereas the rest of the surface area of the depression would be free from cracks. The crack or cracks formed in the small hole would lie in one plane, making it possible, by a later cutting and polishing, to obtain the whole of this "artificial" crack in the polished section of the clinker.

The briquet was then heated to 1,500 °C. A small amount of molten ash was heated separately in a small loop formed at the end of a platinum wire and then dropped into the spherical depression in the briquet's surface. The temperature was maintained for a further period of 10 sec, when the briquet was removed from the furnace and cooled rapidly in about 15 sec to a temperature below 1,000 °C.

After this treatment the briquet was cut, polished, and etched with nitric acid in order to show the dicalcium and tricalcium silicates. For this test series A, clinker C1 and ash A1 were used (for compositions see table 3).

From the photographs, figures 1, 2, and 3, it can be seen that the molten ash has been able to penetrate momentarily down into the crack, when the reaction between the ash and the clinker minerals has started in the usual way through the surface of contact. It will also be seen that the width of the crack is only about 0.35 mm.

At the bottom of the hole characteristic zones of reaction have already developed and can be seen. These will be described in greater detail later in connection with the contact reaction. Dendritic crystals of C_2S appear in the original layer of ash and in the clinker a layer of C_2S crystals can be seen, having been formed by the removal of CaO from the original C_3S crystals. Outside this layer the clinker substance is in its original state.

By comparing the reactions seen in these photos with corresponding photos from test series B, (for instance fig. 4), where the molten ash has been in contact with a clinker substance free from cracks but with the same reaction time of 10 sec, it can be seen that the thickness of the reaction layers and the degree of reaction is very nearly the same in the two cases, indicating that the molten ash has penetrated into the crack almost instantaneously. If this was not the case, reactions so far progressed would not have been observed at the bottom of the hole.

Test Series B1 and B2

Description of Test Procedure

In order to study the direct contact reactions between ash and clinker minerals, it was necessary to prepare a contact area which was, as far as possible, free from any kind of cracks into which the ash could penetrate and thus obliterate the picture.

The preliminary steps in the preparation of the test specimens were the same as those outlined for test series A (see page 89), a small briquet of calcined raw mix being made and the surface drilled to form a spherical depression, 1 cm² in surface area. The spherical shape was chosen in order to insure an even distribution of the molten ash over the clinker surface. A cylindrical depression would, owing to the low contact angle between the molten ash and the clinker substance, give an uneven distribution of the ash over the surface.

Two series of test burnings were carried out. The first, *test series B1*, when the briquet of calcined raw mix was prepared in the abovementioned way, was heated with the desired amount of ash to the required burning temperature in a period of about 2 hr. This temperature was then maintained for a definite time, which varied from 20 min to 6 hr, and the test piece was then cooled at moderate speed over a period of about 20 min.

These tests would to some extent imitate the heating taking place in industry. This is especially so in the case of a wet process kiln, when ash is precipitated onto the surface of nodules from the time they leave the chain system. The amount of ash used in these tests was varied from 2.4–200 mg/cm², and the long burning time of 6 hr. was chosen in order to study the ultimate state of reaction between the ash and the clinker.

Another series of test burnings *test series B2* were carried out in order to imitate the conditions prevailing in the burning zone of a kiln when the molten ash would be precipitated directly onto the surface of the nodules. By these tests the speed of the reaction between the ash and the clinker minerals was investigated and the various steps in the chemical reactions were studied.

In order to fix the original surface of the clinker substance exactly a small hole of 0.5 mm diam was drilled in the briquet and a platinum wire of the same diameter was placed into the hole. The briquet was then burnt (without any ash) at a temperature of 1,500 °C for half an hour and the depression was reground in such a way that the end of the platinum wire was flush with the surface of the clinker.

The briquet was then heated in an electrical furnace to the temperature at which the reactions were to be investigated and the desired amount of ash was heated separately as explained previously on pages 89–90. When the desired temperature was reached the molten ash was dropped into the depression on the briquet's surface and the temperature maintained for the desired test period. After this the briquet was removed from the furnace and cooled rapidly in about 15 sec to a temperature below 1,000 °C. This rate of cooling was chosen in order to prevent the test pieces from developing cracks and to prevent any phenomena of dusting.

The amount of ash used was maintained at a constant value of 150 mg/cm², as this rather high amount would insure a continual surplus of ash, available to react with the clinker, throughout the

FIGURE 1. × *50. Test series A. Clinker C1.*
Ash A1.—1,500 °C—10 sec.

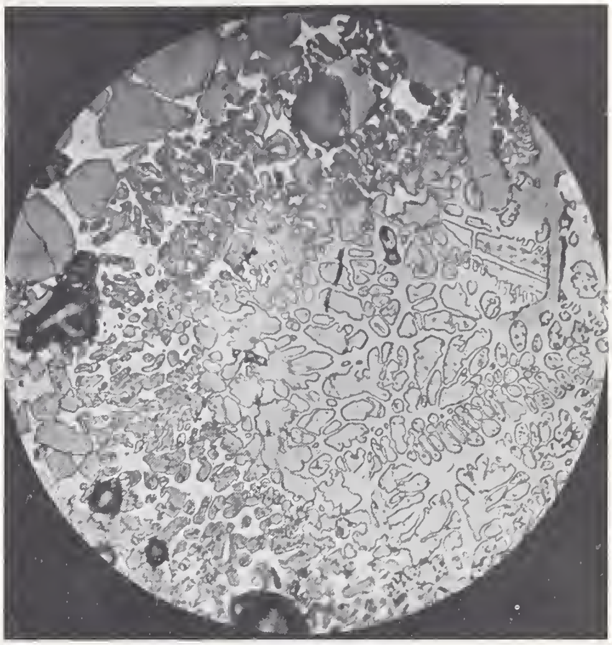

FIGURE 3. × *350. Test series A. Clinker C1.*
Ash A1.—1,500 °C—10 sec.

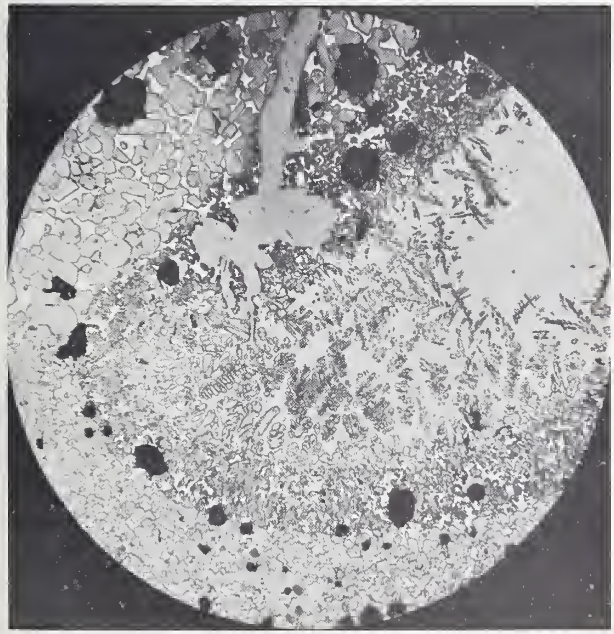

FIGURE 2. × *125. Test series A. Clinker C1.*
Ash A1.—1,500 °C—10 sec.

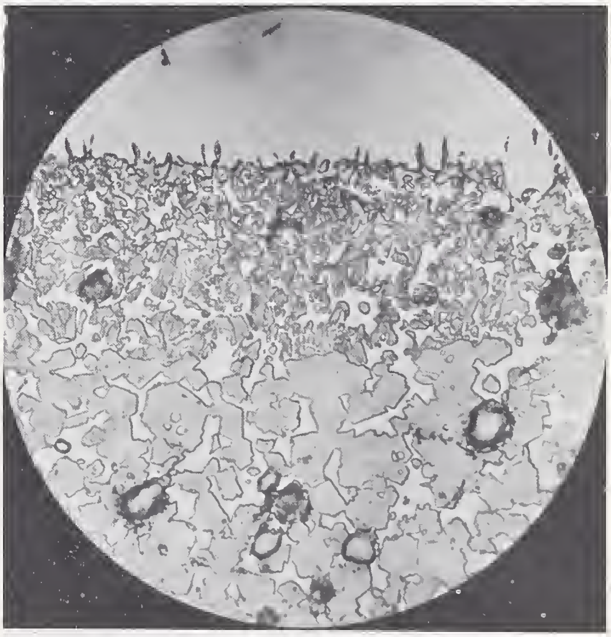

FIGURE 4. × *500. Test series B2. Clinker C1.*
Ash A1.—1,500 °C—10 sec.

chosen reaction times. The reaction temperatures chosen were 1,300, 1,400, and 1,500 °C, and the time of reaction was varied from 10 sec to 60 min.

After burning, the test specimens were cut, polished, and etched in the same way as the specimens of test series A, always insuring that the polished surface cut through the platinum wire.

For the tests, clinker of two compositions, one high in lime, C1, and one of low lime content, C2, were used. Two ashes were also used, one of normal composition, A1, and one with a special high content of CaO, A2. The compositions of the clinker and the ashes are given in table 3.

TABLE 3. *Compositions of clinker and ash used for test series A and B*

	Clinker		Ash	
	C1	C2	A1	A2
	%	%	%	%
SiO_2	19.7	24.8	48.8	39.1
Al_2O_3	5.5	3.6	27.2	20.0
Fe_2O_3	3.4	2.6	12.6	9.6
CaO	69.3	66.8	5.6	26.8
LSF	105	89	--------	--------
Free CaO	3.8	--------	--------	--------
C_3S	74.9	55.7	--------	--------
C_2S	0	29.2	--------	--------
C_3A	8.9	5.1	--------	--------
C_4AF	10.4	7.9	--------	--------
Ratio: CaO/SiO_2	--------	--------	0.12	0.69

General Description of the Reactions Between Ash and Clinker Substance

Figure 5, corresponding to a 1-hr reaction time at 1,500 °C between the clinker C1 and the ash A2, shows under small magnification (12 times) most of the briquet with the platinum wire in the middle of the depression. The uppermost layer is the original ash in which crystals of C_2S have already developed considerably, and below this is the reaction layer corresponding to the original clinker substance from which CaO has been removed.

There are indications that during the first part of the reaction time, presumably during the first few seconds, a thin layer of the clinker substance is dissolved directly into the molten ash. However, during further reactions between ash and clinker, certain characteristic zones of reactions are very quickly formed. These zones are clearly defined in relation to each other, and generally there are no signs of a continuous passing stage between one zone and the next.

Figure 6 shows the zones of reactions in greater enlargement. To the right of the picture the platinum wire can be seen, the top of which indicates the original border between ash and clinker substance. Similar zones are seen in figure 7. This photo is taken at some distance from the platinum wire so the wire itself does not appear in the photo.

FIGURE 5. × *12. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—1 hr—150 mg ash/cm².

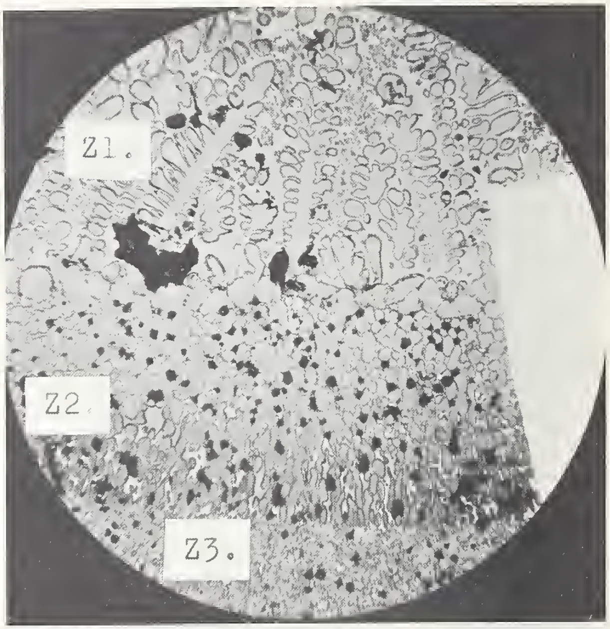

FIGURE 6. × *63. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—1 hr—150 mg ash/cm².

Description of the Zones of Reactions

The uppermost zone, Z1, is the original layer of ash into which CaO has been absorbed with the formation of characteristic C_2S crystals. The next zone, Z2, comprises a layer of the original clinker substance from which crystals of free CaO and CaO from C_3S crystals have been extracted, with the transformation of this C_3S into C_2S crystals.

Farther down is found a zone, Z3, which is only characteristic for clinker of high lime saturation factor. This zone will contain the original clinker substance with its content of C_3S and, possibly, C_2S crystals. Only the crystals of free CaO have been removed. This zone is difficult to distinguish in a black and white photo but is clearly seen in a color photo.

Figures 8 and 9 show the border line between zones Z2 and Z3 in greater enlargement. Below the border line the great amount of well-developed C_3S crystals of the original clinker substance can be seen quite clearly, and above the border line, C_2S crystals formed by the extraction of CaO from the C_3S crystals.

Figures 10 and 11 show the border line between zones Z1 and Z2, also in greater enlargement. Above the border line can be seen the ash into which characteristic C_2S crystals have developed, and below the border line, the C_2S crystals remaining from the original C_3S crystals of the clinker.

Right on the border line there is a characteristic layer of coherent C_2S crystals of the same type which also develops on the outer border of a coarse grain of silica in an ordinary cement raw mix. In the great enlargement, figure 11, narrow channels are seen between these crystals, indicating the possibility of some transport of CaO by liquid diffusion. It must be assumed, however, that probably part of the transport of CaO through this layer takes place as diffusion through the solid C_2S phase.

It will further be noticed, from figure 9 and figure 7, that the C_2S crystals of zone Z2, positioned immediately above the border line between Z2 and Z3, have a typically elongated shape, showing that this shape is particularly characteristic of the initial reaction. Later these crystals are converted to the rounded shape generally seen in portland cement clinker. The elongated crystals, developed to a total length of 250μ or more, are seen only in the tests with the clinker C1 of high lime content. In the lower-lime clinker C2, with both C_2S and C_3S crystals, the elongated C_2S crystals do not develop to the same extent (see fig. 8).

During the reaction, CaO is given off from zone 2 to zone 1, thus the volume of zone 2 will decrease. It is assumed that this is one of the reasons why, as can be seen in figure 5, the border line between zones Z1 and Z2 is situated somewhat below the top of the platinum wire. Another reason is probably that by direct solution a thin layer of clinker has been dissolved by the ash during the very initial stages of the reactions.

A clinker such as C1, containing 3.8 percent of free CaO and 75 percent of C_3S, would by transformation of all C_3S crystals to C_2S and by giving off all the free CaO, shrink in volume by about 23 percent.

In figure 6 the thickness of zone Z2 has been measured and found to be about 510μ. Assuming a shrinkage of 23 percent the original thickness of that layer would have been 660μ. The distance from the border line Z2 and Z3 to the top of the platinum wire has also been measured and found to be about 700μ. Thus, it would seem that by direct solution a layer of clinker, corresponding to a thickness of 40μ, has been dissolved directly by the ash.

These figures correspond to a reaction temperature of 1,500° C. At 1,400° the dissolved layer is somewhat thinner. Furthermore, the dissolved layer is somewhat thicker in the case of ash A1, of low lime content, than in case of ash A2, but this is also to be expected.

In these calculations it has been assumed that the porosity of zone Z2 is the same as that of the original clinker. However, figure 5 indicates a somewhat greater porosity for zone Z2, which means that the dissolved layer would actually be slightly greater than found in the above mentioned calculations.

As the reactions proceed, the distinct border line between zones Z1 and Z2 is gradually obliterated, since the C_2S crystals in zone Z1 gradually assume the same rounded shape as in Z2. The disappearing of the border line Z1 and Z2 is generally found to take place earlier when smaller amounts of ash per unit area are used.

During the later reactions, when the ash layer has been saturated with CaO (with complete formation of C_2S) the transformation of C_3S into C_2S crystals in the clinker will stop, i.e., the border line Z2 and Z3 will not move further down into the clinker substance. However, in the case of the high-lime clinker C1, free lime from farther down in the clinker may be used for re-establishing crystals of C_3S in zone Z2 and in particular near the border line between zones Z2 and Z3. Such characteristic crystals of C_3S, which generally appear as particularly large-size crystals, can be seen in figures 12 and 13. In these figures, inclusions of the original C_2S substance may be seen in C_3S crystals of this type.

In the case of a long reaction time and a comparatively small amount of ash per unit area, this reaction may lead to a complete transformation of the C_2S in Z2 into C_3S. The transformation may even continue into zone Z1, the original ash layer, as seen in figure 14.

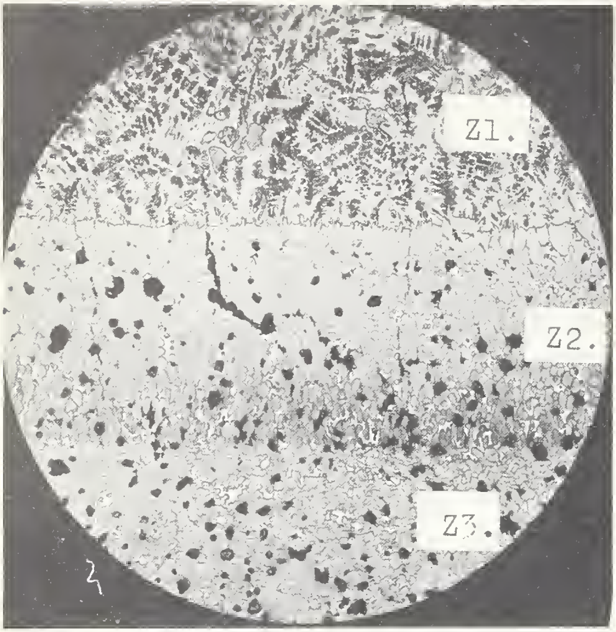

FIGURE 7. × *100. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—6 min—150 mg ash/cm².

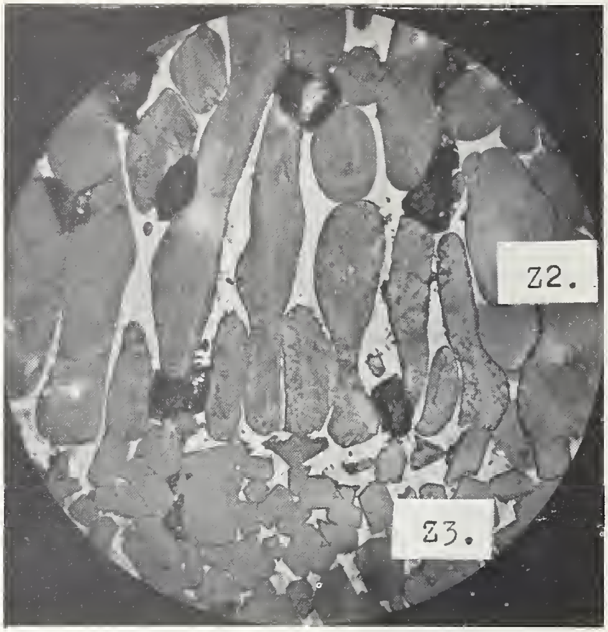

FIGURE 9. × *500. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—1 hr—150 mg ash/cm².

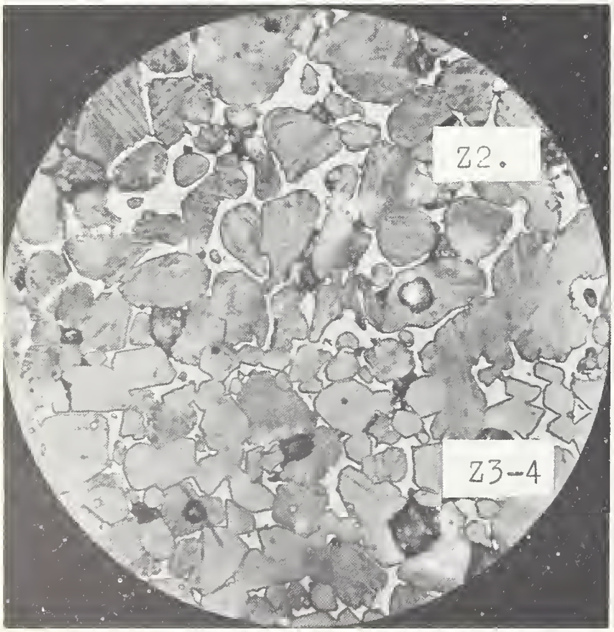

FIGURE 8. × *500. Test series B2. Clinker C2.*
Ash A1.—1,500 °C—6 min—150 mg ash/cm².

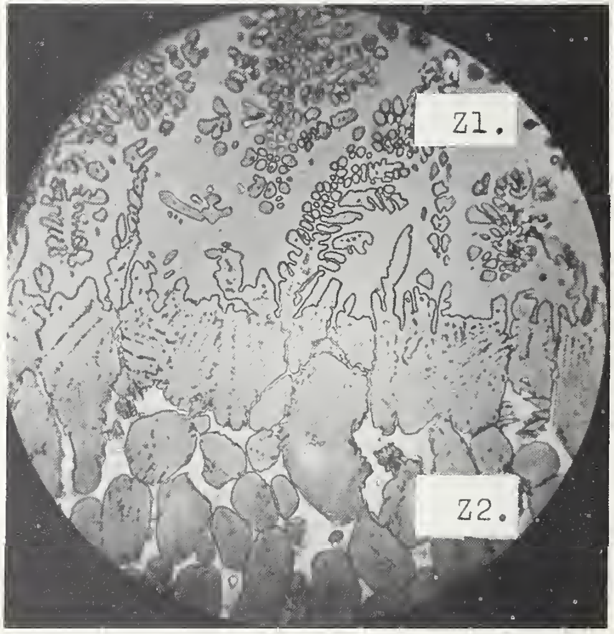

FIGURE 10. × *560. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—6 min—150 mg ash/cm².

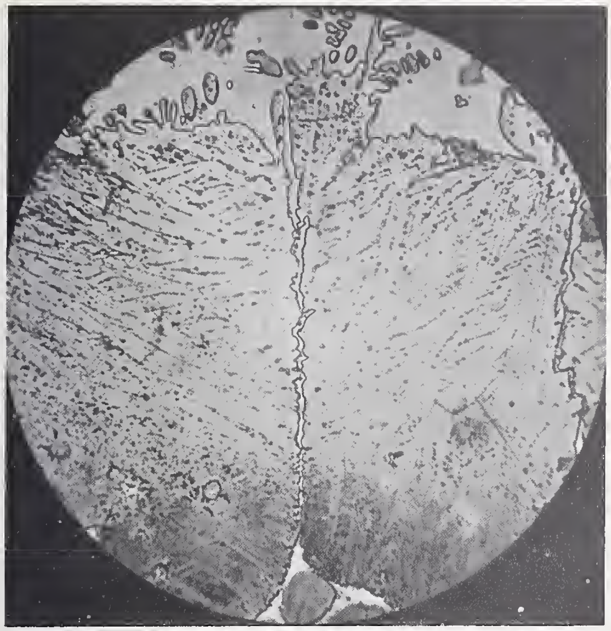

Figure 11. × *560. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—1 hr—150 mg ash/cm².

Figure 12. × *100. Test series B1. Clinker C1.*
Ash A1.—1,400 °C—6 hr—50 mg ash/cm².

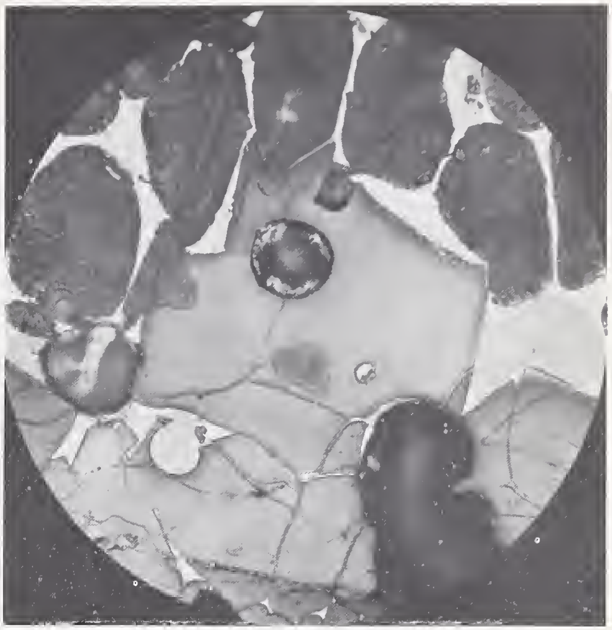

Figure 13. × *500. Test series B1. Clinker C1.*
Ash A1.—1,400 °C—6 hr—50 mg ash/cm².

Figure 14. × *500. Test series B1. Clinker C1.*
Ash A1.—1,400 °C—1 hr—2.4 mg ash/cm².

Depth of the Zones Z2 and Z3

The graphs in figures 15, 16, and 17 show the depth of penetration of zones Z2 and Z3 as a function of the time of reaction, plotted on a double logarithmic scale. The depth of penetration of zone Z2 has been measured as the distance from the top of the platinum wire to the border line between Z2 and Z3, whereas for zone Z3 it has been measured as the distance from the border line Z2 to Z3 to the border line Z3 to clinker.

It will be seen that the depth of penetration "p" in relation to the time of reaction "t" is almost a straight line, indicating that the reaction takes place according to an equation of the following type:

$$p=Kt^k \tag{3}$$

the constant "k" corresponding to the slope of the lines, and having values varying from 0.32 to 0.42.

The test series B1 (without the platinum wire), have shown that the zone Z3 may increase still further in thickness, and at 6 hr reaction time reach a value of up to 1,300 μ.

It must be assumed that the greater part of the transport of CaO, through the zone Z2, from the border line Z2 to Z3 to the border line Z1 to Z2, takes place as diffusion through the liquid between the C_2S crystals.

The diffusion may be estimated approximately in the following way:

An area, comprising one cm² of zones Z1, Z2, and Z3, is shown schematically in figure 18.

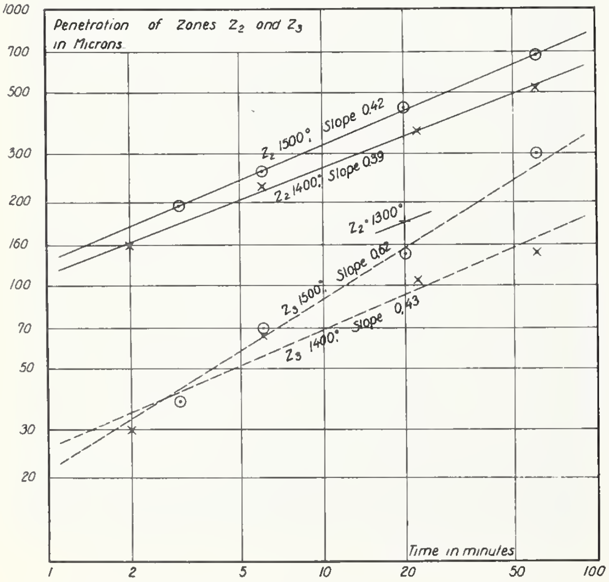

FIGURE 15. *Test series B2. Clinker C1—Ash A1.*

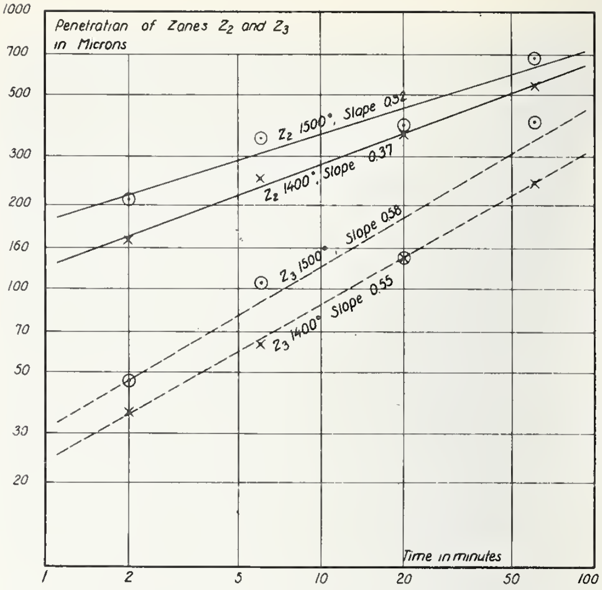

FIGURE 16. *Test series B2. Clinker C1—Ash A2.*

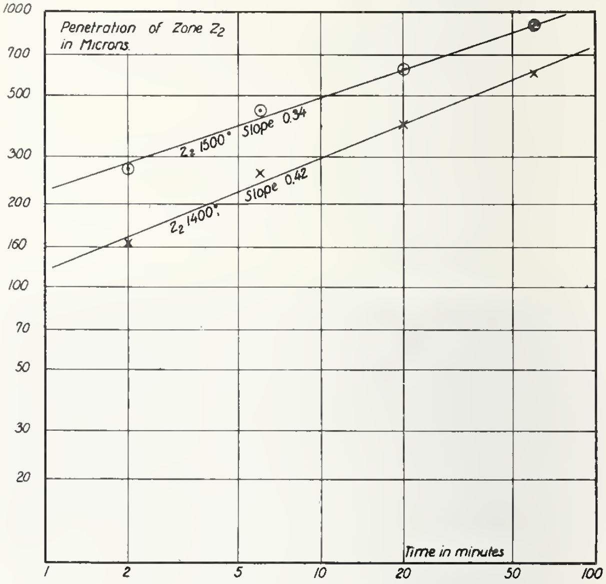

FIGURE 17. *Test series B2. Clinker C2—Ash A1.*

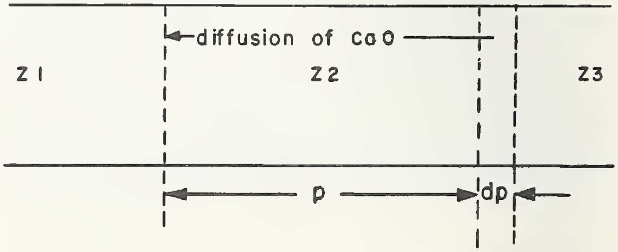

FIGURE 18. *Schematic representation of diffusion of* CaO.

At a certain time (t) the border line Z2 to Z3 is situated at a distance (p) from Z1 to Z2. In zone Z3, C_a g of CaO/cm^3 is assumed to be available for diffusion into zone Z1. Further, the concentration of CaO in the liquid phase at the border line Z1 to Z2 is taken as c_1 and at the border line Z2 to Z3 as c_0, assuming c_1 and c_0 to be constant.

During a time element (dt) the border line Z2 to Z3 moves a certain distance (dp), thus an amount of lime $C_a \times dp$ will move by diffusion into zone Z2.

The law of diffusion states that

$$C_a \frac{dp}{dt} = D \frac{c_0 - c_1}{p}, \tag{4}$$

where D is the coefficient of diffusion. By integration, within the limits $t=0$, to $t=t$,

$$\frac{p^2}{2} = D \frac{c_0 - c_1}{C_a} t, \tag{5}$$

or

$$p = k \frac{t^{\frac{1}{2}}}{C_a^{\frac{1}{2}}} \tag{6}$$

are obtained, k being a constant.

The connection between p and t in general agrees with the results show in figures 15, 16, and 17. The reason why the lines shown on these figures have a slope which for the penetration of Z2 is somewhat below 0.5 may be that the figures for the penetration of Z2 should have been corrected for the thickness of the layer of clinker directly dissolved during the initial stages of the process. If a correction corresponding to about 50 μ is subtracted from all the figures, the slope of the lines will approach the value of 0.5.

The depth p, being a function of C_a, is in agreement with the fact that for the low lime clinker C2 a greater depth of penetration has been found than for the high lime clinker C1. The difference in penetration for the two types of clinker is, according to the graphs, somewhat smaller than the value calculated at 1,400°, and somewhat higher at 1,500 °C.

It would be natural to expect that as the lime content in the ash layer (zone Z1) increases, there would be a corresponding decrease in the rate of CaO absorption by the ash. However, this does not seem to be the case, at any rate not for the range of lime concentrations up to a ratio CaO/SiO$_2$ in the ash of about 1.5, as can be seen by comparing figures 4 and 5.

During one hour at 1,500 °C, the penetration of Z2 increases to a depth of about 700 μ in both cases, while the ratio CaO/SiO$_2$ in the ash layer increases from a value of 0.12 to about 0.7 in case of ash A1, whereas in case of ash A2 it increases from 0.7 to about 1.5.

Test Results in Relation to Industrial Experience

As a conclusion it would, of course, be of interest to judge how the various test results could assist in the general understanding of the various problems which are met in practice when burning portland cement clinker in a rotary kiln with coal of high ash content. The main problems arising from the use of such a coal would generally be (a) the tendency to ring formation in the kiln, thus disturbing its operation, and (b) the influence on the physical properties of the resulting cement, mainly through its strength and expansion properties.

The layer of ash precipitated onto the surface of nodules or clinker will for a certain time, as long as the lime content of the ash layer is low, have a melting point which is lower than that of the clinker. Therefore, in the burning zone there will be a tendency for this clinker covered with ash to stick together and to the surface of the lining; this behavior is well known. The tendency for the ash to cause these troubles will naturally be expected to be less the smaller the amount of ash per unit area of the clinker surface.

It has been seen that the molten ash has a pronounced tendency to penetrate into even the very small pores and cracks in the clinker. Thus as the porosity of the clinker increases, the area for reaction between ash and clinker also increases, thereby reducing the amount of ash per unit area of clinker. This means that the layer of ash would in a short time reach such a degree of lime saturation that the tendency for the clinker to stick either together or to the surface of the lining would be greatly reduced. It is also evident that the higher the temperature in the burning zone, the quicker the ash will react with the clinker.

Now it is a well-known fact that a high silica ratio as well as a high lime saturation will generally counteract the tendency to ring formation in cases where fuel of high ash content is used. Both these measures will. in fact, raise the burning temperature and, therefore, the speed of reaction between ash and clinker while furthermore, a high silica ratio will also increase the porosity of the clinker.

The porosity and the surface properties of the molten ash in relation to the clinker are, undoubtedly, very important factors in avoiding an excessive tendency to ring formation when using coal of high ash content in a rotary kiln.

As the tests show, the depth to which the ash is able to react with the clinker under the conditions prevailing in a kiln, is comparatively small, generally not more than about ½–1 mm. If it were not for the comparatively great porosity of the clinker and the tendency for the molten ash to penetrate into the pores, the ash would remain on the surface of the clinker and, undoubtedly, cause great inconvenience during the operation of the kiln.

Portland cement clinker burnt for instance to an average liter weight of 1,350 g (measured on a fraction from 5–10 mm in size) may have a total porosity of about 20 percent, of which open pores would amount to 16 percent. Thus there would be every chance for the ash to penetrate deeply and react with the clinker. However, the absorption of ash onto the nodules or the clinker and the resulting reactions will lead to certain inhomogeneities in the clinker, which will influence the physical properties of the cement made from the clinker in question.

The pores and the cracks in the surface of the clinker cannot be expected to be evenly distributed, and, therefore, in some places comparatively large amounts of ash will penetrate into the clinker, resulting in areas of C_2S crystals. Therefore, under equal conditions, the average lime saturation of the clinker cannot be kept as high, without the risk of getting clinker with a high content of free CaO, in the case of a fuel of high ash content, as it could have been with a fuel of lower ash content. Even with the same average lime saturation, however, the inhomogeneity of the clinker caused by the ash reactions may cause some reduction in the strength properties of the cement.

Concluding Remarks

Besides adding to the better understanding of the practical problems involved in the application of high-ash coal to the burning of portland cement clinker in a rotary kiln, the investigations have also contributed to the understanding of the mechanism of the reactions which take place during the formation of the clinker minerals during the burning process. In particular, the important part which the movement of CaO plays in the formation of the clinker minerals has been demonstrated.

Furthermore, it would perhaps be justified to point out once more the importance of the microscopical examination of portland cement clinker as a valuable instrument in the investigation of problems which it would be very difficult to solve solely by chemical analyses.

In the planning and execution of the tests which have been carried out in the laboratories of F. L. Smidth and Co. A/S., Copenhagen, very valuable assistance has been rendered by K. A. Simonsen, and further by A. F. Mansell, especially in compiling the test results.

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Paper II–S5. Solid Solution of Alumina and Magnesia in Tricalcium Silicate*

F. W. Locher

Synopsis

Mixtures of tricalcium silicate and tricalcium aluminate were burnt at 1,500 °C and quenched. The composition of the melt which is thus formed is indicated by the invariant point *D* at 1,470 °C of the ternary system $CaO–Al_2O_3–SiO_2$. As it is relatively poor in lime and, due to the rapid quenching, can not react with the solid phases C_3S and CaO, the mixture must contain a corresponding amount of free CaO, although practically no free CaO is present in the constituents C_3S and C_3A of the initial mixture. Consequently, the occurrence of free CaO indicates that the heated sample contained a liquid phase. As the liquid is formed principally from the aluminate that was not taken up into the C_3S, it can be determined with the help of the chemical-analytically determined content of free CaO what is the maximum amount of C_3A that can be taken up by the C_3S in solid solution. The investigations indicated a maximum of about 2 percent C_3A, equivalent to 0.7 to 0.8 percent Al_2O_3. The entering Al atoms occupy the positions of Si atoms. X-ray diffraction investigations revealed that the dimensions of the C_3S lattice were hardly changed, if at all, by the takeup of C_3A.

Magnesium ions can replace the calcium ions in the lattice of the tricalcium silicate, which are then present in the burnt mixtures as free CaO. With the help of the content of free CaO it was established that at 1,420 °C, C_3S can take up about 1.5 percent MgO, at 1,500 °C up to 2.5 percent MgO, and also if the mixture further contains 4 percent C_3A.

Résumé

Des mélanges de silicate tricalcique et d'aluminate tricalcique ont été soumis à une température de 1,500 °C, puis à un refroidissement trempé. La composition de la masse fondue ainsi formée est indiquée par le point invariant *D* (1,470 °C) du système ternaire $CaO–Al_2O_3–SiO_2$. Etant donné que le mélange est de teneur relativement faible en chaux et que, par suite du refroidissement rapide, il ne peut pas produire de réaction avec les phases solides C_3S et CaO, il doit contenir une quantité correspondante de CaO libre; bien qu'il n'y ait pratiquement pas de CaO libre dans les constituants C_3S et C_3A du mélange initial. Par conséquent la présence de CaO libre indique que l'échantillon soumis à la cuisson contenait une phase fondue. Puisque la masse fondue est principalement formée à partir de l'aluminate qui n'a pas été absorbé dans le C_3S, on peut déterminer (à l'aide de la teneur en CaO libre, laquelle est déterminée par méthode chimique analytique) la quantité maximum de C_3A qui peut être absorbée par le C_3S en solution solide. Les résultats des recherches indiquent un maximum d'environ 2 % C_3A, équivalent à 0.7–0.8 % Al_2O_3. Les atomes de Al qui sont entrés occupent la position des atomes de Si. Les études de la diffraction aux rayons X ont révélé que l'absorption de C_3A n'avait qu'à peine modifié les dimensions du réseau de C_3S, s'il y eusse aucune modification de ces dimensions.

Des ions de magnésium peuvent remplacer les ions de calcium dans le réseau de silicate tricalcique, ces derniers se trouvant alors sous forme de CaO libre dans les mélanges cuits. A l'aide de la teneur en CaO libre on a établi qu'à 1,420 °C,C_3S peut absorber environ 1.5% de MgO, à 1,500 °C il peut prendre jusqu'à 2.5% de MgO, également si le mélange contient de plus 4% de C_3A.

Zusammenfassung

Mischungen aus Tricalciumsilikat mit Tricalciumaluminat wurden bei 1,500 °C gebrannt und schnell gekühlt. Die Zusammensetzung der Schmelze, die sich dabei bildet, wird durch den Invarianzpunkt *D* (1,470 °C) des Dreistoffsystems $CaO–Al_2O_3–SiO_2$ angegeben. Da sie verhältnismäßig kalkarm ist und infolge der schnellen Kühlung nicht mit den festen Phasen C_3S und CaO reagieren kann, muß die Mischung eine entsprechende Menge freies CaO enthalten, obwohl in den Komponenten C_3S und C_3A der Ausgangsmischung praktisch kein freies CaO vorliegt. Das Auftreten von freiem CaO zeigt infolgedessen an, daß die erhitzte Probe eine Schmelzphase enthielt. Da sich die Schmelze im wesentlichen aus dem Aluminat bildet, das nicht in das C_3S eingebaut wurde, kann mit Hilfe des chemisch-analytisch bestimmten Gehalts an freiem CaO festgestellt werden, wieviel C_3A das C_3S höchstens in fester Lösung aufnehmen kann. Die Untersuchungen ergaben als Grenze etwa 2 % C_3A entsprechend 0,7–0,8 % Al_2O_3. Die eingebauten Al-Atome besetzen die Plätze von Si-Atomen. Röntgenographische Untersuchungen zeigten, daß die Abmessungen des C_3S-Gitters durch Aufnahme von C_3A nicht oder nur wenig geändert werden.

Magnesiumionen können im Gitter des Tricalciumsilikats die Calciumionen vertreten, die dann in den gebrannten Mischungen als freies CaO vorliegen. Mit Hilfe des Gehalts an freiem CaO wurde festgestellt, daß C_3S bei 1,420 °C bis zu etwa 1,5 %, bei 1,500 °C bis zu 2,5 % MgO aufnehmen kann, und zwar auch dann, wenn das C_3S außerdem 4 % C_3A enthält.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Forschungsinstitut der Zementindustrie, Düsseldorf, Germany.

Introduction

The formula

$$54CaO \cdot 16SiO_2 \cdot Al_2O_3 \cdot MgO,$$

abbreviated to

$$C_{54}S_{16}AM$$

has been attributed by J. W. Jeffery [1] [1] to the alite of portland cement clinker. According to this formula, in 18 formula units of tricalcium silicate 2 Si atoms are to be replaced by 2 Al atoms and as charge compensation 1 Mg atom is to be placed in an intermediate lattice position. It was found, however, that it is not possible to produce a pure alite of this formula. Mixtures of this composition always contain after burning about 5 percent free CaO that does not decrease even after frequently repeated heating up to 1,500 °C.

This finding, which shows that the formula of J. W. Jeffery attributes too high a lime content to the alite, must be interpreted as follows: An Al atom entering into the alite in solid solution replaces a Si atom and can therefore bind 3CaO, that is to say, to one mole Al_2O_3 belong 6 moles CaO. In the lime-richest independent alumina compound, tricalcium aluminate, only 3 moles CaO are bound with 1 mole Al_2O_3. If the tricalcium silicate takes up less alumina in solid solution than is indicated in the aforementioned formula, tricalcium aluminate is formed, with a corresponding amount of free CaO.

Free CaO can also occur if the magnesium ions do not occupy intermediate lattice positions but replace the calcium ions in the lattice of the tricalcium silicate. However, this could only explain a free CaO content of about 1.4 percent. As about 5 percent of free CaO always occurred in burned mixtures with the composition $C_{54}S_{16}AM$, it was to be assumed that alite contains less alumina than is indicated in the formula. It was necessary, therefore, to investigate how much alumina tricalcium silicate can take up and whether an addition of MgO has an influence on the solubility of alumina in tricalcium silicate.

The point of departure for the determination of the maximum alumina content that can be taken up in tricalcium silicate was the following consideration. In mixtures of tricalcium silicate and tricalcium aluminate, heating to 1,470 °C yields a melt which contains all the tricalcium aluminate and only a small amount of tricalcium silicate. However, the alumina content of the tricalcium silicate will not participate in the formation of the melt. The composition of this melt at 1,470 °C is determined by the position of the invariant point *D* (1,470 °C) in the ternary system $CaO–Al_2O_3–SiO_2$ (fig. 1). According to the data given by G. A. Rankin and F. E. Wright [2] on the ternary system it contains

$$59.7\% \ CaO$$
$$32.8\% \ Al_2O_3$$
$$7.5\% \ SiO_2.$$

According to the investigations of E. Spohn [3] and H. Kühl [4], at sintering temperature the solid phases are in equilibrium with the melt. As the melt, however, is poorer in lime than the initial mixtures of tricalcium silicate and tricalcium aluminate, this condition being recognizable by the fact that point *D* lies on the low-lime side of the connecting line C_3S—C_3A, CaO must occur as a further solid phase. If the mixtures are cooled under equilibrium conditions, the CaO is re-absorbed by the melt, but with sufficiently rapid cooling it remains free. The occurrence of free CaO in the burnt and quickly cooled mixtures indicates, therefore, that a liquid phase was formed.

Accordingly, it should be possible to establish, with only the help of chemical determinations of the free CaO, how much tricalcium aluminate can be taken up into the lattice of the C_3S. The free CaO should also be able to furnish information as to whether the magnesium ions taken up by the C_3S occupy intermediate lattice positions, that is to say, enter additionally into the lattice, or whether they replace the calcium ions and displace an equivalent amount of CaO from the tricalcium silicate.

Method of Investigation

For the purpose of the investigations the compounds tricalcium silicate and tricalcium aluminate were prepared by the usual method and then mixed with each other in various proportions with or without an addition of MgO or CaO. All the mixtures were homogenized by repeated sieving and cautious grinding in a porcelain mortar, stirred with distilled water to a plastic paste, shaped into granules, burnt for one hour at 1,500 °C and then rapidly quenched in air. The burning temperature of 1,500 °C, which thus lay 30 °C above the temperature of the invariant point *D*, was chosen to ensure that all the tricalcium aluminate was melted. Consequently, although the composition of the melt also changed, the course of the boundary curve C_3S—CaO (fig. 1) shows that principally only the C_3S content of the melt increased and that there was little change in the content of free CaO.

In the burnt mixtures the free CaO was determined by the method of B. Franke [5] in which process the CaO is dissolved in a mixture of acetoacetic ester and isobutyl alcohol and titrated with 0.1 N hydrochloric acid. In addition, a number of mixtures were investigated by X-ray diffraction with a Geiger-counter goniometer. The exact position of the lines was established with NaCl as standard substance.

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[1] Figures in brackets indicate the literature references at the end of this paper.

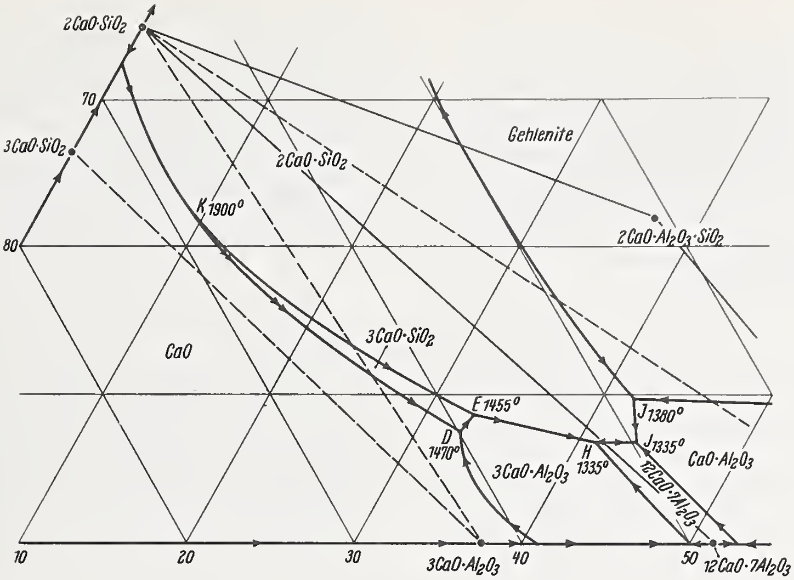

FIGURE 1. *Section of the ternary system $CaO—Al_2O_3—SiO_2$ with the invariant point D (1,470 °C), in which CaO, tricalcium silicate and tricalcium aluminate are stable beside each other.*

Results

The Amount of Tricalcium Aluminate Taken Up by Tricalcium Silicate

Figure 2 shows the results of tests with mixtures of tricalcium silicate without and with CaO or MgO and various amounts of tricalcium aluminate. It is seen that in mixtures of C_3S and MgO (C_3A content=0) the content of free CaO increases with the MgO content. This finding would appear to indicate that in the lattice of the pure tricalcium silicate the magnesium ions can replace the calcium ions. In mixtures of C_3S, C_3A, and MgO, the content of free CaO first decreases with increasing C_3A content, reaches a minimum value at about 2 percent C_3A, and then rises in a line with the C_3A content. This curve shows that C_3A contents of more than 2 percent already form a melt, that is to say, that the alite can contain approximately 2 percent C_3A at the most, i.e., 0.7 to 0.8 percent Al_2O_3.

The thin straight lines indicate the amounts of free CaO calculated on the assumption that the melt has the composition of the invariant point *D* in the ternary system $CaO–Al_2O_3–SiO_2$, that pure C_3S, C_3S with 2 percent or with 4 percent C_3A crystallizes in solid solution, and that in cooling, the melt no longer reacts with the solid phases C_3S and CaO. The chemically determined increase in the content of free CaO tallies very well with the calculated rise of the straight lines and thus shows that the occurrence of the free CaO in burnt mixtures of C_3S and C_3A can be explained by the formation of a melt poor in lime.

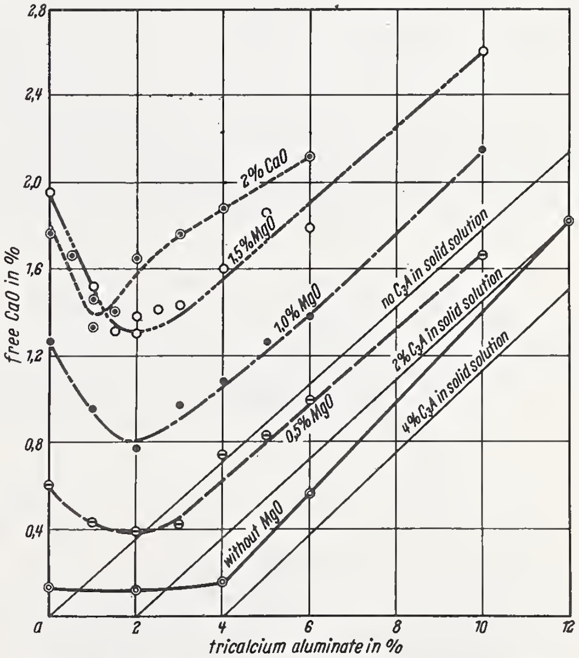

FIGURE 2. *Content of free CaO in mixtures of tricalcium silicate, tricalcium aluminate and MgO or CaO after burning at 1,500 °C and rapid quenching in air.*

Small MgO contents have only a slight influence on the position of the invariant point *D*. Investigations by H. F. McMurdie and H. Insley [6] showed that in the presence of 5 percent MgO the melt is still slightly poorer in lime at point *D*. The solid phases should, therefore, be richer in lime, i.e., in the formation of a melt more free CaO should occur in the system with MgO than in the MgO-free system.

In mixtures with less than 2 percent C_3A the free CaO decreases with an increasing C_3A content. This finding would appear to indicate that an MgO content stimulates the entry of alumina into the alite.

The Amount of MgO Taken Up by Tricalcium Silicate

It has already been pointed out in the foregoing section that free CaO is formed in mixtures of tricalcium silicate and MgO during heating. For the purpose of investigating the connection between the contents of MgO and of free CaO, the free CaO was determined in burnt mixtures of pure C_3S with various amounts of MgO. The results are presented in figure 3. It is perceived that the content of free CaO first rises steeply with an increasing MgO content, reaches a maximum value at a certain MgO content, then falls steeply, and, with still higher MgO content, continues to fall only slightly. This curve reveals that the magnesium ions are taken up into the C_3S lattice in place of the calcium ions, that is to say, they displace the calcium ions up to a maximum extent which depends on the temperature treatment. The higher the temperature, the more MgO the C_3S lattice can take up.

In order to check whether the magnesium ions also displace the calcium ions if the lattice of the tricalcium silicate simultaneously contains alumina, three mixtures of 96 parts C_3S and 4 parts C_3A, to which had been added 1, 2, and 3 percent MgO, were burnt at 1,500 °C and after quenching as rapidly as possible in air, the content of free CaO was investigated. The results are shown by the thin curved line of triangles in figure 3. It is seen that with an addition of MgO the content of free CaO increases from 0.15 to 1.77 percent, showing that the magnesium ions also take the place of the calcium ions when there is a simultaneous takeup of Al_2O_3 and MgO.

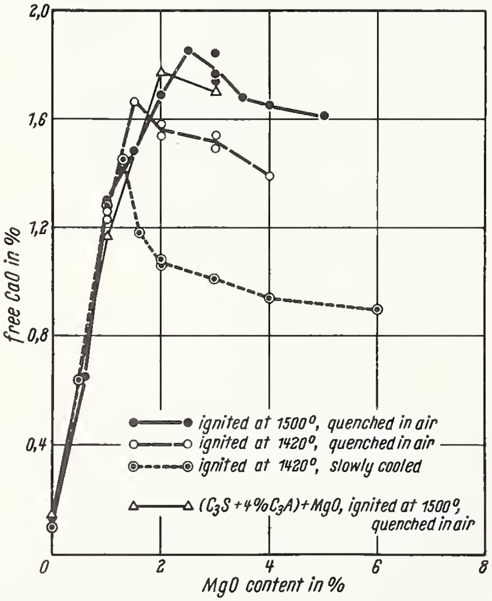

FIGURE 3. *Content of free CaO in burnt mixtures of tricalcium silicate with magnesium oxide.*

X-ray Diffraction Investigations

Figure 4 presents the Geiger-counter diagrams of a number of mixtures which were burnt at 1,500 °C. The two lower diagrams of pure tricalcium silicate and of an MgO-free mixture of C_3S and C_3A reveal, in agreement with the findings of W. Jander and J. Wuhrer [7], that the takeup of alumina in C_3S has no influence or only a very slight influence on the position of the lines, that is to say, on the dimensions of the crystal lattice. The two

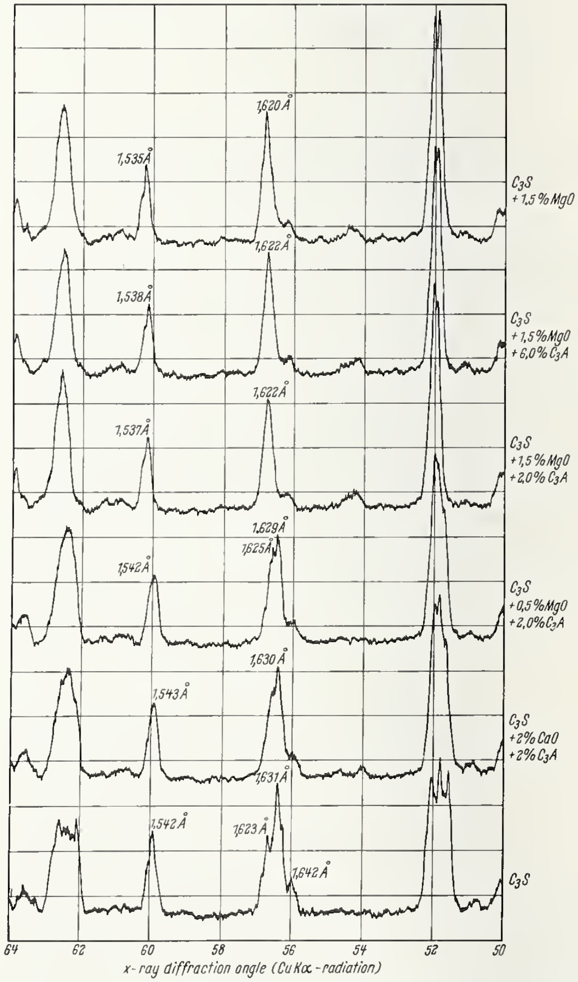

FIGURE 4. *X-ray diagrams of mixtures of tricalcium silicate, tricalcium aluminate and MgO or CaO after burning at 1,500 °C and rapid quenching in air.*

middle lines in the diagram of the C_3S–C_3A–CaO mixture at 1.630 A and 1.542 A (($\bar{2}213$) and ($\bar{2}214$), according to G. Yamaguchi and H. Miyabe [8]), in the diagram of the pure C_3S lie at 1.631 A and 1.542 A. The pattern of the lines changes, however, with glancing angles of reflection, 2θ, of about 51.5° (d=1.76 A) and 62.5° (d=1.49 A), which form multiplets in pure C_3S but occur in the mixtures as simple lines.

The top four X-ray diagrams of samples with MgO show, like the results of K. Koyanagi and T. Sudoh [9], that with a takeup of MgO the lattice of the tricalcium silicate contracts, this being recognizable by the fact that the two marked lines shift over to smaller d-values. The top three diagrams reveal that even alumina-free tricalcium silicate that contains 1.5 percent MgO already produces an X-ray diagram of an alite.

Discussion of Results

The tests led to the following results:

1. Tricalcium silicate cannot take up more than about 0.7 to 0.8 percent Al_2O_3, equivalent to 2 percent tricalcium aluminate, in its crystal lattice. The Al atoms here occupy the positions of the Si atoms. R. Naito, Y. Ono, and T. Iiyama [10] indicate approximately the same low values for the alumina content of the alite, i.e., 2.5 to 3.0 percent C_3A. These values were calculated on the basis of a diagram that was presented in a short review of the work of the Japanese scientists. A. Guttmann and F. Gille [11] found about 2.5 to 5.0 percent tricalcium aluminate in relatively pure alite samples which they produced from technical clinker by centrifuging with heavy solutions. H. E. Schwiete and W. Büssem [12] established on a selected part of a furnace coating with some 90 percent alite that about 4.5 percent tricalcium aluminate was contained in the alite in solid solution. Still higher values, namely 6 to 7 percent tricalcium aluminate, are indicated by W. Jander and J. Wuhrer [7]. This value tallies with the formula of J. W. Jeffery which attributes a 6.5 percent content of tricalcium aluminate to the alite.

2. Magnesium oxide can enter the lattice of the tricalcium silicate at 1,420 °C up to about 1.5 percent and at 1,500 °C up to 2.5 percent. As the content of free CaO increases hereby from about 0.1 percent in the pure C_3S to 1.5 to 2.0 percent it is assumed that the magnesium ions displace the calcium ions.

   According to K. Koyanagi and T. Sudoh [9] the tricalcium silicate can take up less MgO, namely, only 1.0 to 1.5 percent. They established this with the aid of X-ray diffraction investigations.

3. The investigations showed that MgO can enter into the tricalcium silicate independently of the Al_2O_3 and that it is not taken up additionally as charge compensation and placed on intermediate lattice positions, but that it replaces the calcium ions. The difference in charge between the quadrivalent silicon ion and the trivalent aluminium ion taken up in its place is therefore compensated in some other way. As the structure of the tricalcium silicate contains oxygens outside the tetrahedron it is probable that with the takeup of Al^{3+} an equivalent number of these oxygen positions will not be occupied.

The above work was published in somewhat more detail in Zement-Kalk-Gips, September, 1960, under the title "Die Einlagerung von Al_2O_3 und MgO in Tricalciumsilikat."

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Discussion

Guenter Ahlers

The purpose of this discussion is to report the results of some studies on the periclase content of portland cement. The difference between this and the total MgO content is an upper limit for the amount of MgO in the alite, since it is equal to the total combined MgO. It is felt that the fact that even this upper limit was found to be less than the amount indicated by Jeffery's formula is of some interest in relation to Dr. Locher's work on a simpler system.

The cement samples were analyzed for periclase by means of X-ray diffraction. The procedure was very similar to the one used by Copeland, et al. [1].[1] The samples were ground together with 10 percent silicon as internal standard in a vibratory ball mill. The material was vibrated into a sample holder, as described by Copeland and Bragg [2]. The ratio of the line areas of the (200) periclase line and the (311) silicon line was used for analysis. A calibration was obtained by adding three different known amounts of periclase to a cement sample, and obtaining the line intensity ratios to the standard line. The periclase used was obtained by heating C.P. basic magnesium carbonate at 950 °C. for several hours.

The chemical analysis[2] for MgO was done according to the usual ASTM procedure.

Eighteen cement samples from six different mills were analyzed. The results are shown in table 1. Each value is the average of three analyses. The uncertainties in the data are larger than the amount of combined MgO, and thus some of the differences are negative. The differences have an average of 0.05 percent MgO, and this is the best estimate of the average amount of combined MgO. Consideration of the scatter of the calibration data about a straight line and of the three analyses per sample leads to a probable error of ±0.17 percent for the average of the combined MgO. Allowing for some error in the chemical analyses, it then appears that on the average the amount of combined MgO does not exceed 0.3 percent, and probably is in the neighborhood of 0.1 percent.

TABLE 1. *Analyses of portland cement for periclase and total magnesium oxide*

Sample	Periclase X-ray	Total MgO chemical	Difference
	%	%	
I–1	1.24	1.21	−0.03
I–2	2.36	2.38	+.02
I–3	2.30	2.38	+.08
I–4	1.29	1.21	−.08
II–1	3.52	3.30	−.22
II–2	3.82	3.91	+.09
II–3	3.60	3.55	−.05
II–4	3.29	3.30	+.01
III–1	4.14	4.43	+.29
III–2	3.76	3.95	+.19
III–3	4.11	4.07	−.04
III–4	4.32	4.43	+.11
IV–1	2.94	3.02	+.08
IV–2	2.62	2.82	+.20
V–1	3.74	4.11	+.37
V–2	4.27	4.19	−.08
VI–1	4.09	4.13	+.04
VI–2	3.93	3.95	+.02

The samples all contained between 35 and 50 percent C_3S as calculated by the Bogue method, and on the average they contained 42.5 percent C_3S. Thus, if all the combined MgO combined with the C_3S, then the alite in the cements should on the average have contained 0.2 percent MgO, with a maximum possible content of 0.7 percent MgO. This is definitely less than Jeffery's value, and it is in good agreement with the amount of stabilizer used by Copeland, et al., [1]. Copeland's replacement of two SiO_4 groups in 54 such groups would result in about one third of one percent MgO.

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The author is indebted to the control laboratories of the Riverside Cement Company for these analyses.

Discussion

E. Woermann

During our work on the effects of reduction on the equilibrium in portland cement clinker and especially on the alite phase [1] [1] it has been found that:

1. By action of reducing atmosphere in presence of iron-bearing compounds the free lime content of clinker—especially of clinker very rich in alite—is raised considerably.
2. Solid solution of Fe^{++} and Fe^{+++} in tricalcium silicate causes some changes in the lattice of the compound, resulting in a powder pattern resembling that of alite containing Mg^{++} and Al^{+++} in solid solution.
3. Solid solution of Fe^{++} in alite brings about an extremely high instability of this compound as compared with alite containing Mg^{++} in solid solution instead.

It seemed desirable to gain some further information on the influence of different ions on alite and its stability. Searching for some experimental method we tried to determine the influence of certain additions on the free lime content of our samples. Thus we made use of some methods very nearly resembling those of Locher.

Furthermore, as Mg^{++} and Al^{+++} are much easier to treat experimentally than Fe^{++} and

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[1] Figures in brackets indicate the literature references at the end of this paper.

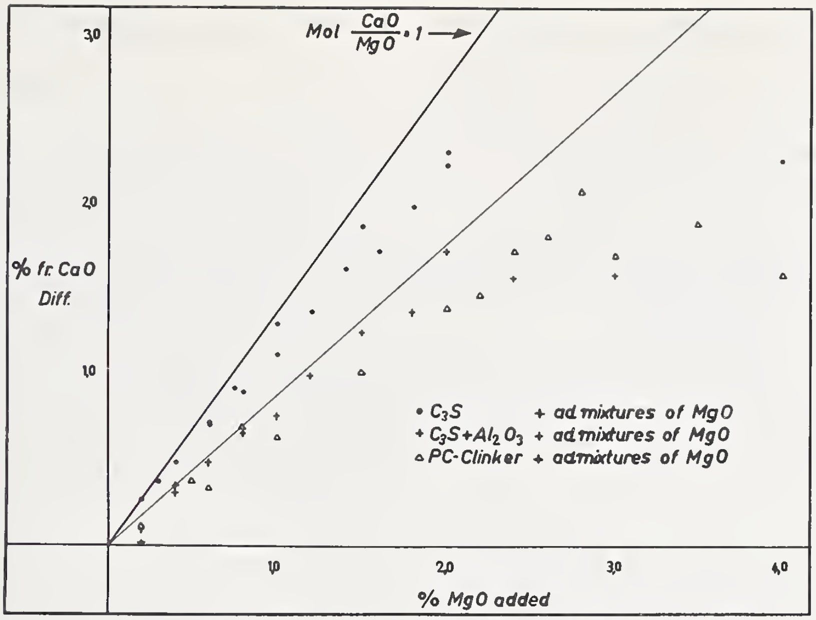

FIGURE 1. *Change in free lime content of* C_3S *and clinker resulting from addition of magnesia.*

Fe^{+++}, we started our experiments by testing the influence of magnesia and alumina on tricalcium silicate. Thus our results may directly be compared with those of Locher, and it seems that they compare very well (fig. 1).

In figure 1 the abscissa represents the amount of magnesia added to the charges, while the ordinate shows the change in content of free lime (=CaO difference) effected by this addition of magnesia as determined by analysis.

We find that after addition of magnesia to a sample of pure tricalcium silicate and burning until the value of free lime determined by analysis remains constant, this content of free lime is higher than in the original sample containing no magnesia. By plotting the results (fig. 1) we find that our points lie very close to a line which represents equivalence between the CaO of the ordinate and MgO of the abscissa. A slight deviation may partly be explained by experimental error, partly by lack of real equilibrium in the sample. Regarding the fact that nearly all of our points lie below the line, we may not exclude the possibility that there is a real deviation of our points from the line which, however, must be very small. We may conclude that up to a certain maximum limit of addition of MgO, Mg^{++} ions may replace Ca^{++} ions in tricalcium silicate. This is in perfect agreement with the results of Locher.

When MgO is added to a charge of C_3S containing alumina in solid solution we find, however, that after burning of the charge and determination of the free lime the points do not follow the line of equivalence of CaO and MgO any more, all of them lying distinctly lower, apparently following their own line of reference. This means that for any amount of magnesia added, *less* than the equivalent amount of lime is liberated. Thus, while still a greater part of the magnesium ions added is replacing calcium ions in the alite lattice, another fraction of the magnesium seems most probably to be included in the lattice of alite, other than by occupying Ca^{++} positions. Moreover there seems to exist a certain relationship regarding the amount of Mg^{++} substituting for Ca^{++} and of Mg^{++} included into the alite lattice.

Furthermore, figure 1 demonstrates that the limit of solubility of magnesium in alite is higher than in tricalcium silicate, while in both cases the maximum amount of lime that may be liberated by the magnesia is the same.

Considering the fact that alite is a major phase in portland cement clinker, we extended our studies to learn something about the influence of MgO on the phase composition of normal clinker. Plotting the points obtained from this experiment on the same graph (fig. 1) we find them closely following the alite line. Thus additions of magnesia in portland cement clinker may cause a rise of free lime content of about 2.0 to 2.5 percent. Considering this influence on the lime saturation of a clinker it seems to be important to include the value of MgO in any method for computation of cement composition.

The theory that a certain fraction of the Mg^{++} ions are included in the alite lattice other than by substituting for Ca^{++} may be supported by some observations on the decomposition of alite.

It seemed rather puzzling to find that a solid solution of ferrous iron in alite results in an extreme instability of this compound, so that it may hardly be possible to prevent the alite from being decomposed, while on the other hand alite containing magnesium in solid solution shows a comparatively weak tendency to decompose. Thus we tried to gain some more knowledge on the effect of admixtures of other divalent ions on alite.

Table 1 shows a list of divalent ions which have been tested for their influence on the stability of alite, arranged according to their ionic radii.

TABLE 1. *Influence of divalent ions on stability of alite*

Admixture	Ionic radius (after Ahrens 1952)	Disintegration of alite after cooling at 5 °C/min
Mg^{++}	0.66	−
Ni^{++}	.69	−
Co^{++}	.72	+
Fe^{++}	.74	+
Mn^{++}	.80	+

According to these results, Ni^{++} has much the same effect on alite as Mg^{++}, while Mn^{++} and Co^{++} resemble ferrous iron in exerting an accelerating influence on the decomposition of alite.

Thus, strikingly, all divalent ions with an ionic radius *greater* than about 0.7 A do exert this destructive influence on alite under given cooling conditions, some of them even to a still higher degree than Fe^{++}, which may lead to the conclusion that these ions were rather too *large* to be included into the lattice. By thermal expansion of the lattice during sintering temperature a certain amount of these ions may have been included in the lattice, but with subsequent cooling and contraction they induce a destruction of the lattice.

Since all of these ions are distinctly smaller than Ca^{++} (ionic radius=0.99 A) they cannot be too large as substituents for Ca^{++}. But assuming that these ions entered some of the holes in the lattice denoted by Jeffery [2] it may be imagined that really some ions may be too large for these holes. This observation thus confirms the theory that some of the Mg^{++} ions are included in the lattice of alite other than by substituting for Ca^{++}.

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Closure

F. W. Locher

It is to be expected that in the heating of mixtures of MgO and tricalcium silicate an equilibrium will occur between the MgO taken up in solid solution and the whole MgO present in the sample. The position of the equilibrium will depend on the following factors:

1. MgO concentration in the sample
2. Temperature treatment
3. Kind and amount of foreign ions present

It follows from this that the investigations hitherto carried out reveal only what MgO concentration in the sample is necessary to saturate the tricalcium silicate or the alite with MgO. They give no indication of the amount of MgO taken up in solid solution.

The investigations of G. Ahlers, for instance, show very clearly that the alite of the cement clinker takes up only very little MgO although relatively large amounts up to more than 4 percent were available to it. Taking into account that the aluminate ferrite phase also takes up MgO and, according to H. E. Schwiete and H. zur Strassen [1], thus give the cement its greenish color, and that, according to H. Müller-Hesse and H. E. Schwiete [2], the tricalcium aluminate can take up as much as 2.5 percent MgO it follows that the alite of the cement clinkers investigated by G. Ahlers can contain only an extremely small amount of MgO. The major part of the MgO was present as periclase. Nor is it to be expected, therefore, that in the mixtures used by E. Woermann, the MgO available was completely taken up by the tricalcium silicate or by the alite in solid solution. In this way it might also be explained why not all the MgO added to the mixture forms free CaO.

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Paper II–S6. Reaction Velocity in Portland Cement Clinker Formation *

Renichi Kondo

Synopsis

In the investigation of the burnability of portland cement, detailed studies on the reactions of clinker formation were performed, intending, first to clarify the differences in the reaction mechanism when selecting clays or granulated blast furnace slag as the sources of silica and alumina, and second to establish a method of measurement of reactivity. The results are as follows:

(1) The reaction between lime and clays containing quartz to form C_2S is noticeable above 1,100 °C. With reaction products burned in this temperature range, despite rapid cooling, slight expansion and dusting occur. The reactivity of highly siliceous clay is superior to that of low-silica clay combined with silica sand. Slag crystallizes out as melilite, and then absorbs lime to form C_2S. Considerable expansion occurs, but dusting can not be observed on cooling. The reactivity of the raw mixtures containing slag besides silica sand is excellent, especially in the stage of C_2S formation, up to 1,250 °C. The differences of reactivity due to the differing type of raw material diminished above about 1,250 °C to form C_3S.

(2) The rate of reaction in burning may be expressed by the formula, $(1-\sqrt[3]{1-x})^N=Kt$. At constant temperature, it seems that the contact-reaction and diffusion processes are predominant in the initial and successive stages respectively, because N is smaller and K is larger in the former than in the latter. N is found to have an abnormally high value of about 5, in contrast to the ordinary value of 2, K a minimum value at medium temperatures, and the activation energy a value as high as 200 kcal/mole. It may be speculated that these apparent abnormalities result from the too formal treatment disregarding two successive reactions leading to C_2S below and C_3S above about 1,250 °C.

(3) It is found that the amount of free lime remaining in the raw mixture sometimes passes through a minimum value during the burning at about 1,100 to 1,200 °C. This result is thought to be caused by the change of solubility of free lime in glycerin accompanying a change of state of the lime in burning at about 1,200 °C. The use of tribromophenol as a powerful solvent instead of glycerin resulted in the absence of a minimum.

Résumé

Après l'évaluation de 13 facteurs, au moyen d'expériences en ordre orthogonal combinées au hasard, des études détaillées concernant l'aptitude à la cuisson du ciment Portland ont été faites sur la réaction de la clinkérisation. Elles ont pour but d'abord de mettre en lumière la différence que produit dans le mécanisme de réaction le choix d'argiles ou le choix de laitiers de haut-fourneau granulés en tant que sources de silice et d'alumine, et ensuite d'établir une méthode de mesure de la réactivité. Les résultats sont les suivants:

(1) La réaction entre la chaux et les argiles contenant du quartz pour former C_2S est sensible au-dessus de 1,100 °C. Avec les produits de réaction à cet ordre de température, malgré le traitement de refroidissement rapide, on rencontre réduction en poussière et une expansion légères. La réactivité d'une argile à forte teneur en silice est supérieure à celle d'une argile à faible teneur en silice combinée à un sable siliceux. Le laitier se cristallise en melilite et absorbe ensuite la chaux pour former C_2S. A ce moment, une expansion considérable se produit mais on n'observe pas de réduction en poussière. La réactivité des mélanges bruts contenant du laitier, outre du sable siliceux, est excellente, spécialement au stade de la formation de C_2S, jusqu'à une température de 1,250 °C. La différence de réactivité due au type de matériaux bruts diminue au-dessus de 1,250 °C environ pour former C_3S.

(2) La vitesse de réaction dans la cuisson est exprimée par la formule, $(1-\sqrt[3]{1-x})^N=Kt$. A température constante, il semble que la réaction de contact et les procédés de diffusion sont prédominants respectivement aux stades initial et successif, parce que pour celui-là N est plus petit et K est plus grand que pour celui-ci. N montre une valeur anormalement élevée d'environ 5, contrastant avec sa valeur ordinaire de 2, K montre une valeur minimum à températures moyennes, et l'énergie d'activation montre une valeur aussi élevée que 200 kcal/mole. On peut se demander si ces anormalités ne proviennent pas du traitement trop conventionnel qui ne tient pas compte de deux réactions successives arrivant chacune à C_2S et C_3S, au-dessous et au-dessus de 1,250 °C environ.

(3) On observe que la quantité de chaux libre dans le mélange brut passe parfois par une valeur minimum durant la cuisson à environ 1,100–1,200 °C. On pense que ce résultat est causé par le changement de solubilité de la chaux libre dans la glycérine accompagnant le changement d'état de la chaux à la cuisson à environ 1,200 °C. Par conséquent on recommande comme dissolvant puissant le tribromophenol au lieu de la glycérine, ce qui évite la présence d'un minimum.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Tokyo Institute of Technology, Japan.

Zusammenfassung

Das Brennen des Portlandzements hängt von 13 Faktoren, die durch Experimente mit Zufallskombinationen durch orthogonale Anordnung ausgewertet werden, ab. Untersuchungen über die Reaktion der Klinkerbildung wurden angestellt, die dem Zwecke dienten, die Unterschiede im Reaktionsmechanismus ausfindig zu machen, wenn Ton oder granulierte Hochofenschlacke das Rohmaterial für Kieselsäure oder Tonerde ist, und die auch dazu dienen sollten, eine Methode der Reaktionsgeschwindigkeitsmessung ausfindig zu machen. Die folgenden Ergebnisse werden erzielt:

(1) Die Reaktion zwischen Kalk und quarzhaltigen Tonen, die zur Bildung des C_2S führt, macht sich oberhalb 1,100 °C bemerkbar. Die Reaktionsprodukte, die bei einer solchen Temperatur erhalten werden, bringen eine leichte Ausdehnung und ein Zerrieseln hervor, die nicht durch ein schnelles Abkühlen überkommen werden können. Die Reaktionsfähigkeit eines Tones, der viel Kieselsäure enthält, ist größer als die eines Tones, der wenig Kieselsäure enthält, und den man mit Quarzsand gemischt hat. Die Schlacke kristallisiert zuerst als Melilit, und bindet dann Kalk unter C_2S–Bildung. Wenn sich das ereignet, nimmt eine beträchtliche Ausdehnung statt, aber ein Zerrieseln kann nicht beobachtet werden. Die Reaktionsfähigkeit der rohen Mischungen, die Schlacke mit Quarzsand zusammen enthalten, ist vorzüglich, besonders auf der Stufe der C_2S–Bildung, bis zu 1,250 °C. Die Differenzen, die man auf Grund der verschiedenen Rohstoffe beobachtet, verschwinden, wenn die Temperatur auf mehr als 1,250 °C erhöht wird, sodaß sich C_3S bilden kann.

(2) Die Reaktionsgeschwindigkeit beim Brennen wird durch die Formel $(1-\sqrt[3]{1-x})^N=Kt$ ausgedrückt. Bei konstanter Temperatur hat man den Eindruck, daß die Kontaktreaktion in der Anfangsstufe überwiegt, und daß die Diffusionsprozesse in den späteren Stufen die Oberhand gewinnen, weil nämlich N am Anfang klein ist, und weil K dann groß ist, in den späteren Stufen wächst N, während K kleiner wird. Bei nicht zu hohen Temperaturen wurde für N der ungewöhnlich hohe Wert 5 gefunden, der viel höher als der normale Wert 2 ist, während K durch ein Minimum geht, und die Aktivierungsenergie einen hohen Wert annimmt, bis zu 200 kcal/mole. Man kann annehmen, daß diese Ausnahmen in Wirklichkeit keine Ausnahmen sind, daß sie bemerkbar werden, weil man die Prozesse nur rein formell behandelt and zwei gekoppelte Reaktionen, die unterhalb und überhalb 1,250 °C stattfinden und in denen C_2S und C_3S entsteht, vernachlässigt hat.

(3) Es wurde gefunden, daß der Betrag des freien Kalks in der ungebrannten Mischung manchmal durch ein Minimum beim Brennen bei 1,110–1,200 °C geht. Es wird angenommen, daß dieser Effekt hervorgebracht wird durch eine Veränderung der Löslichkeit des freien Kalkes in Glyzerin, da er nämlich beim Brennen bei 1,200 °C seinen Zustand ändert. Es wird daher Tribromphenol als Lösungsmittel vorgeschlagen; es löst den Kalk genau so gut wie Glyzerin, und vielleicht sogar noch besser, und bringt dieses Minimum nicht hervor.

Introduction

In spite of abundant papers on the burning of portland cement clinker [1, 2],[1] there are rather few studies dealing mainly with the reaction velocity, a knowledge of which is believed to be most important for the improvement, and for the development of an entirely new design of the furnace. For instance, there is a future possibility of using the highly efficient suspension type or cyclone furnace heated with fuels or atomic energy.

The reaction velocity in the solid state has been investigated only for the simple systems [3], and similar studies have not yet been successfully applied to the formation of clinker.

Moreover, an abnormal fact has been reported [4] that the content of free lime takes a minimum value at a certain period during heating of the raw mixture at about 1,200 °C, but the causes could not be explained.

It has also been reported that a partial substitution of limestone and clay by blastfurnace slag can reduce the fuel consumption [5, 6], but the reaction process has not yet been demonstrated. This study was performed with the purpose of solving the problems mentioned above.

Burning of the Raw Mixtures

TABLE 1. *Chemical compositions and fineness of raw materials, percent*

	CaO	Al_2O_3	TiO_2	Al_2O_3 + Ti_2O_3	Fe_2O_3	Mn_2O_3	Fe_2O_3 + Mn_2O_3	SiO_2	MgO	S	Loss	Others	Fineness Blaine	Coarser than 88 μ
													cm²/g	%
Limestone (L)	54.88	0.22	--------	0.22	0.64	--------	0.64	0.74	0.65	0.02	42.10	P_2O_5 0.07	3680	2.0
Siliceous clay (S)	3.35	13.86	--------	13.86	4.78	--------	4.78	65.96	1.74	.59	5.66		8190	0.1
High-aluminous clay (A)	tr.	29.50	--------	29.50	9.88	--------	9.88	48.20	0.62	tr.	12.36		20000	8.9
Granulated slag, coarse (C)	39.90	14.72	1.62	16.18	0.91	1.01	1.92	32.33	6.16	1.11	tr.		2950	tr.
Granulated slag, fine (F)	39.90	14.72	1.62	16.18	.91	1.01	1.92	32.33	6.16	1.11	tr.		4940	tr.
Silica sand (Q)	tr.	2.24	--------	2.24	.86	--------	0.86	94.88	0.40	tr.	0.65		5620	1.1
Blast-furnace dust (I)	1.40	3.57	--------	3.57	75.05	0.51	75.56	10.10	.82	0.21	2.83	C 4.18 ZnO 0.84 P_2O_5 0.10	4360	1.0

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[1] Figures in brackets indicate the literature references at the end of this paper.

Comparative burning studies were made using clays and granulated blastfurnace slag as raw materials for the sources of silica and alumina.

The chemical compositions and finenesses of the raw materials used in this experiment are shown in table 1.

The compositions of raw mixtures to be burned were H.M. 2.10, S.M. 2.42, and I.M. 1.90, i.e., C_3S 53–55, C_2S 23–24, C_3A 10–11, and C_4AF 9–10 percent, as illustrated in table 2.

The raw mixtures were pressed at 500 kg/cm^2 to form tablets with an area of 1 cm^2, height of 5.5 mm, and weight of 1 g. The burning conditions were in the range of 1,100 to 1,450 °C with 7 levels at 50 °C intervals, and in the range of 10 to 60 min. with 6 levels at 10 min. intervals. The burning was done in a carborundum electric furnace with an automatic temperature controller.

TABLE 2. *Combinations of raw materials*

Main raw material as the source of silica and alumina	Limestone	Siliceous clay	High-aluminous clay	Granulated slag, coarse	Granulated slag, fine	Silica sand	Blastfurnace dust
	L	S	A	C	F	Q	I
	%	%	%	%	%	%	%
Siliceous clay (S)	77.37	18.62	3.64				0.37
High aluminous clay (A)	78.92		12.12			8.56	.40
Granulated slag coarse (C)	66.95			23.74		7.63	1.68
Granulated slag fine (F)	66.95				23.74	7.63	1.68

(H.M. 2.10, S.M. 2.42, I.M. 1.90, C_3S 53-55, C_2S 23-24, C_3A 10-11, C_4AF 9-10)

Shrinkage During Burning

The shrinkage during burning is illustrated in figure 1. There is a tendency for the shrinkage to increase with rising temperature and with prolonged time, but expansion or dusting takes place also after burning at 1,100 to 1,350 °C. Dusting could not be found in the specimens containing slag. In connection with this fact, C_2S crystals formed from the quartz particles were generally large, while C_2S crystals from melilite as the devitrified product of slag were finely divided.

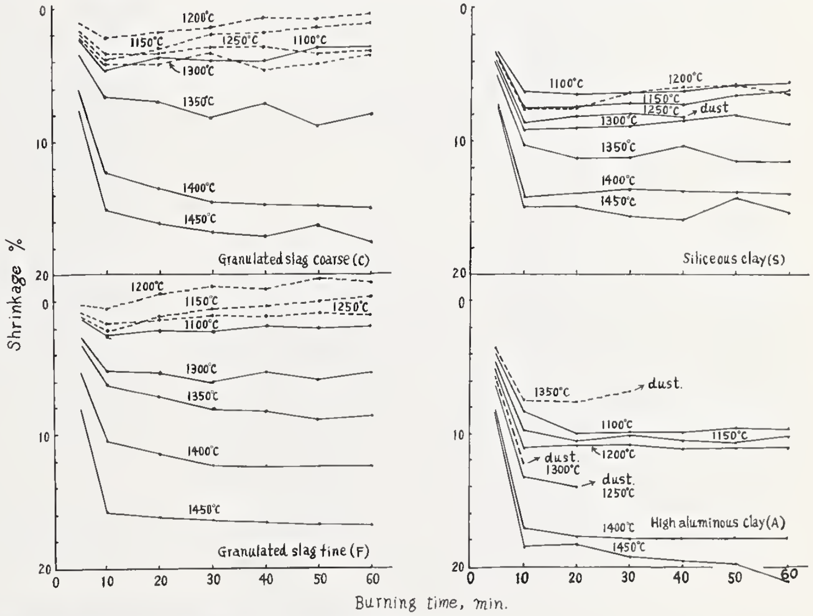

FIGURE 1. *Burning shrinkage.*

Changes of the Mineral Composition

The mineral composition of the raw materials and the changes of the mixtures in the burning process were determined by means of the reflecting and polarizing microscopes and also by the X-ray diffractometer. The principal results obtained were as follows:

Clay S contained quartz as a main constituent, together with feldspar, pyroxene, and a clayey mineral containing iron, and the maximum grain size before grinding was about 100μ. Clay A was composed chiefly of allophane containing iron, with a small amount of quartz, etc. Blastfurnace slag was almost entirely in the glassy state.

During the burning of the mixtures under about 1,000 °C, the component materials changed independently the reactions $CaCO_3 \rightarrow CaO$ and slag→ melilite taking place. In the mixtures containing clay S or clay A, the reaction $2CaO + \text{quartz} \rightarrow C_2S$ takes place at 1,100 to 1,200 °C, and then the reaction $CaO + C_2S \rightarrow C_3S$ above 1,300 °C. The resulting crystals were very fine at 1,350 °C but grew larger at 1,450 °C. In the mixtures containing Slag C or Slag F, the reaction $CaO + \text{melilite} \rightarrow C_2S$ occurred a little after the reaction $2CaO + \text{quartz} \rightarrow C_2S$ took place above about 1,100 °C, and all of the melilite disappeared with the reaction $CaO + C_2S \rightarrow C_3S$ at 1,300 °C.

Content of Uncombined Lime

The free lime content in samples was generally reduced with increased temperature and time of burning. An abnormal minimum value, however, sometimes appeared for samples burned at 1,100 to 1,200 °C. Figure 2 illustrates the results obtained.

The existence of a minimum value was reproducibly confirmed and this result was supposed to be based on experimental error in the determination of free lime. The degree of dispersion of lime tends to change in the range of 1,100 to 1,200 °C, consequently the solubility of lime in a solvent such as glycerin is expected to be different. By using tribromophenol as a somewhat more powerful solvent, it could be confirmed that this abnormal phenomenon is eliminated.

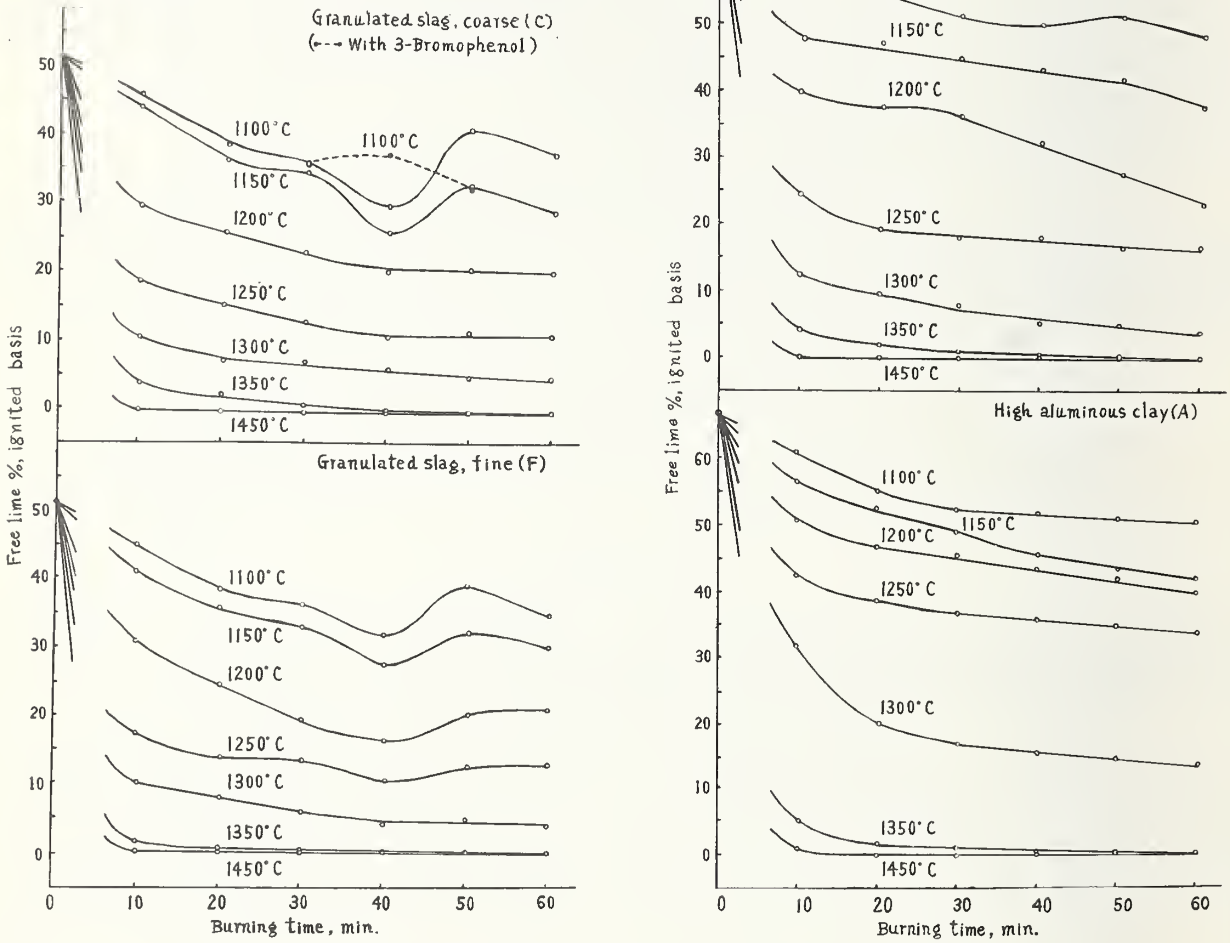

FIGURE 2. *Content of uncombined lime.*

The Reaction Velocity

The reaction ratios are shown in table 3, calculated from the results illustrated in figure 2.

Figure 3 shows the relationship between $1-\sqrt[3]{1-x}$ as the ratio of the depth of reaction to the mean radius of the particles, and t as the burning time, with temperature T as the parameter.

The equation $(1-\sqrt[3]{1-x})^2=Kt$ can be applied to the reaction velocity, if Jander's theory [3] holds. The lines are not parallel, however, and have a sharp bend, and the slope becomes gentle at high temperature where alite forms. It is therefore necessary to select the more general experimental formula $(1-\sqrt[3]{1-x})^N=Kt$. If the angle between the straight line and the ordinate is put as θ, then $N=\tan\theta$. The logarithm of the velocity constant K, i.e., $\log K$, can be obtained by the length of the section between the original point 1,1 and the intersection of the abscissa with the straight line. The calculated values are shown in table 4.

The values of N and $\log K$ varied widely with the raw materials and the temperature and time

Table 3. *Reaction ratio x*

Temp	Time	Main raw material			
		S	A	C	F
°C	*min*				
1,100	10	0.05	0.08	0.10	0.10
	20	.16	.18	.27	.25
	30	.20	.22	.30	.29
	40	.21	.22	.32	.38
	50	.19	.23	.19	.25
	60	.25	.25	.26	.32
1,150	10	.26	.16	.14	.20
	20	.26	.20	.29	.30
	30	.31	.27	.32	.35
	40	.33	.34	.49	.47
	50	.34	.37	.36	.37
	60	.42	.37	.43	.43
1,200	10	.38	.25	.43	.40
	20	.43		.48	.50
	30	.44	.32	.55	.62
	40	.52	.36	.61	.69
	50	.57	.37	.50	.61
	60	.65	.41	.57	.58
1,350	10	.62	.38	.64	.69
	20	.71	.42	.68	.73
	30	.71	.45	.74	.75
	40	.73	.47	.80	.80
	50	.75	.49	.75	.76
	60	.72	.50	.77	.73
1,300	10	.81	.53	.80	.80
	20	.85	.71	.86	.84
	30	.86	.75	.84	.88
	40	.93	.77	.88	.93
	50	.91	.79	.90	.88
	60	.93	.80	.90	.91
1,350	10	.92	.93	.93	.98
	20	.97	.97	.96	1.00
	30	.98	.98	.98	0.99
	40	1.00	1.00	.99	1.00
	50	1.00	1.00	1.00	1.00
	60	1.00	1.00	1.00	1.00
1,450	10	1.00	0.99	1.00	1.00
	20	1.00	1.00	1.00	1.00
	30	1.00	1.00	1.00	1.00
	40	1.00	1.00	1.00	1.00
	50	1.00	1.00	1.00	1.00
	60	1.00	1.00	1.00	1.00

of burning, especially at lower temperatures. At constant temperature, it seems that the contact reaction and the diffusion process are predominant in the initial and the successive stages, respectively, because N is smaller and K is larger in the former than in the latter.

The relation between the velocity constant and the temperature is shown in figure 4.

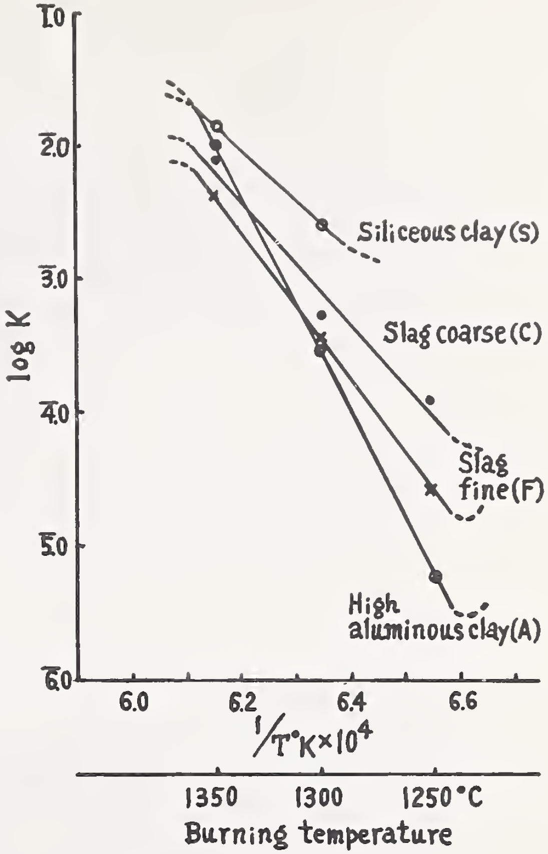

Figure 4. *Log K vs 1/t.*

It was found that the value of log K does not always increase with temperature, but passes through a minimum at about 1,100 to 1,250 °C.

The activation energy of the diffusion is calculated from the Arrhenius equation, $\log K = \log A - E/4.574\ T$. If in this figure, the angle between the line and abscissa is put as θ, then $\tan \theta = E/4.574\ T$. The activation energy was cal-

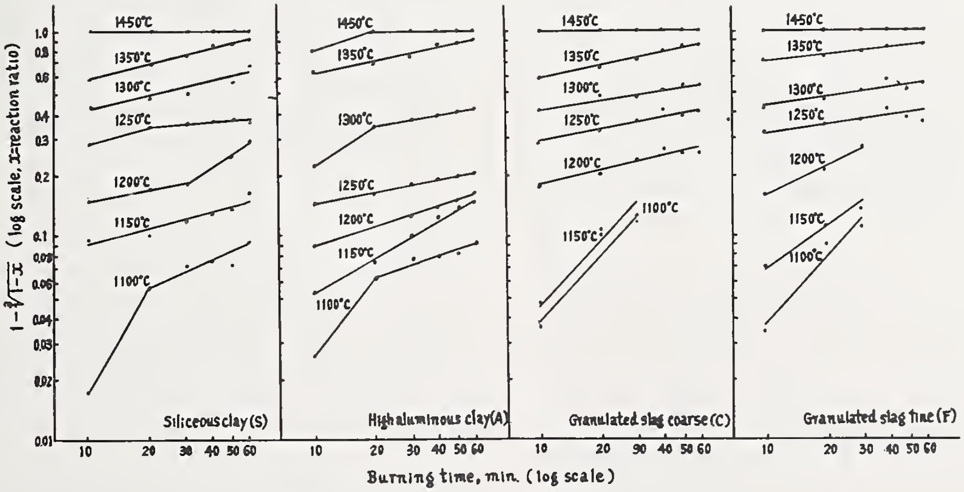

Figure 3. *Log* $(1-\sqrt[3]{1-x})$ *vs log t.*

Table 4. *Reaction order and velocity constant*

Temp	$\frac{1}{T^\circ K}\times 10^4$	Stage	Main raw material							
			S		A		C		F	
°*C*			*N*	log *K*	*N*	log *K*	*N*	log *K*	*N*	log *K*
1,100	7.29	Initial	0.6	$\bar{2}.00$	0.8	$\bar{3}.84$	0.9	$\bar{3}.80$	0.9	$\bar{3}.68$
		Later	2.2	$\bar{5}.89$	3.5	$\bar{5}.26$				
1,150	7.03		3.8	$\bar{5}.11$	1.6	$\bar{4}.87$	.09	$\bar{3}.87$	1.4	$\bar{3}.34$
1,200	6.80	Initial	4.9	$\bar{6}.80$	2.8	$\bar{5}.86$	4.2	$\bar{5}.70$	11.9	$\bar{3}.34$
		Later	1.5	$\bar{5}.50$						
1,250	6.56	Initial	3.0	$\bar{3}.08$	4.9	$\bar{6}.75$	5.5	$\bar{4}.15$	6.8	$\bar{5}.40$
		Later	11.7	$\bar{7}.40$						
1,300	6.35	Initial	4.4	$\bar{3}.42$	1.5	$\bar{2}.00$	5.7	$\bar{4}.69$	6.5	$\bar{4}.45$
		Later			5.3	$\bar{4}.46$				
1,350	6.16		3.7	$\bar{2}.11$	5.0	$\bar{2}.00$	4.8	$\bar{3}.90$	9.4	$\bar{3}.70$
1,450	5.80	Initial			2.7	$\bar{2}.80$				

($\log t = N(1-\sqrt[3]{1-x}) - \log K$)

Table 5. *Activation energy*

Raw material:	S	A	C	F
E kcal/mole	180	380	210	240

culated in the range of alite formation at 1,250 to 1,350 °C, as shown in table 5.

The fact that the value of *N* was established at nearly 5, at higher temperature, apparently shows that the reaction mechanism is similar regardless of the difference of raw materials. The activation energy to form chiefly alite reaches 200 kcal/mole, which is considerably higher than the expected value. A much higher value was obtained with the composition A, which may be explained by the fact that the formation of C_2S is not sufficiently completed under 1,250 °C because of the inferior reactivity of the raw material.

Thus, the Jander formula cannot be applied to the burning of portland cement clinker, as *K* takes a minimum value at medium temperatures, and the values of *N* and activation energy reach very high values at higher temperatures. Such an abnormal result, however, is believed to be occasioned by the treatment, as there exists one sort of reaction, disregarding the reactions of the formation of C_2S and C_3S, taking place in 2 steps separately below and above about 1,250 °C. Reasonable results would be obtained, if we could distinguish the reactions $2CaO+SiO_2 \rightarrow C_2S$ and $CaO+C_2S \rightarrow C_3S$ and estimate the reaction ratios separately.

The author expresses his gratitude to President Toshiyoshi Yamauchi of Tokyo Institute of Technology for his invaluable advice and encouragement. He is also indebted to Mr. Toshio Tsuji for his assistance in carrying out the experiments.

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Paper II–S7. Solid Solutions of the Minerals of Portland Cement Clinkers*

N. A. Toropov

Synopsis

This account contains the results of experimental work by the author and his collaborators, establishing numerous cases of formation of solid solution between different constituents of portland cement clinker. The authors have established the dissolution of chromium in alite and belite, and of orthosilicates of barium and strontium and of calcium orthophosphate in belite, have determined the concentration limit of solutions of calcium aluminate in dicalcium ferrite, etc. These studies were accomplished with the aid of the polarizing microscope, X-rays, and thermal analysis.

Résumé

Cet exposé contient les résultats des travaux expérimentaux de l'auteur et de ses collaborateurs, établissant de nombreux cas de formation de solutions solides entre différents constituants du clinker de ciment portland. Les auteurs ont notamment constaté la dissolution d'oxydes de chrome dans l'alite et la bélite, d'orthosilicates de baryum, de strontium et d'orthophosphate de calcium dans la bélite, déterminé la concentration limite des solutions d'aluminate de calcium dans le ferrite bicalcique etc. Ces études ont été effectuées à l'aide du microscope polarisant des rayons X et de l'analyse thermique.

Zusammenfassung

In der Arbeit wird das Versuchsmaterial, das vom Verfasser und seinen Mitarbeitern zusammengetragen worden ist, beschrieben; sehr viele Beispiele von festen Lösungen der verschiedenen Portlandzementklinkerbestandteile in einander sind aufgefunden worden. Ganz besonders muß hervorgehoben werden, daß das Auflösen von Chromoxyden in Alit und Belit, und auch die Lösungsbildung des Bariumorthosilikats, des Strontiumorthosilikats und des Kalziumorthophosphats im Belit entdeckt worden sind; auch wurde die Maximumkonzentration des Kalziumaluminats im Dikalziumferrit bestimmt, und andere ähnliche Messungen wurden vorgenommen. Man hat in diesen Untersuchungen Röntgendiagramme und Thermoanalyse benutzt.

Results of some experimental work of the author and his collaborators are given in this report, from which it is seen that formation of solid solutions between different components of the portland cement clinker have been shown in numerous cases. In particular, the authors demonstrate the solution of chromic oxide in alite and belite, and of barium and strontium orthosilicates and calcium orthophosphate in belite; and the limited concentration of calcium aluminate solution in dicalcium ferrite was determined. These studies were made by the use of the polarizing microscope and by X-ray and thermal analyses. The varieties of cement clinker minerals obtained can be named: chromalite, chrombelite, barium belite, phosphate belite, and strontium belite. The results of these studies considerably reinforce the conception of minerals of portland cement clinker as solid solutions, not as definite compounds of simple chemical composition. The modern development of microscopical, X-ray, and thermal methods of examination of the polycomponent mineral systems, as well as of crystalline and amorphous phases formed in them, has made it possible to attain considerable progress in determining the mineralogical composition of portland cement clinker. The initial conceptions of this problem that have dominated for some decades (1915–1945), were principally based on the data obtained by the study of simple physicochemical systems formed by oxides of portland cement clinker. These conceptions favor the propagation of the theory that different clinker minerals are identified with simple silicates, aluminates, and calcium aluminoferrites formed in the respective physicochemical systems. In particular, this theory is assumed as a principle of the method for calculating the mineralogical composition of the clinker according to its gross chemical composition.

However, numerous experimental works in recent years show that this theory is only a first approximation to the solution of this problem. In reality, the chemical composition of the clinker minerals is more complicated. Mostly, they represent no simple chemical compounds but solid solutions formed between different compounds and oxides. As is known, the solution of aluminum oxide or calcium aluminates in alite and belite is a problem of great importance. Many investigators have dealt with this problem, including Jeffery [1] [1] who studied the crystalline structure of alite and tricalcium silicate. However, the close proximity of the optical properties of tricalcium silicate to those of tricalcium aluminate, as well as the absence of coloration, makes it diffi-

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Institute of Silicate Chemistry, U.S.S.R. Academy of Sciences, Leningrad, U.S.S.R.

[1] Figures in brackets indicate the literature references at the end of this paper.

cult to study their mutual solubility in solid solution. The thermal investigation of the phase diagram of the system $3CaO \cdot SiO_2$–$3CaO \cdot Al_2O_3$ is also difficult because of its pseudobinary character and the instability of these chemical compounds on heating to the melting point.

According to our opinion the possibility of partial dissolving of the aluminum oxide or a replacement of silicon atoms by aluminum atoms, with the supplementary introduction of magnesium atoms in the crystalline lattice of tricalcium silicate, finds its confirmation in the replacement of silicon by chromium in the structure of alite with the formation of chromalite, as we call it.

This replacement is a result of the interaction of the chromium oxide with basic silicates of calcium. Also, for example, during the study of samples of portland cement clinker with additions of chromite in small quantities (in the order of 3 to 5 percent of chromium oxide) obtained by S. S. Tcherepovski [2], we found already in 1933 that alite and belite crystals took on an intense bright-green emerald coloration. There was also observed a considerable augmentation of the index of refraction of the alite crystals from $n_m = 1.720 \pm 0.003$ to $n_m = 1.735 \pm 0.005$ and of belite from $n_m = 1.725$ to $n_m = 1.750 \pm 0.005$.

Later analogous observations were made by D. S. Belyankin and B. V. Ivanov [3] who had been studying structures of chromodolomitic refractories, produced by P. P. Budnikov. These refractories were obtained by firing of bricks prepared of mixtures of dolomite, chromite, and quartzite. In the chromalite crystals formed in this refractory, it was also possible to observe sometimes the formation of zonal structures with the internal substance consisting of discolored mineral of the belite type. The index of refraction of the chromalite varied within the limits $n_m = 1.745$ to $n_m = 1.760$–1.770. Chemical analyses of the refractory made by V. A. Moleva showed the presence of two chromium oxides: $Cr_2O_3 = 2.47$ percent and $CrO_3 = 5.79$ percent.

The formation of chromalite is of great interest in the study of the structure of chromite refractories, as well as for the knowledge of the service conditions of these refractories in furnaces for burning cement. According to Bunting [4] the ionic radii of trivalent aluminum (0.57A) and trivalent chromium (0.65A) are close together, and as a result there can be isomorphous, reciprocal, and complete miscibility of chromium oxide and aluminum oxide. This fact, according to our observations, appears to be an indirect indication of the possibility of solution of alumina (aluminum atoms) in the calcium silicates. It is also necessary to take into account the observations of V. V. Lapin [5], who showed the presence of feeble coloration of the alite crystals in clinkers; at the time of their burning there were introduced small additions of cobalt and nickel oxides. As is known, the solid solutions formed by dicalcium silicate have been the object of numerous and detailed observations. As a result, different authors obtained many varieties, α' and β, of the dicalcium silicate modifications, which represent themselves as various forms of the clinker mineral, belite.

In many works dedicated to the study of the solid solutions of dicalcium silicate, the solubility of the isolated oxides in the crystalline lattice of this compound has been investigated. However, the solubility of different oxides in a given case does not correspond at all with that of the orthosilicates of the same oxides in $2CaO \cdot SiO_2$. This is explained by the broad development of isomorphous interrelations between orthosilicates of the different elements, while the oxides of the same elements have a highly symmetrical structure. Therefore, in our work on solid solutions of dicalcium silicate, we considered it more expedient to study binary systems formed by this silicate with other orthosilicates rather than with different oxides. This procedure permitted us to establish the limited concentrations of solid solutions formed between orthosilicates under conditions of isomorphism. The study of solid solutions of dicalcium silicate with barium and strontium orthosilicates had been realized earlier in our laboratory. Toropov and Konovalov [6], with the help of a polarizing microscope, found evidence of the formation of a continuous series of solid solutions in the system dicalcium silicate–barium orthosilicate, and these authors also described the optical properties of these crystals (fig. 1). Later, we found similar crystals, which we named barium belites, in cements prepared with the addition of barium oxide.

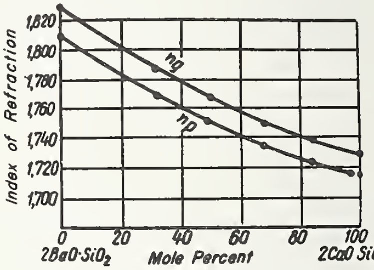

FIGURE 1. *Index of refraction as a function of composition in* $2CaO \cdot SiO_2$–$2BaO \cdot SiO_2$ *solid solutions.*

In 1953, Toropov and Borisenko [7] studied this series of solid solutions, called by us barium belites, in a more detailed way with the use of thermographic and X-ray analyses. Two series of samples were made for this purpose, namely: (a) by quenching from 1,450 °C, and (b) by annealing with slow cooling (1.5° per min, beginning from 1,450 °C) of the same samples in the platinum resistance furnace.

Data of thermographic investigations of the tempered samples are given in table 1.

Table 1. *Polymorphous transformations of dicalcium silicate, found by the method of thermal analysis*

No.	Composition		Temperatures of the polymorphous transformations	
	$2CaO \cdot SiO_2$	$2BaO \cdot SiO_2$	$\gamma - \alpha'$	$\alpha' - \alpha$
1	2	3	4	5
	Mole %	*Mole %*	*°C*	*°C*
1	100	0	810	1,440
2	90	10	absent	1,340
3	80	20	absent	1,230
4	70	30	absent	1,130
5	60	40	absent	1,040
6	50	50	absent	950
7	40	60	absent	900
8	30	70	absent	Thermal effects not observed.
9	20	80	absent	
10	10	90	absent	
11	0	100	absent	

Transformations at 810 and 1,440 °C corresponding to the transformations $\gamma \rightarrow \alpha'$ and $\alpha' \rightarrow \alpha$-$2CaO \cdot SiO_2$ were found in the first sample. By addition of barium orthosilicate into the composition of the experimental solid solutions a stabilization down to low temperatures was observed on annealing the α' modification of $2CaO \cdot SiO_2$. The evidence of this stabilization is shown by: (1) The absence of disintegration of the sample on cooling, (2) the disappearance of the thermal effect corresponding to the transformation $\gamma \rightarrow \alpha'$-$2CaO \cdot SiO_2$, (3) the conservation (up to the concentration of 70 mole percent $2BaO \cdot SiO_2$) of the thermal effect corresponding to the transformation $\alpha' \rightarrow \alpha$-$2CaO \cdot SiO_2$. A lowering of the temperature of this effect, proportional to the increased addition of $2BaO \cdot SiO_2$, is characteristic of the formation of solid solutions.

The absence of the thermal effect for the samples containing more than 70 mole percent of $2BaO \cdot SiO_2$ shows that at this concentration the solid solutions of the type α'-$2CaO \cdot SiO_2$-$2BaO \cdot SiO_2$ become unstable even at high temperatures, but solid solutions of the type α-$2CaO \cdot SiO_2$-$2BaO \cdot SiO_2$ only are preserved at elevated temperatures.

Toropov and Konovalov [8] made an additional investigation of the system: dicalcium silicate–strontium orthosilicate where they also observed the formation of continuous solid solution. The same authors studied the optical properties of the crystals obtained (fig. 2). Later Toropov, Galakhov, and Bondar [9] studied the ternary system: calcium oxide–barium oxide–silica, in which they determined particularly the crystallization region of the barium belites, that is, the solid solutions of barium orthosilicate in dicalcium silicate. The development of production of portland cement containing barium and strontium oxides ("Edelzemente") permits the use of our physicochemical data for the determination of the mineralogical composition of the cements.

Solid solutions of calcium aluminoferrites are formed in the ternary system: calcium oxide–aluminum oxide–ferric oxide by the mutual dissolution of dicalcium ferrite, $2CaO \cdot Fe_2O_3$, and pentacalcium trialuminate in the solid phase, and probably of a small quantity of surplus calcium oxide in the crystal lattice of these solid solutions.

The first investigators of the system: calcium oxide–alumina-ferric oxide, Hansen, Brownmiller, and Bogue [10] found evidence of the formation of only a single ternary compound, tetracalcium aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, afterwards called brownmillerite. It forms a continuous series of solid solutions with dicalcium ferrite.

In subsequent studies, Lea and Parker [11] and Guttmann and Gille [12], investigating synthetic and clinker aluminoferrites, managed to obtain crystals with indices of refraction considerably lower than those of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. Therefore, in 1937 we undertook, together with Shishakov and Merkov [13], a special investigation of the pseudobinary system: brownmillerite-pentacalcium trialuminate, and ascertained a partial dissolution in brownmillerite of components with lower indices of refraction, namely, calcium aluminates.

A study of the system brownmillerite–pentacalcium trialuminate by microscope and X-ray methods permitted us to establish that the maximum quantity of pentacalcium trialuminate that can be dissolved in brownmillerite is 35 weight percent. The formula of the limited solid solution, consisting of 35 weight percent of C_5A_3 and 65 weight percent of C_4AF is $43CaO \cdot 16Al_2O_3 \cdot 7Fe_2O_3$. If the percentage of ferric oxide in brownmillerite is 32.8 weight percent, then the content of ferric oxide in this aluminoferrite is 21.7 percent. Aluminoferrite of this composition has the following indices of refraction: $n_g = 1.93$ and $n_p = 1.87$. The existence of these solid solutions was confirmed by the authors with the aid of X-ray analysis.

Almost simultaneously with our work, McMurdie [14] also demonstrated the existence of solid solutions between brownmillerite and pentacalcium trialuminate. But the limits of solubility found by him were considerably less. According to data of Yamauchi [15], who published his work at the same time, the existence of the solid solution of the composition $6.2CaO \cdot 2.2Al_2O_3 \cdot Fe_2O_3$ (21.8 weight percent of ferric oxide) would be possible.

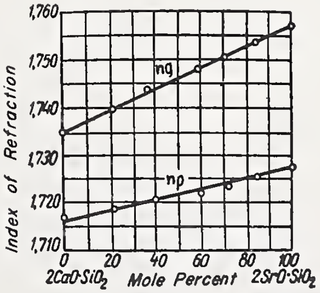

Figure 2. *Index of refraction as a function of composition in* $2CaO \cdot SiO_2$-$2SrO \cdot SiO_2$ *solid solutions.*

The results of the study completed by Toropov, Shishakov, and Merkov [13] had been repeatedly criticized until 1946, when Swayze [16] confirmed our results as well as those of Yamauchi. According to Swayze, a continuous series of solid solutions extends from $2CaO{\cdot}Fe_2O_3$ to the composition $6CaO{\cdot}2Al_2O_3{\cdot}Fe_2O_3$ (22.8 weight percent of ferric oxide) or $42CaO{\cdot}14Al_2O_3{\cdot}7Fe_2O_3$. If this formula is compared with the formula $43CaO{\cdot}16Al_2O_3{\cdot}7Fe_2O_3$ proposed by us in 1937, no great difference between them will be observed.

Furthermore, the last formula is considerably nearer to the aluminoferrite composition with maximum content of aluminate in solid solution (called limiting solid solution). Actually, according to Swayze the limiting solid solution should contain 22.8 weight percent of Fe_2O_3 but according to Toropov, Shishakov, and Merkov it contains 21.7 percent by weight. Thus, the composition proposed by Swayze as a final term of the series of solid solutions is only a first approximation to the limiting composition of the solid solutions. This fact becomes more evident if one examines the works of Italian investigators. Thus, Malquori [17], Cirilli and Burdese [18], studying by X-rays solid solutions of aluminoferrites, drew the conclusion that it is possible to obtain a homogeneous solid solution with a content of 20–21 percent of Fe_2O_3. Malquori [17a] proposed the following formula for aluminoferrite with the maximum content of aluminate: $6CaO{\cdot}2.1Al_2O_3{\cdot}0.9Fe_2O_3$ ($Fe_2O_3=20.7$ percent).

The next work on this problem was done by Toropov and Boikova [19] in the Institute of Silicate Chemistry of the Academy of Sciences, USSR. The investigation of aluminoferrite solid solutions was performed mainly by the use of the polarizing microscope, this being the most precise method. The sensitivity of the roentgenographic method for the quantity determination of aluminates and aluminoferrites is not great and is limited to contents not lower than the following percentages in the mixture: C_4AF–15 percent, C_5A_3 and C_3A–6 percent [20]. Malquori, Cirilli, and Burdese disregarded the possibilities of the roentgenographic method for the quantity determination of aluminates and ferrites. It is also important to provide for sufficiently slow rate of cooling. The cooling velocity in our experiments was 1.5° per min.

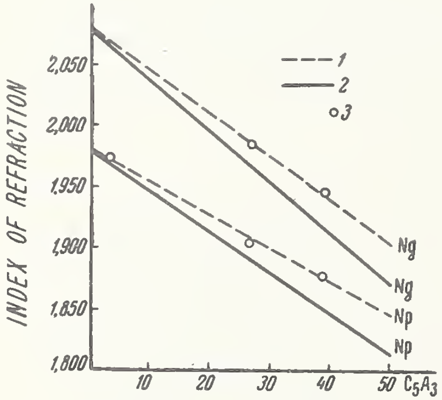

FIGURE 3. *Relation between indices of refraction of aluminoferrites and quantity of* C_5A_2 *incorporated in the solid solution containing* C_4AF.

-- A curve obtained on the supposition that the rhombic modification of C_5A_3 is incorporated into the solid solution.
— A curve obtained on the supposition that the cubic modification of C_5A_3 is incorporated into the solid solution.
° Experimental points.

At first we carried out experiments to establish which of the modifications α-C_5A_3 or α'-C_5A_3 was a part of the solid solution of aluminoferrites (together with an insignificant quantity of lime). It was natural to suppose that solid solutions of aluminoferrites are formed with the rhombic modification of pentacalcium trialuminate, which has a structure closer to that of $2CaO{\cdot}Fe_2O_3$.

To verify this hypothesis we have calculated a theoretical curve of index of refraction, drawing a chart of curves of variations of these indices as functions of the concentration of C_5A_3, for the α' form and for the α form (fig. 3).

This calculation is based on additivity, that is, on the existence of a linear relation between the composition of the solid solutions and their indices of refraction. As is known, such a relation is very clearly expressed for a whole series of systems with solid solutions. The experimental verification showed that it is necessary to consider α'-C_5A_3 as the aluminate component of the solid solution of aluminoferrites.

To answer a principal question, what is the maximum content of C_5A_3 in the solid solution, and also what are the limits of the reduction of the quantity of the ferric oxide in the limiting composition of the aluminoferrite, we have synthesized and studied samples containing 42, 32, 24, 20, 16, 14 and 12 weight percent of Fe_2O_3. In table 2 are given compositions of the mixtures.

TABLE 2

Sample No.	CaO	Al_2O_3	Fe_2O_3	$\frac{Al_2O_3}{Fe_2O_3}$
	Weight percent			
12	50.0	38.0	12.0	3.17
14	49.73	36.27	14.0	2.59
16	49.4	34.6	16.0	2.162
20	48.6	31.4	20.0	1.57
24	47.8	28.2	24.0	1.175
32	46.32	21.68	32.0	0.68
42	44.43	13.57	42.0	0.32

Each sample was subjected to four annealings with intermediate fine grinding. The samples were observed by the microscope in immersion and by reflected light, in polished sections. The study showed that the samples containing more than 20 percent of Fe_2O_3 consisted of homogeneous phases: solid solutions of the aluminoferrites.

Samples with 16, 14, and 12 weight percent of Fe_2O_3 contained, together with aluminoferrite, also the aluminates C_5A_3 and C_3A which were well identified in reflected light (when the section was etched with a solution of oxalic acid in alcohol). The indices of refraction of the aluminoferrites determined by immersion in liquids with a high index of refraction, continuously increased in the samples containing 14 and more percent of Fe_2O_3. Only samples with 14 and 12 percent of Fe_2O_3 attained a constant (minimum) value of indices of refraction. This permitted us to establish that the compositions of the aluminoferrites in these samples were the same. Therefore, we concluded we had attained the limiting composition of solid solution (with maximum content of aluminate). The maximum reduction of the indices of refraction of aluminoferrites is from $n_g=2.08$ and $n_p=1.98$ for $4CaO\cdot Al_2O_3\cdot Fe_2O_3$ to $n_g=1.914$ and $n_p=1.854$ for the limiting solid solution.

The calculation based on the linear relation between the indices of refraction and the concentration of the solid solution gave a chemical composition of the limiting solution as follows: $7.8CaO\cdot 3.24Al_2O_3\cdot Fe_2O_3$. Approximately, it can be represented by the following formula: $8CaO\cdot 3Al_2O_3\cdot Fe_2O_3$ (ferric oxide, 17.5 weight percent).

A special roentgenographic study of this limiting concentration accomplished by Boĭkova and Poraĭ-Koshits [21] confirmed the results of the microscopical study. In figure 4 is shown the relative position of the characteristic peaks of the X-ray diagram obtained by the diffractometer. These curves are taken from samples of aluminoferrites with different contents of ferric oxide. (The number of the sample corresponds to percentage of ferric oxide.) As may be seen in figure 4, the position of the peak corresponding to pentacalcium trialuminate remains invariable. The position of the maximum for aluminoferrite is constant only in samples with a content of 12 and 14 percent of ferric oxide; if the content is more, then the peak is displaced, showing a change in concentration of the solid solution.

The choice of the formula, shown above, for the limiting solid solution is also confirmed by some crystallochemical considerations. Probably the relations of atoms in the elementary cell can be presented in the following way: $8CaO\cdot 3Al_2O_3\cdot Fe_2O_3$ or $Ca_8Fe_2Al_6O_{20}$.

Büssem [22] thought that aluminum atoms in aluminoferrites are only in octahedral coordination. We consider that the point of view of Malquori and Cirilli corresponds better to reality. These authors think that aluminum atoms are to be found in aluminoferrites with coordination numbers four and six. In reality, this point of view is confirmed by the existence of the aluminoferrite solid solution of the type $Ca_8Al_6Fe_2O_{20}$. In this compound 4 aluminum atoms are in tetrahedral coordination and 2 in octahedral. The structural forms of the considered compounds can be represented as follows:

Chemical composition	Quantity of Fe_2O_3 in weight percent	Number of "molecules" in the elementary cell	Structural formulas
$2CaO\cdot Fe_2O_3$	58.8	4	$Ca_8Fe^{IV}_4Fe^{VI}_4O_{20}$
$4CaO\cdot Al\_O_3\cdot Fe_2O_3$	32.8	2	$Ca_8Fe^{IV}_4Al^{VI}_4O_{20}$
$8CaO\cdot 3Al_2O_3\cdot Fe_2O_3$	17.5	1	$Ca_8Fe^{IV}_2Al^{IV}_2Al^{VI}_4O_{20}$

For the composition $6CaO\cdot 2Al_2O_3\cdot Fe_2O_3$ (ferric oxide 22.8 percent) or $6CaO\cdot 2.1Al_2O_3\cdot 0.9Fe_2O_3$ (ferric oxide 20.7 percent) it was impossible to establish a disposition of atoms in the elementary cell of the type $Ca_8Me^{IV}_4\cdot Me^{VI}_4\cdot O_{20}$.

It is necessary to consider that the formulas shown above express only a relation of oxides in aluminoferrites.

In 1958 Newkirk and Thwaite of the National Bureau of Standards, USA [23], published a new

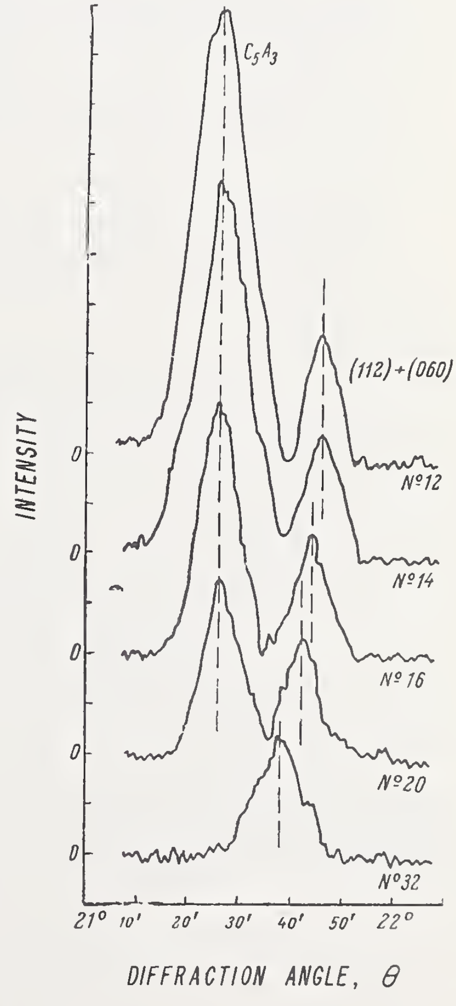

FIGURE 4. *Relative positions of calcium aluminate and calcium aluminoferrite lines.*

communication on solid solutions in aluminoferrites. According to the data of thermal and X-ray analyses the authors drew a conclusion that the limiting composition of the aluminoferrite solid solution corresponds to the formula $6.45CaO \cdot 2.31Al_2O_3 \cdot Fe_2O_3$. Thus, it corresponds to a composition occupying an intermediate position between the limiting compositions indicated by Malquori [17] and by us.

From our point of view, results of joint investigations by X-ray and microscope afford the greatest precision.

All examples, given above, show that the chemical nature of the different crystalline phases of portland cement clinker is very complex. Chemical phenomena in solid solutions are broadly developed, and there is a great possibility for variations of the structure and for chemical reactivity of the clinker minerals.

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Discussion

Myron A. Swayze

Dr. Toropov's approval of the petrographic microscope as the most precise instrument in checking homogeneity of the aluminoferrite solid solutions is heartily seconded by this writer, especially if powder mounts of these compositions are made in Hyrax resin. This material has a refractive index of 1.713, and thus allows observation of all the colorless clinker minerals with almost complete elimination of refraction shadows around these compounds. It has the further advantage of producing permanent mounts for everything except free CaO, which hydrates very slowly in contact with the solid resin.

High index resins for identification of particular compositions within the aluminoferrite solid solution series are not as reliable as X-ray analyses because of difficulty in standardizing these resins and the volatility of the lower index portion of these mixtures in preparing powder mounts. The X-ray patterns as shown in Toropov's figure 4 should furnish a much more exact indication of the A/F ratio of ferrite phases.

In this connection, it is regrettable that he fails to include compositions in table 2 between Fe_2O_3 contents of 20.0 and 24.0 percent, and that these compositions were not subjected to X-ray analysis. A study of this kind should automatically settle the present question of the minimum Fe_2O_3 content of the aluminoferrite series of solid solutions, by revealing C_5A_3 peaks when this minimum was passed.

Incidentally, the compositions shown in table 2 are not prepared from mixtures of C_5A_3 with C_2F or C_4AF at all, as might be concluded from the discussion, but are rather on or very close to a line of compositions running from C_2F to a hypothetical C_2A. Since this line of compositions is of such great interest, it is hoped that the author and his colleagues will fill in the information on compositions between 20 and 24 percent Fe_2O_3 and present these new data as a revision of the present paper.

Paper II–S8. Decomposition of Alite in Technical Portland Cement Clinker*

E. Woermann

Synopsis

The conditions occurring in technical clinker for the decomposition of alite to secondary belite and free lime have been traced. It is shown that alite tends to decompose only in such iron-bearing clinker samples as show typical indications of reducing heating conditions.

Laboratory experiments were conducted to confirm the hypothesis that the abnormal instability of alite is produced by ferrous iron ions entering the alite lattice.

Reducing conditions during the sintering process result in: dusting of clinker containing primary belite; a considerable increase in periclase; changing quantitative ratio of ferrite and aluminate; and a change of the properties of ferrite.

Under favourable conditions alite may decompose so rapidly that freezing of the high temperature equilibrium cannot be achieved simply by quenching in air.

The lower limit of stability of alite containing ferrous iron in solid solution is determined to be 1,183 °C (±5 °C). Alite containing ferric iron has been destroyed by annealing at a temperature of 1,180 °C.

Evidence has been offered that the Fe^{++} ions are for the greater part substituting for Ca^{++} ions in the alite lattice.

Résumé

Les conditions présidant à la décomposition de l'alite du clinker de l'usine en belite secondaire et en chaux libre sont connues. On montre que l'alite ne tend à se décomposer que dans les échantillons de clinker ferrifère qui donnent des indications typiques de chauffage réductif.

On a procédé à des expériences au laboratoire pour corroborer l'hypothèse que l'instabilité anormale de l'alite est produite par les ions de fer ferreux pénétrant le réseau d'alite.

Les conditions réductives au cours de l'agglomération par frittage donnent les résultats suivants: pulvérisations spontanée du clinker contenant du belite primaire; périclase extrêmement accrue; rapport quantitatif de ferrite et d'aluminate changeant; et un changement dans les propriétés du ferrite.

Sous des conditions favorables l'alite peut se décomposer si rapidement que le simple refroidissement à l'air est incapable de réaliser la fixation de l'équilibre à haute température.

La limite inférieure de stabilité de l'alite contenant du fer ferreux en solution solide est déterminée comme étant de 1,183 °C (±5 °C). L'alite contenant du fer ferrique est détruit par recuit à une température de 1,180 °C.

On présente de l'évidence que l'ion Fe^{++} remplace en partie le Ca^{++}, en entrant pourtant en partie les troux du réseau d'alite.

Zusammenfassung

Die Bedingungen, die in technischem Klinker zum Zerfall des Alit in sekundären Belit und freien Kalk führen, wurden untersucht. Es konnte dabei gezeigt werden, daß Alit vorwiegend in eisenführenden Klinkerproben, die typische Anzeichen reduzierender Brennbedingungen aufweisen, zum Zerfallen neigt.

Die Annahme, daß die abnormale Instabilität des Alit durch in das Gitter eintretendes, zweiwertiges Eisen verursacht wird, konnte durch Laboratoriumsversuche bestätigt werden.

Reduzierende Brennbedingungen rufen einige weitere, charakteristische Eigenschaften im Klinkerbild hervor: Klinker mit höheren Belitgehalten neigen zum Zerrieseln; die Periklasgehalte nehmen zu; das Mengenverhältnis Aluminat: Ferrit wird zugunsten des Aluminat verschoben; die optischen Eigenschaften des Ferrit sind verändert.

Unter günstigen Umständen kann Alit so schnell zerfallen, daß der Zustand bei Sintertemperatur auch durch Abschrecken an Luft nicht eingefroren werden kann.

Die Stabilitätsgrenze von Fe^{++} haltigem Alit liegt bei 1,183 °C (±5 °C). Alit mit Gehalten von dreiwertigem Eisen konnte durch Tempern bei 1180 °C zerstört werden.

Die Fe^{++} Ionen scheinen im wesentlichen Ca^{++} Ionen des Alitgitters zu vertreten.

Decomposition of Alite

During the last three decades much work has been devoted to the phenomenon of the decomposition of alite in portland cement clinker to secondary belite and free lime according to the simplified equation

$$3\ CaO{\cdot}SiO_2 \rightarrow 2\ CaO{\cdot}SiO_2 + CaO.$$

Except for the special case of admixture of CaF^2 to the clinker it has always proved necessary for the laboratory specimens to be tempered for a very long run—generally for several days—at temperatures between 1,300 and 1,000 °C before any decomposition of alite was detectable. Thus for these laboratory experiments time factors have been involved that are incomparable with any technical process.

Decomposition of alite in technical products, however, has been observed repeatedly during

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Hauptlaboratorium, Portland-Zementwerke Heidelberg A. G., Germany.

Figure 1. *Idiomorphic crystal of alite (dark grey) partially disintegrated (diffused part).*

Shaft kiln clinker. Etched with dimethyl ammonium citrate. 1500 ×.

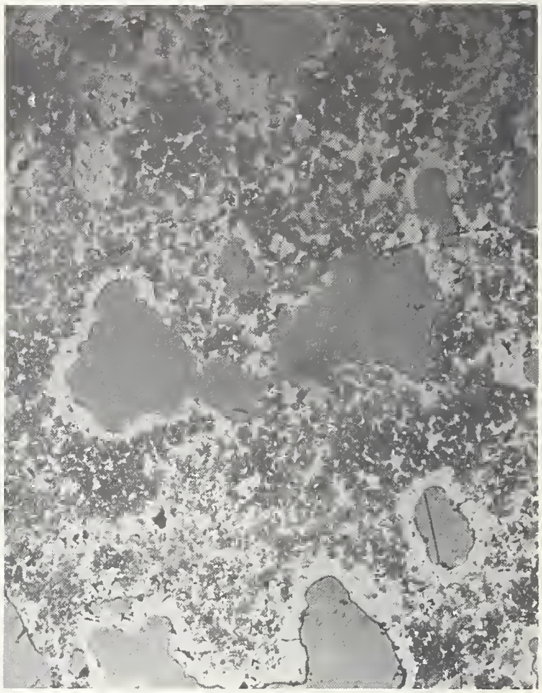

Figure 3. *The same specimen as shown in figure 2.*

Intense decomposition of alite in a shaft kiln clinker. 50 ×.

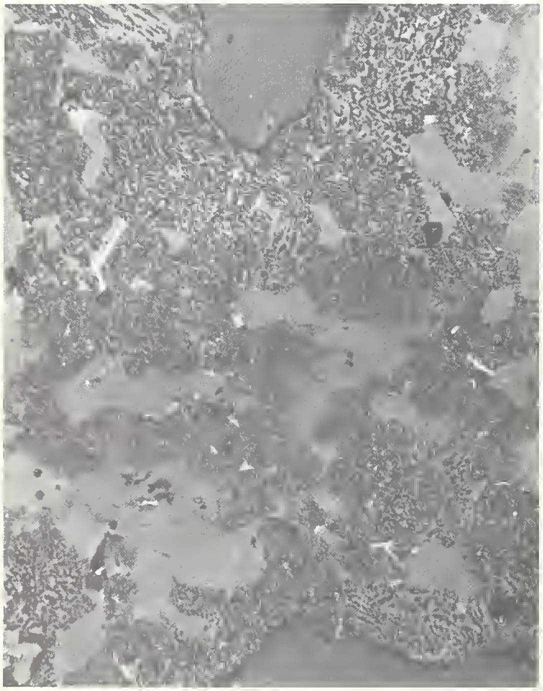

Figure 2. *Secondary free lime showing as fine black inclusions after exposure to moist air for 24 hr.*

Shaft kiln clinker. 200 ×.

microscopic control of shaft kiln and sinter grate clinker (figs. 1 to 4). Spohn [1],[1] Spohn and Woermann [2].

The products of this decomposition form intimate myrmekitic intergrowth structures, pseudomorphous after the primary alite, of very small, but even in single specimens widely varying dimensions. Typically the decomposition starts from certain centers that show relatively coarse intergrowth structures. From here it spreads like an infectious disease from one crystal to another, the intergrowth structures becoming ever finer with increasing distance from the centers until at last it is impossible to resolve them by optical methods. In this case the decomposition may still be detected in polished sections by the rough surface and the diffused reflection of the alite pseudomorphs and the quite different etching properties of the secondary products (fig. 5).

Table 1

Clinker	A	B	C	D
Alite	82.5	76.5	73.9	77.6
Decomposed alite	32.3	44.2	25.9	52.8
Secondary free lime	7.9	10.9	6.4	13.0
Primary free lime	5.0	3.3	2.4	1.1
Sum: free lime (micr.)	12.9	14.2	8.8	14.1
Free lime (chem. anal.)	5.8	5.4	3.2	7.1

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[1] Figures in brackets indicate the literature references at the end of this paper.

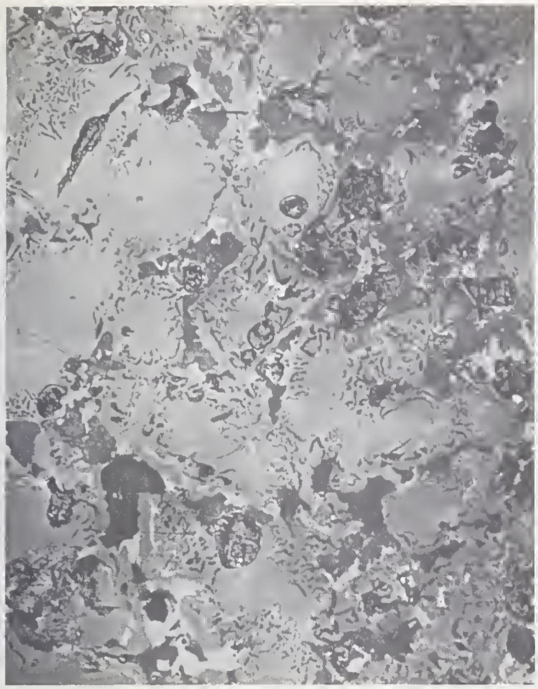

Figure 4. *Disintegration of alite starting from the crystal surfaces.*

Typical coating of the alite crystals by belite in spite of a high content of primary free lime. Sinter grate clinker. Etched with H_2O. 500 ×.

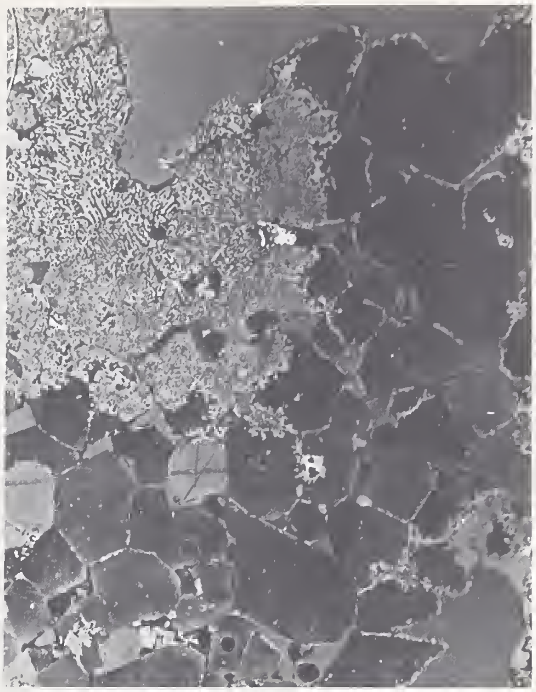

Figure 5. *Alite crystals (dark grey) being decomposed to belite (light grey) and free lime (black).*

The center from which the disintegration has started shows coarser structures. Shaft kiln clinker. Etched with H_2O. 500 ×.

Methods of Investigation

The observation of these phenomena has only been possible by microscopic methods on suitably etched polished sections.

In thin sections, areas with decomposed alite were characterized by blurred dark spots. The decomposition products are in any case much finer than the thinnest practically attainable thin section (fig. 6).

The chemical determination of free lime must necessarily give values that are too low and will, in the case of the finest intergrowth-structures of the secondary products, fail altogether as a method for the detection of the decomposition of alite. Table 1 compares some values, obtained by analytical and microscopic methods, of free lime in clinker containing amounts of decomposed alite.

The phenomenon of the decomposition of alite in technical clinker has been described by several authors, e.g., Tröjer [3] and Alègre and Terrier [4]. In all cases slow cooling in the temperature interval below the stability limit of alite has been quoted as a determining factor. Tröjer observed decomposition of alite in clinker specimens containing relicts of coke or traces of a "sulfite" phase. From this he concluded that the burning of these inclusions in air would produce enough heat to prevent effective cooling of alite in the critical interval.

Figure 6. *In thin sections decomposition of alite may be recognized by dark blurred spots.*

Shaft kiln clinker. 200 ×.

Tracing the phenomena accompanying the decomposition of alite soon led to doubt that slow cooling alone is responsible for this effect in technically cooled clinker.

It was proved that alite may be destroyed even in cases of fast cooled clinker, as for example in sinter grate clinker, where the typical dendritic intergrowth of the matrix confirms the quenching from sintering temperature. The abnormal instability of alite seems to be sensibly dependent on other factors, e.g., the presence of foreign components that may enter the alite lattice. Some most typical characteristics may be observed in clinker showing structures of alite decomposition.

Generally the clinker is densely burnt, being of a light brown colour.

Under the microscope the ferritic phase shows a distinctly lower reflectivity than in normal clinker, a typical characteristic of reducing conditions during the sintering process.

At the same time some further compounds may be identified which can only be formed in reducing atmosphere, as for example calcium or iron sulfides (fig. 7).

Under conditions of extreme reduction, however, the ferritic phase disappears. All iron is transformed to the metallic state. The colour of the clinker is white. At the same time all structures of the decomposition of alite disappear.

Black, fully oxidized parts of the same sample, on the other hand, show a quite normal clinker with the usual combination of its components—a high reflectivity of the ferritic phase and eutectic intergrowth of ferrite and aluminate in the matrix—without any trace of decomposed alite. In some cases however fine lamellae are exposed in the alite crystals (fig. 8). They occur in three different—but apparently not equivalent—sets with strict crystallographic orientation with respect to the host. Coarser individual lamellae could be identified as belite.

Nearly all of the phenomena accompanying the decomposition of alite thus point to moderately reducing burning conditions, while on the other hand intense reduction, transforming iron to the metallic state, does not seem to exert an accelerating influence on the destruction of alite.

Furthermore the pseudomorphs after alite most frequently contain fine inclusions or margins of ferrite in addition to the belite and free lime to be expected here (figs. 9 and 10). Apparently iron is playing an active role in this reaction.

These observations lead to the conclusion that alite by action of moderate reduction and in the presence of iron—probably by introduction of ferrous iron into the alite lattice—is becoming highly unstable so that it will tend to decompose to belite, free lime and a ferritic phase, even under normal technical cooling conditions.

Figure 7. *Intense disintegration of alite in a specimen bearing calcium sulfide (white, round spots).*

Shaft kiln clinker. Etched with H_2O. 500 ×.

Figure 8. *Fine lamellae of belite in three parallel sets in alite crystals.*

Shaft kiln clinker. 500 ×.

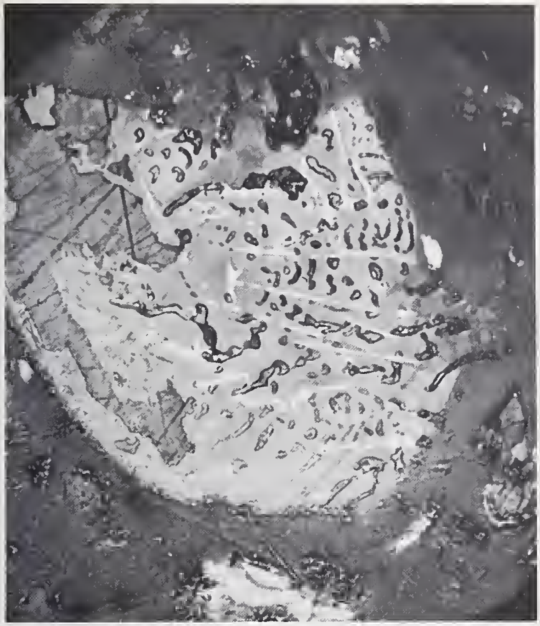

FIGURE 9. *Alite (medium grey relicts) being disintegrated to a myrmekitic intergrowth structure of belite (light grey), free lime (dark grey) and a ferritic phase (white).*

Shaft kiln clinker. Etched with H_2O. 500 ×.

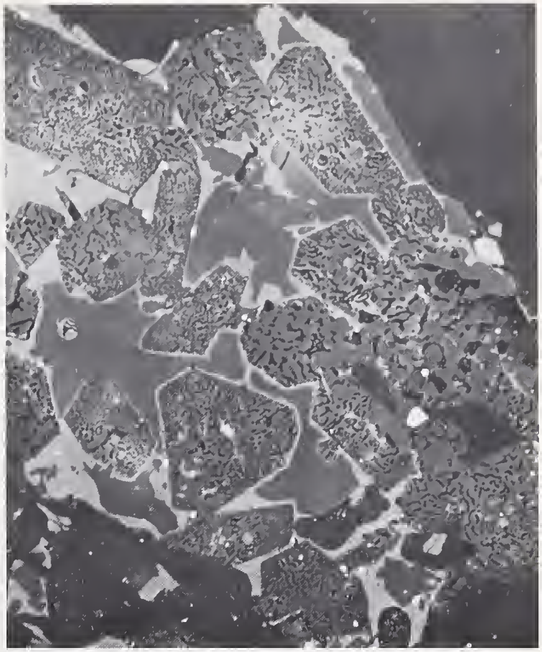

FIGURE 10. *Decomposed alite crystals with tiny inclusions and distinct margins of ferrite.*

Laboratory clinker. 500 ×.

Laboratory Experiments

It seemed desirable to prove the deduction, that the decomposition of alite under technical conditions is decidedly influenced by the action of Fe^{++}, by laboratory experiments.

Laboratory clinkers of very different compositions in the range of normal portland cement were prepared from pure chemical substances. Different fractions of each were subsequently treated according to the following scheme:

1. heated in air, quenched
2. heated in air, slowly cooled
3. heated in reducing atmosphere, quenched
4. heated in reducing atmosphere, slowly cooled

A uniform sintering temperature of 1,450 °C was chosen for all charges, which were kept at this point for 30 min, in some special cases even much longer. Quenching was achieved simply by dropping the charge—about 7 g of clinker—from the maximum temperature to open air. Slowly cooled specimens were kept in the furnace, where the temperature dropped constantly at a rate of 5 °C/min until a temperature of 1,000 °C was attained.

Different methods were adopted to obtain moderate reduction in these charges. Either nitrogen containing small amounts of hydrogen was passed through the furnace tube or, with much better results, H_2O/H_2 or CO_2/CO mixtures were used. Excellent results were obtained by heating the charge in a closed iron crucible, but here it was most difficult to have control of the metallic iron of the crucible itself taking part in the reaction. Considerable difficulties have also been experienced with long run heatings in platinum crucibles and H_2O/H_2 gas, especially with high temperatures. The vapour pressure of FeO proved here to be high enough to cause considerable differences in composition of the charge before and after heating or in the composition of its outer shell and its centre. For these reasons the results of our experiments can have only a purely qualitative character. Never the less the deductions made from our experience with shaft kiln clinker were confirmed.

Clinker heated in air with subsequent quenching shows normal idiomorphic alite, round belite crystals and a most typical dendritic intergrowth of the matrix (fig. 11).

With heating in air and slow cooling a clinker is produced showing all well known characteristics: Alite is still fresh without any trace of decomposition. Aluminate and ferrite have crystallized separately. They show tiny exsolutions of belite (fig. 12).

The structure of clinker heated in reduced atmosphere and quenched (fig. 13) differs greatly from the above.

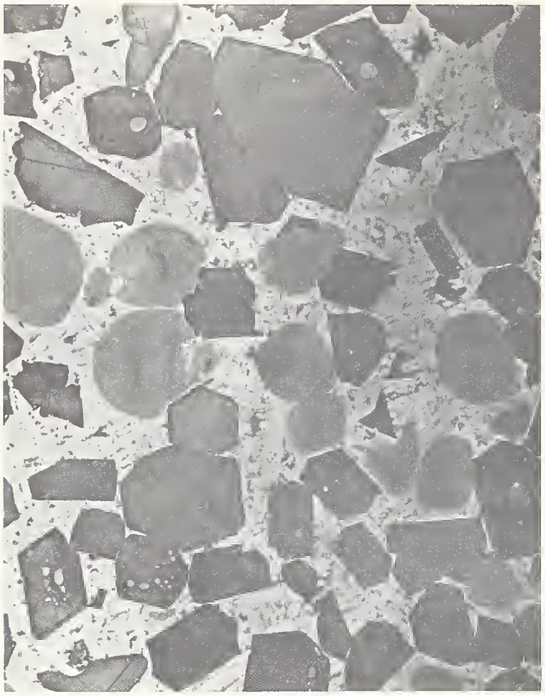

FIGURE 11. *Laboratory charge heated in air, quenched from sintering temperature.*

Etched with H_2O. 500 ×.

FIGURE 12. *Laboratory charge heated in air, cooled at a rate of 5°C/min.*

Etched with H_2O. 500 ×.

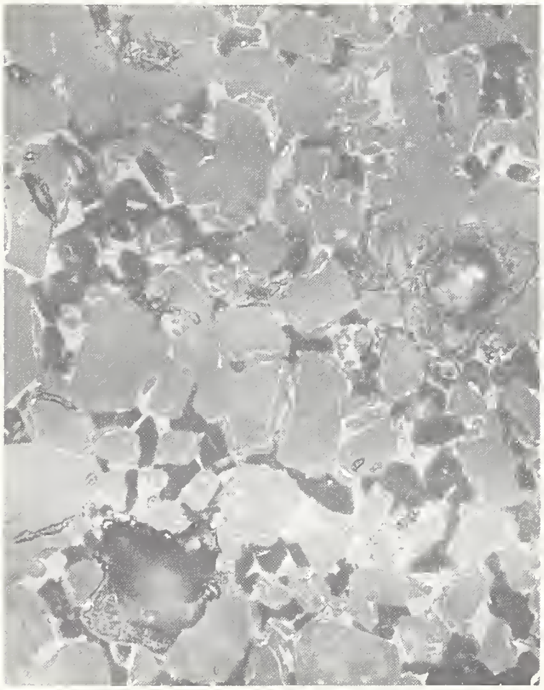

FIGURE 13. *Laboratory charge heated in reducing atmosphere, quenched from sintering temperature.*

Etched with H_2O. 500 ×.

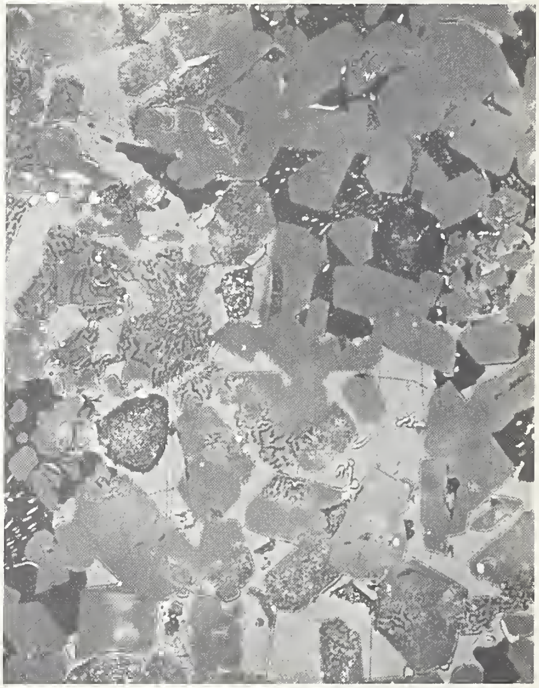

FIGURE 14. *Laboratory charge (initial composition analogous to that of figures 11–13) heated in reducing atmosphere, slowly cooled.*

Inclusions of periclase (grey) and metallic iron (white). Etched with H_2O. 500 ×.

In spite of the fast cooling the phases of the matrix are distinctly separated from each other without showing the typical eutectic intergrowth structures. The etching properties are changed, the alite now being considerably less sensitive to the influence of water. No traces of decomposition are shown by the alite crystals in quenched charges. The content of free lime is always considerably higher than in oxidized charges of the parallel run. The alite crystals are coated—mostly after a thin ferrite seam—by a thick belite cover, a phenomenon that can be observed in some technical clinker as well. The melt must have been rich in silica and comparatively poor in lime. With quick cooling a resorption has been prevented.

Charges treated in a current of reducing gas during the heating and with subsequent slow cooling also produce highly characteristic structures (fig. 14). The most striking one is the decomposition of alite, which can be traced here in almost every charge: In 24 charges treated accordingly the degree of decomposition with respect to the original alite varied between 10 to 85 percent. Exceptions are noted only in clinker without iron or with very low iron content. Thus it is evident that here a combination of iron content, moderate reduction and slow cooling is a prerequisite for the decomposition of alite.

In some cases the structures of secondary belite and free lime are extremely coarse. Thus it may occasionally be difficult to detect their source (fig. 15).

Clinker containing MgO shows a distinctly lower rate of decomposition of alite, which could, however, never be prevented altogether. We may conclude that alite containing Mg^{++} cannot dissolve as much Fe^{++} as alite free of Mg^{++}.

Furthermore clinker containing Mg^{++} generally contains appreciable amounts of periclase, even if the parallel charge, run in oxidizing atmosphere, is altogether free of periclase. The periclase itself is characterized by high reflectivity and low polishing hardness. It thus obviously contains appreciable amounts of wüstite in solid solution.

The ferritic phase here possesses a considerably lower reflectivity than in analogous specimens heated in air. It is stable in the presence of metallic iron. The amount of aluminate increases on account of ferrite.

The massive belite seams around alite crystals shown by quenched specimens have disappeared completely. Obviously equilibrium conditions could be attained by resorption of belite by free lime.

Charges with a relatively low content of lime regularly tend to dust, even if samples of the same composition heated in oxidized atmosphere remain hard. This is in good agreement with the results of Suzukawa's [5] experiments, stating that the β–γ inversion of belite is sensibly promoted by small amounts of $2FeO \cdot SiO_2$ in solid solution with $2CaO \cdot SiO_2$. It has been established in technical clinker as well as in laboratory specimens that in general primary belite tends to dust much easier than belite derived from the decomposition of alite (fig. 16). Charges with high content of lime frequently remain hard, even if alite has been decomposed completely to secondary belite and free lime. It is obvious that dusting of a clinker specimen cannot be a direct measure for the degree of decomposition of alite.

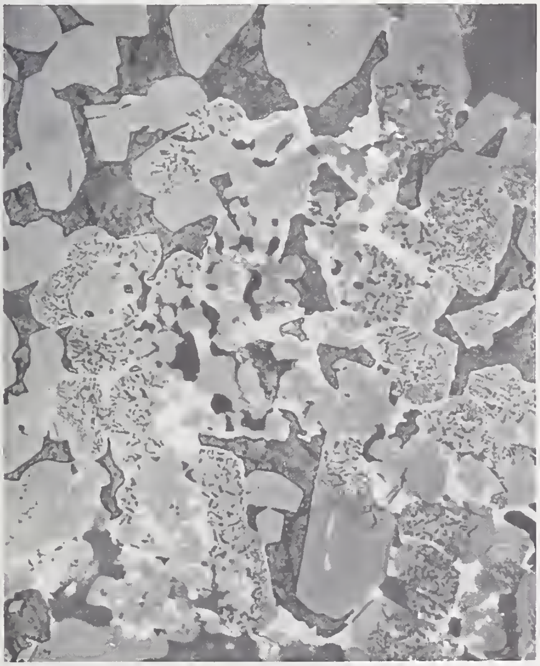

FIGURE 15. *Coarse intergrowth structures in centers of decomposition.*
Inclusions of metallic iron. Laboratory charge. Etched with H_2O. 500 ×.

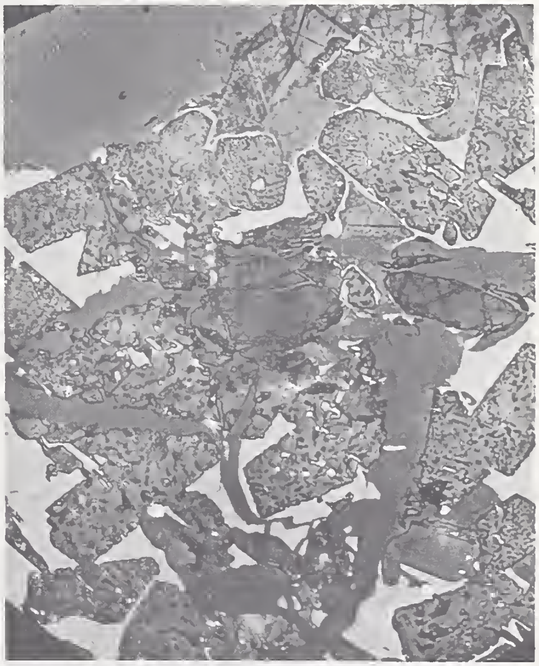

FIGURE 16. *Single grain from dusted clinker.*
The inversion to γ-C_2S has been limited to primary belite. Shaft kiln clinker. Etched with alcoholic HNO_3. 500 ×.

The Velocity of Decomposition of Alite

FIGURE 17. *Complete decomposition of a laboratory specimen after quenching from 1600 °C*

Etched with alcoholic HNO_3. 1000 ×.

The rate of cooling of laboratory charges was chosen to be about 5 °C/min in order to pass the temperature interval between 1,450 to 1,000 °C in 90 min, corresponding to slow technical cooling conditions. Later some experiments were made in order to determine the tendency of alite to decompose even in shorter time intervals. Even after cooling at a rate of 10 °C/min a considerable amount of the alite is destroyed. The intensity of this decomposition is dependent on the composition of the specimen and on the heating temperature. Thus complete decomposition of alite could be observed in a sample prepared by heating a mixture of pure tricalcium silicate with 6 percent of ferrous oxide ($Fe_2O_3+Fe \rightarrow 3\ FeO$) in H_2/H_2O gas at 1,600 °C, although it was quenched subsequently in nitrogen (fig. 17). A charge of analogous composition was heated in air, where the first traces of decomposition could be observed only after annealing of the charge for 30 to 45 hr at 1,180 °C.

The Limit of Stability of Alite

A most favourable chance has been offered to determine the limit of stability of alite by a quick method by treating the alite with ferrous iron. Knowing, however, that the decomposition of alite containing Fe^{++} may occur very rapidly it seemed doubtful whether normal quenching would always succeed exactly in preserving the conditions of equilibrium of the temperature of annealing. Thus, after heating a charge at 1,500 °C, it was slowly cooled in reducing atmosphere until the temperature chosen for this run was attained. The furnace temperature having been kept at this point for 2 hr, the charge was oxidized and thus the phases stable at that temperature were preserved and the equilibrium safely frozen to room temperature.

The limit of stability of alite containing Fe^{++} has been determined by this method to be 1,183 °C (±5 °C). It seems, however, that this value is valid only for the special case of instabilization of alite by Fe^{++}. Attempts to decompose alite heated in air, by annealing, show that charges containing ferric iron are unstable at a temperature of 1,180 °C while those containing alumina and magnesia did not show any trace of decomposition after 120 hr annealing at this temperature. This is in good accordance with the observations of Welch and Gutt [6] who found that the limit of stability of alite may be shifted considerably by different admixtures.

The Fe^{++} Content of Alite

An attempt was made to determine the limit of solubility of Fe^{++} in alite. For this purpose pure tricalcium silicate containing admixtures of metallic iron and ferric oxide was heated to temperatures of 1500 °C and 1600 °C, respectively, while a water-vapor/hydrogen mixture of varying composition was passed over the charge. Succeeding inspections by analytical methods and by microscope always revealed that certain quantities of ferric iron or of ferric iron and metallic iron were present. It seems to be impossible to obtain a compound containing iron only in its bivalent state. Our analytical data, however, prove that at least 2.60 percent FeO together with 0.40 percent Fe_2O_3 may enter the tricalcium silicate as solid solution, thus producing the typical powder diagram of alite.

It has already been mentioned that considerable amounts of free lime are liberated by the reduction of iron-containing clinker. This phenomenon can be observed even much better in charges prepared from pure tricalcium silicate, containing no more than traces of free lime, and iron oxide only. After heating in reducing atmosphere, considerable

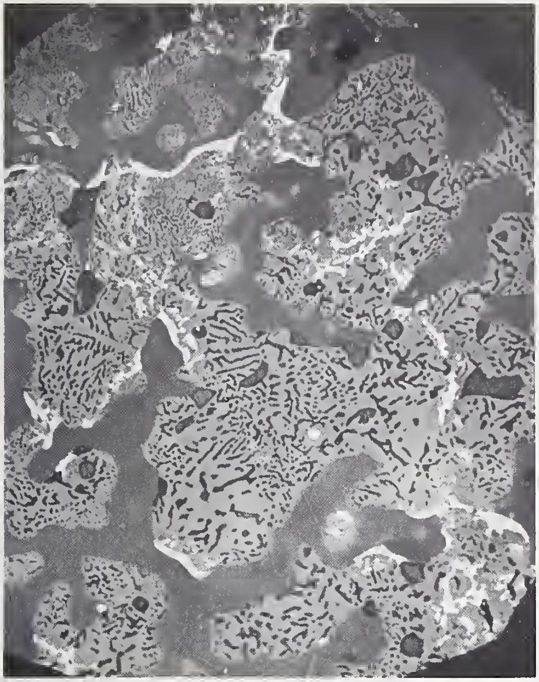

Figure 18. *Complete disintegration of iron-bearing alite in a laboratory charge resulting in a myrmekitic intergrowth of secondary free lime, belite, and ferrite.*

Primary and secondary free lime may easily be distinguished from one another. Etched with H_2O. 800 ×.

amounts of free lime are produced (fig. 18) while the phases of air-treated clinker in the parallel run consist of alite, belite, and ferrite. Thus it may be concluded that at least a considerable fraction of the Fe^{++} formed during this process replaces Ca^{++} of the tricalcium silicate.

The reoxidation at lower temperature of primarily reduced, iron-bearing alite produces characteristic structures which may help to arrive at an analogous deduction. Alite treated in this way shows three sets of fine, strictly parallel belite lamellae, strikingly similar to those described from technical clinker samples (fig. 19). This feature may be explained as follows:

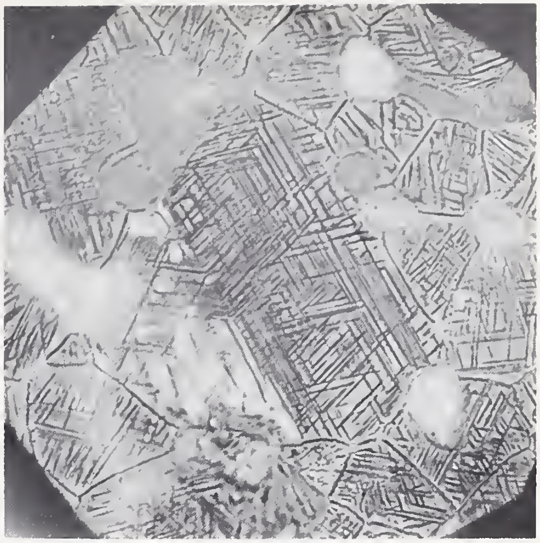

Figure 19. *Three different sets of parallel belite lamellae follow the orientation of the alite crystal.*

Laboratory charge. Etched with H_2O. 1000 ×.

During the heating of the clinker under conditions of reduction, Fe^{++} ions have been replacing some of the Ca^{++} ions of the tricalcium silicate. Oxidation at lower temperatures transforms the divalent iron ions to trivalent ones which can no longer substitute for calcium. The ferric ion, on the contrary, changes its chemical nature from a cation to an anion, now detaching further amounts of divalent ions from the tricalcium silicate. As the formula of tricalcium silicate containing Fe^{++} as a substitute for Ca^{++} may be written $(Ca,Fe)_3SiO_5$ or $xCa_3SiO_5 \cdot yFe_3SiO_5$ the equation for this transformation will be

$$10\,Ca_3SiO_5 + 2\,Fe_3SiO_6 \xrightarrow[ox]{} 12\,Ca_2SiO_4 + 3\,Ca_2Fe_2O_5$$

or

$$10\,C_3S + 2\,f_3S \xrightarrow[ox]{} 12\,C_2S + 3\,C_2F,$$ (where $f = FeO$).

This clearly demonstrates the reaction forming belite lamellae in alite crystals at lower temperature, where the low mobility of the lattices prevents the complete separation of the resulting phases from one another as would have happened at higher tempertaures. Thus theoretically the oxidation of 1.0 percent Fe^{++} in alite will result in the transformation of tricalcium silicate to 6.17 percent dicalcium silicate. Again this reaction points to the substition of Ca^{++} by Fe^{++} in alite.

The Influence of Sulfides on the Stability of Alite

Sulfides are formed only under conditions of reduction, thus occasionally being encountered in samples showing disintegration of alite. Generally, however, they rather seem to repress this reaction.

Rather as a curiosity we want to present a photograph here (fig. 20), demonstrating the decomposition of alite in a clinker sample containing an unusually high amount of sulfides. Here belite, free lime, ferrite and an iron sulfide may be identified as disintegration products pseudomorphous after alite.

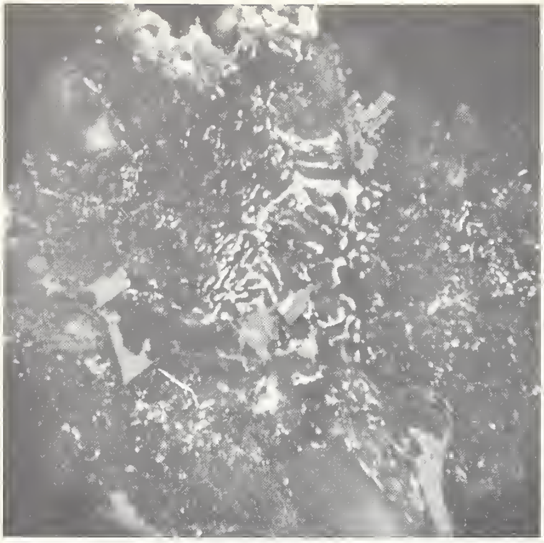

FIGURE 20. *Myrmekitic intergrowths of belite, free lime, ferrite, and iron sulfide pseudomorphous after alite.*

Oil, immersion, crossed nicols. 500 ×.

Decomposition of Alite in Clinker Containing Potassium

It is well known fact that the formation of alite is prevented when a certain limiting concentration of potassium in the clinker is passed. A belite phase and free lime are formed instead. (Zur Strassen [8])

This limit of concentration of potassium seems to be dependent on temperature in such a way that alite crystals may contain a higher amount of K^+ at higher temperatures without being destroyed. Thus there is a possibility that with lower temperature, in the equation alite = belite + free lime the equilibrium may be shifted to the right. An alite crystal containing certain amounts of potassium will thus tend to decompose. Likewise a later addition of potassium to the clinker will result in a change of equilibrium.

The decomposition of alite by the influence of higher concentrations of potassium has been observed in laboratory clinker. The minimum amount of potassium resulting in this disintegration may even be attained by technical clinker. The author, however, has not yet found a sample in which the decomposition of the alite had to be ascribed without doubt to the fact that the limit of potassium content had been passed.

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Discussion

G. Ahlers

In this discussion it is desired to report on some other experiments on the decomposition of alite. It was felt that this decomposition, if it could be brought to completion, would be a way of obtaining a direct method of analysis for alite. Whereas it was found that normal clinkers did not decompose at an appreciable rate at any temperature, it was possible to decompose at least some cements quantitatively at 900 °C. The difference in the rate of decomposition between cement and clinker is due to the catalytic effect of $CaSO_4$ [1].[1] It was ascertained that the decomposition was complete by examining the cement after ignition by means of X-ray diffraction. After two hours at 900 °C, the alite lines were completely gone, there were strong CaO lines, and there were lines due to a substance which is believed to be some form of C_2S. The C_2S found was by no means the same material as that already present in the cement. Its pattern also did not agree too well with those reported for other forms of C_2S; however, this problem was not pursued any further.

The CaO formed during the decomposition was determined by the Bogue and Lerch modification of the Emley method [2]. The C_3S was calculated from this analysis by multiplying the free lime content by 4.072. This factor is based on the simplified reaction as written by Woermann; however, the error in the C_3S if one assumes Jeffery's formula to be correct would be only about 2 percent. Since this is an extreme assumption, it is felt that the factor for pure C_3S is a sufficiently good approximation.

It is, of course, conceivable that there are other minor reactions occurring under the suggested conditions in which CaO is involved. Notably there is a good possibility of a change in the composition of the ferrite phase. Indeed such a change was occasionally suggested by a change in the ferrite X-ray pattern. But nonetheless an estimate within several percent of the alite content could be obtained by this method. The results of 11 analyses are listed in table 1. They are compared with the results of Bogue calculations.

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *C_3S analyses by decomposition and by Bogue calculations*

This method	Bogue's method
47.8	45.5
53.7	49.5
19.0	21.0
50.1	48.1
56.2	54.8
55.8	53.1
48.0	55.8
55.7	57.3
50.1	48.2
60.7	61.1
56.2	51.2

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Closure

E. Woermann

According to the results of Ahlers' experiments it is possible to determine the amount of alite in a sample of portland cement by analyzing the free lime liberated by the decomposition of the alite during heat treatment in a laboratory furnace. For this purpose the amount of secondary free lime necessarily has to be determined most exactly and quantitatively.

At first glance this seems to be in contradiction to our statement, that it is impossible to trace the decomposition of alite in technical clinker by conventional analytical methods, because generally the intergrowth structures of secondary belite and free lime are much finer than the average grain size of cements.

It must be kept in mind, however, that the laboratory technique applied by Ahlers is totally different from any technical process.

(1) Ahlers points out the fact that normal clinker does not decompose at an appreciable rate at any temperature. In portland cement, however, alite may be quantitatively decomposed, owing to the catalytic action of the gypsum added.

(2) The samples of portland cement selected by Ahlers at one time have been cooled from sintering temperature in technical cooling aggregates—in most cases even at a relatively rapid rate. Only later they have been reheated to 900 °C in order to bring about the disintegration of the alite contained in these samples. Considering the influence of fast cooling on the properties of portland cement clinker, it does not seem improbable that rapid cooling may even affect the properties of alite itself. Thus alite seems to react more sensitively to this heat treatment than to the slow cooling from sintering temperature to about 900 °C that might occur in a technical process.

(3) From experiments of S. L. Meyers [1] and E. T. Carlson [2] we know that the age of the portland cement sample affects the tendency of the alite to dissociate, which is much less in the case of fresh material.

(4) Furthermore it should be borne in mind that the disintegration of alite in technical clinker is due to solution of divalent iron in the alite, which sensibly influences the velocity of the decomposition of the latter and thus at the same time, most probably, the coarseness of the intergrowth structures of the secondary products.

(5) During our own experiments it has repeatedly been observed that, while the disintegration products of alite in technical clinker form very fine intergrowth structures pseudomorphous after alite, these structures are very coarse in samples subjected to prolonged heat treatment according to the proposals of Ahlers. It is evident that in this case the amount of secondary free lime can be determined by conventional analytical methods. Thus our experiments are in good agreement with the results of Ahlers and of Meyers [1].

At this point it seems interesting to review the literature regarding the decomposition of alite and of tricalcium silicate. We find that nearly all research work devoted to this feature is done by reheating charges of the material in question, with or without further additions, at different temperatures. The recorded increase in the analyzed amount of free lime is accepted as a direct measure for the degree of disintegration of alite or of tricalcium silicate. (e.g., S. L. Meyers [1], E. T. Carlson [2], D. Steiner and B. Bartos [3], N. Yannaquis [4], F. W. Locher [5], J. H. Welch and W. Gutt [6], and others.) On the other side F. Tröjer [7], investigating the decomposition of alite in technical clinker, finds that in his samples the secondary free lime cannot be determined by conventional analytical methods because the structures of the secondary products are much too fine. Thus the belite to a considerable extent protects the free lime from being dissolved by the reagents.

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Paper II–S9. Note on the Behavior of Tetracalcium Aluminoferrite in an Atmosphere of Hydrogen*

P. Longuet

Synopsis

The weight losses attending the reduction of iron oxide compounds in a hydrogen atmosphere were recorded by thermogravimetric means. The strength of bond between Fe and O was thus revealed, with C_4AF apparently the most stable combination of those investigated. The iron formed by the reduction is quantitatively oxidized to Fe_2O_3 in an atmosphere of CO_2.

Résumé

Les variations de poids provenant de la réduction des composés oxydés du fer en atmosphère d'hydrogène sont enregistrées par thermogravimétrie. L'intensité de la liaison entre Fe et O est ainsi mise en évidence—AFC_4 apparaît comme le terme le plus stable. Le fer formé lors de la réduction est quantitativement oxydé en Fe_2O_3 en atmosphère de CO_2.

Zusammenfassung

Die Gewichtsverluste, die während der Reduktion von Eisenoxydverbindungen in einer Wasserstoffatmosphäre auftreten, wurden vermittelst thermo-gewichtsanalytischen Methoden registriert. Man konnte in dieser Weise die Bindungsfestigkeit zwischen Fe und O feststellen, und es ist auf diese Weise herausgefunden worden, daß augenscheinlich C_4AF die stabilste Verbindung ist. Alles Eisen, welches durch die Reduktion gebildet worden ist, wird in einer CO_2 Atmosphäre quantitativ zu Fe_2O_3 oxydiert.

Experimental Procedure

The use of thermogravimetric analysis as a method of phase analysis has led us to study the action of hydrogen on the reducible components in cement chemistry (alkali and alkaline earth sulfates, iron compounds, etc.). The present note deals with tetracalcium aluminoferrite and certain supplementary tests.

We used the Chevenard thermobalance which we have described elsewhere. We will simply say that the apparatus used permits continuous measurement of weight variation in a specimen subjected to a uniform temperature rise (300 °C per hr) in a definite gaseous atmosphere (air, H_2, CO_2, N_2, A . . . at atmospheric pressure).

The compounds subjected to tests were prepared by coprecipitation. A standard solution of nitrates with desired cations is precipitated *simultaneously* by ammonium carbonate. The precipitate obtained is dried, calcined at about 600 °C to constant weight, finely ground, and kept in an electric furnace for 20 to 30 hr at a temperature somewhat lower than the probable point of fusion. The composition is checked by chemical analysis, and, eventually, the phases present are identified by X-ray diffraction. A summary of our observations follows.

The Compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

Figure 1a shows the curve for reduction of this compound in hydrogen. The trend is regular, without level stretches, as in the case of the reduction of a definite compound. The temperature at the start of the reaction is around 860 °C. This value is the highest encountered in the study of the ferric compounds. Figure 2 shows the behavior of Fe_2O_3 under the same conditions.

The compound obtained after reduction (cooling in an atmosphere of hydrogen) presents an X-ray diffraction pattern whose continuous back-

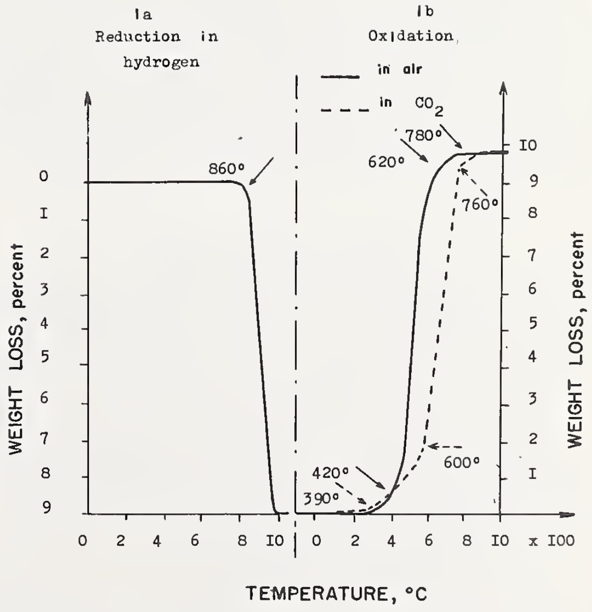

Figure 1. *Thermogravimetric analysis of* C_4AF.

Reduction in hydrogen, and oxidation in oxygen and carbon dioxide. Heating rate 300 °C per hr.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Centre d'Études et de Recherches de L'Industrie des Liants Hydrauliques, Paris, France.

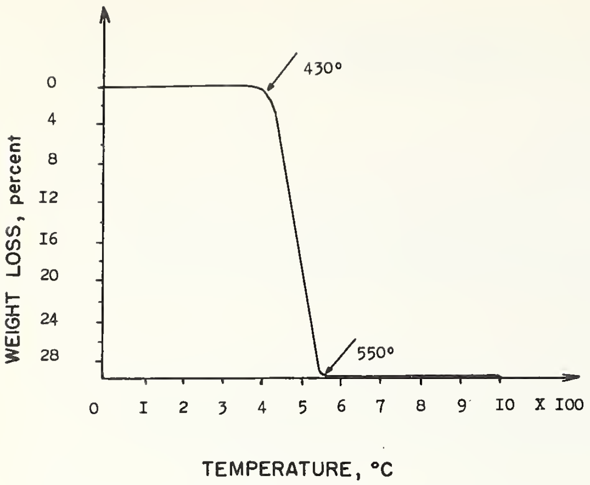

FIGURE 2. *Thermogravimetric analysis of* Fe_2O_3.
Reduction in hydrogen. Heating rate 300 °C per hr.

ground is rather pronounced, yet permits detection of the principal lines of metallic iron (Fe), tricalcium aluminate (C_3A), and calcium oxide (CaO). A quantitative determination of the lime thus liberated by fixation of water vapor at 200 °C at atmospheric pressure yields a value of the order of one mole CaO per mole of reduced C_4AF.

When heated in air the reduced compound oxidizes, following a regular curve (fig. 1b, solid line). Upon complete oxidation the compound presents an X-ray diffraction pattern analogous to the initial C_4AF product, although with a somewhat more pronounced continuous background. No free CaO is observed.

When heated in an atmosphere of CO_2 (we intended at the start to investigate the behavior of free CaO), the very finely divided iron of the reduced compound quickly takes part in oxidation-reduction reactions, finally becoming completely oxidized—the same final state as in air—without revealing any evidence of even partial carbonation of free lime (dashed curve, fig. 1b).

Supplementary Tests

No systematic study of the systems CaO-Fe_2O_3 and CaO-Fe_2O_3-Al_2O_3 was undertaken. Yet we must mention the behavior of certain compositions which we had occasion to examine.

A first binary composition comprising 80.9 percent Fe_2O_3 and 19.1 percent CaO (fig. 3).

Reduction begins at a lower temperature than that of the oxide. The trend of the curve reveals a succession of equilibria during the course of the reaction. The system is complex.

A second binary composition (64.1 percent Fe_2O_3 and 35.9 percent CaO) (fig. 4). The temperature increases at the start of the reduction. The trend is simpler and of a general type related to a sequence of two simple reactions.

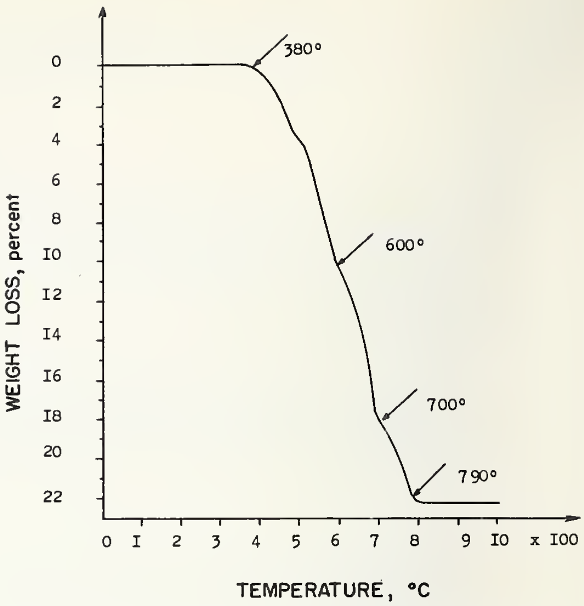

FIGURE 3. *Thermogravimetric analysis of* $CF_{1.49}$.
Reduction in hydrogen. Heating rate 300 °C per hr.

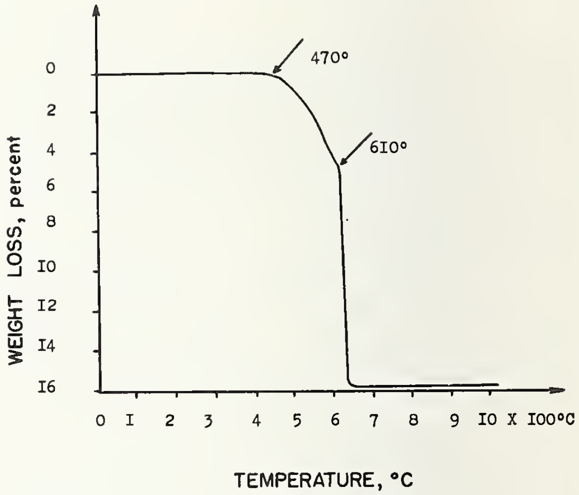

FIGURE 4. *Thermogravimetric analysis of* $C_3F_{1.89}$.
Reduction in hydrogen. Heating rate 300 °C per hr.

A ternary composition (Al_2O_3, 26 percent; Fe_2O_3, 31 percent; CaO, 43 percent or, expressed in millimoles per 100 g, Al_2O_3 257; Fe_2O_3 193; CaO 770). The composition presents the following ratios: $C/F=4$ and $A/F>1$. It corresponds to an addition of 64 mM of Al_2O_3 to 193 mM of C_4AF, with a ratio of excess A to C_4AF that amounts to 1/3.

The thermogram obtained in a hydrogen atmosphere (fig. 5) reveals two successive reactions which are clearly defined. One can see that the ratio of successive losses, 2.75/5.55, has essentially the same value as the ratio 64/(193–64). It seems as if the Al_2O_3 added to C_4AF forms an equivalent quantity of a ferric compound that

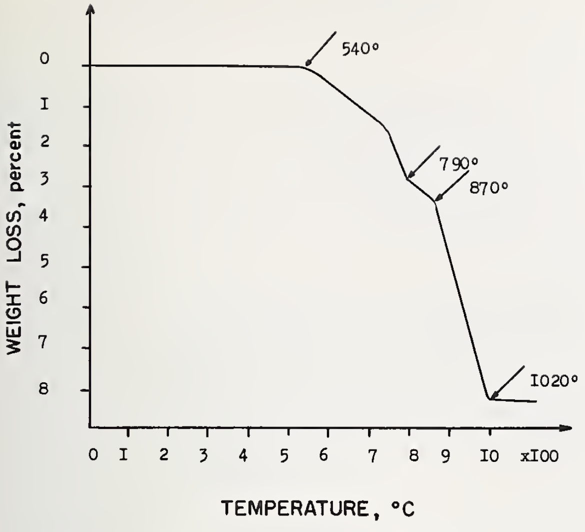

FIGURE 5. *Thermogravimetric analysis of* $C_4A_{1.33}F$.
Reduction in hydrogen. Heating rate 300 °C per hr.

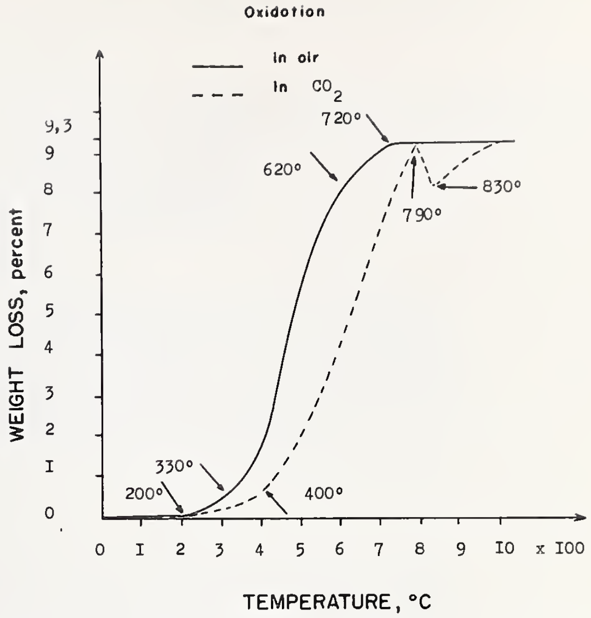

FIGURE 6. *Thermogravimetric analysis of reduced* $C_4A_{1.33}F$.
Oxidation in oxygen and in carbon dioxide. Heating rate 300 °C per hr.

is more easily reducible. The completely reduced composition yields an X-ray diffraction pattern with a very intense continuous background with only the principal lines of metallic iron visible. We could not detect free lime (the ratio excess $A/C_4AF=1/3$ permits acceptance of the hypothesis of formation of C_3A and Fe as end products of reduction).

Oxidation of the reduced composition in air yielded a regular curve (fig. 6, solid line). In a CO_2 atmosphere the curve presents a hook indicating a loss at the same temperature as at the end of the first reducing reaction (dashed curve, fig. 6). Whatever the cause of this hook (action of iron oxide on $CaCO_3$ formed during the reaction, disturbance of oxidation-reduction equilibria between the different iron oxides formed), it reveals the complexity of the system which does not smoothly attain its equilibrium as in the case of C_4AF.

Let us also mention that a comparison of the numerical values of the reduction and oxidation of the same reduced composition with the theoretical value derived from chemical analysis permits us to determine the losses of oxygen undergone by the composition during treatment at high temperature or, conversely, the formation of higher oxides during oxidation.

In summary, the action of hydrogen on some compositions in the two systems Fe_2O_3-CaO and Al_2O_3-Fe_2O_3-CaO suggests a classification of these compounds according to ease of reduction. This reactivity gives an indication—which could be a function of possible disturbances of equilibrium due to reduction—of the strength of the bonds between Fe and O in the composition under study. In the case of a pronounced difference the thermogram permits us to evaluate the relative amounts of the different forms present. We have thus revealed the stability of a compound corresponding to the formula C_4AF and the effect of an addition of Al_2O_3 to this compound. The oxidation curves in air or, even better, in CO_2 may permit us to state precisely the nature of the system under study. An examination of the products of the reduction yields interesting indications of the structure of the compound under study.

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SESSION III. CHEMISTRY OF HYDRATION OF CEMENT COMPOUNDS

Paper III–1. The Hydration of Tricalcium Silicate and β-Dicalcium Silicate at Room Temperature*

Stephen Brunauer and S. A. Greenberg

Synopsis

In the room temperature hydration of C_3S and β-C_2S, the hydration products are a calcium silicate hydrate and calcium hydroxide. Some of the properties of C_3S, C_2S, $Ca(OH)_2$ and the aqueous phase are presented, and the chemical and physical properties of the calcium silicate hydrate are discussed in considerable detail. This hydrate is a member of a series of hydrates, called tobermorites. The properties of other tobermorites are discussed in relation to those of the tobermorites produced in the hydration of C_3S and β-C_2S.

Data are given on the heats of hydration of C_3S and C_2S, and estimates are made of the entropies and free energies of hydration. Finally, the rates and mechanisms of hydration are discussed.

Résumé

Dans l'hydratation de C_3S et β-C_2S à la température du laboratoire, on obtient comme produits d'hydratation un hydrate de silicate de calcium et l'hydroxyde de calcium. L'exposé présente certaines propriétés de C_3S, C_2S, $Ca(OH)_2$, et la phase aqueuse, et discute de façon bien détaillée les propriétés chimiques et physiques de l'hydrate du silicate de calcium. Cet hydrate est membre d'une série d'hydrates, appelés tobermorites. Les propriétés d'autres tobermorites sont discutées par rapport à celles des tobermorites produits dans l'hydratation de C_3S et β-C_2S.

Des résultats sont donnés quant aux chaleurs d'hydratation de C_3S et de C_2S, et l'évaluation des entropies et des énergies libres d'hydration est faite. Enfin, les taux et mécanismes d'hydratation sont discutés.

Zusammenfassung

Bei der Hydratation des C_3S und des β-C_2S bei Zimmertemperatur sind die Hydratationsprodukte Kalziumsilikathydrat und Kalziumhydroxyd. Einige Eigenschaften des C_3S, des C_2S, des $Ca(OH)_2$ und der wäßrigen Phase werden besprochen, und die chemischen und physikalischen Eigenschaften des Kalziumsilikathydrates werden ganz ausführlich dargelegt. Dieses Hydrat ist nur eines einer Hydratreihe, die alle mit dem Namen Tobermorit bezeichnet werden. Die Eigenschaften der anderen Tobermorite werden in ihrer Beziehung zu den Tobermoriten, die bei der Hydratation des C_3S und des β-C_2S entstehen, diskutiert.

Die Werte der Hydratationswärmen des C_3S und des C_2S werden angegeben, und die Entropien und die freien Hydratationsenergien werden abgeschätzt. Schliesslich werden die Hydratationsgeschwindigkeiten und -mechanismen besprochen.

Introduction

In a discussion of the hydration of calcium silicates, it is customary to start by pointing out that tricalcium silicate and β-dicalcium silicate together constitute about 75 percent of a portland cement. To be sure, the reaction is vitally important, because the most important constituent of hydrated portland cement is a calcium silicate hydrate, and the most important constituent of concrete and mortar is hydrated portland cement. The present authors would like to point out that the hydration of calcium silicates is not only an important reaction but a fascinating one, as well. It is not a simple reaction, as will be seen, nor is it hopelessly complicated—but it is complicated enough to be interesting and challenging.

In every chemical reaction, the investigator is interested in three things: changes in matter, changes in energy, and the rate of change. In the present paper, the authors will attempt to report the status of the knowledge of these three aspects of the chemical reactions under consideration, as they see it. Before doing so, however, it seems appropriate to describe some of the pertinent properties of β-C_2S and C_3S.

Some Properties of the Two Calcium Silicates

1. The preparation of tricalcium silicate and β-dicalcium silicate was described by a number of early investigators; among them are Lerch and Bogue [1].[1] Most of the other investigators used slight modifications of this method. The modifications used in this laboratory are described in the literature, ref. [2, 3].

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Research and Development Laboratories of the Portland Cement Association, Skokie, Illinois.

[1] Figures in brackets indicate the literature references at the end of this paper.

2. The crystal structure of β-C_2S, together with the structures of the three other modifications of C_2S, was described by Nurse [4]. The structure of β-C_2S was determined by Mrs. Midgley [5]. The unit cell is monoclinic, with $a=5.48$, $b=6.76$, $c=9.28$, and the angle is 94°33′. Mrs. Midgley states that very slight modifications to the β structure produce an orthorhombic cell, and somewhat larger distortions and rearrangements produce a trigonal cell.

The unit cell contains four molecules. There are four SiO_4 tetrahedra in the cell, not linked with each other; in other words, β-Ca_2SiO_4 is an orthosilicate. Four of the eight Ca^{++} ions in the cell are alternately above and below the SiO_4 tetrahedra (Ca I), and the other four are in holes between the tetrahedra (Ca II). Nurse states, "Formally the co-ordination number of Ca I is six and of Ca II is eight, but the existence of holes fronting on the Ca ions means that the co-ordination is irregular and that O ions at distances greater than normal Ca-O bond lengths must also be considered as contributing to the co-ordination."

The specific gravity of β-C_2S is 3.28. β-C_2S occurs in nature as the mineral larnite.

The C_3S found in portland cement contains small amounts of Al_2O_3 and MgO as necessary constituents of its structure. This phase is called alite, and its crystal structure has been worked out by Jeffery [6]. The unit cell of alite is monoclinic, with $a=33.08$, $b=7.07$, $c=18.56$, and the angle is 94°20′. The cell contains 36 molecules of C_3S, in which four Si^{4+} ions are replaced by four Al^{3+} ions, and two Mg^{++} ions are located in holes to balance the charges. Thus, the chemical formula is $C_{54}S_{16}AM$.

The unit cell of C_3S itself is triclinic, and the crystal structure has not been worked out fully. The pseudostructure has the formula $Ca_3O(SiO_4)$. Bernal, Jeffery, and Taylor [7] state, "Each calcium ion is surrounded by six oxygens, arranged in such a way that the centres of five of them are in one hemisphere, with only one atom closing the gap on the other side. Large holes, equal in size and number to those occupied by the calcium ions, occur adjacent to the loosely coordinated sides of the calcium ions. The oxygen ions attached to silicon are each 3-coordinated on the other side by calcium ions, and those not attached to silicon are octahedrally coordinated by calcium."

The specific gravity of C_3S is 3.15. C_3S does not occur in nature.

3. The fact that β-C_2S occurs in nature, whereas C_3S does not, indicates greater stability of the former. This is borne out also by thermodynamic considerations.

Johannson and Thorvaldson [8] determined the heat of formation of C_3S from β-C_2S and CaO, and they found that the reaction was endothermic to the extent of 470 cal/mole at 20 °C. King [9] redetermined the same quantity and found a value of 3200 cal/mole at 25 °C. Brunauer, Kantro, and Weise [3] used a theoretically more correct calorimetric procedure and they corrected for impurities. Their value was 2100 cal/mole at 23 °C.

Todd [10] determined the low temperature heat capacities and the entropies at 25 °C for C_3S and β-C_2S. He obtained ΔS values of 1.5 and 1.8 e.u. for the formations from the oxides of C_2S and C_3S, respectively. These figures, combined with the ΔH value of Brunauer, Kantro, and Weise, lead to a ΔF of $+2000$ cal/mole for the conversion of β-C_2S and CaO to C_3S. Thus, C_3S is thermodynamically unstable with respect to β-C_2S and CaO.

Actually, C_3S is far more reactive than β-C_2S. Bernal, Jeffery, and Taylor [7] point out that, "The alkaline character of C_3S, together with the high lattice energy associated with a distorted Ca coordination, and possibly also the presence of "holes" in the structure, give the compound a high solubility and reactivity towards water." The authors mean "high energy lattice" instead of "high lattice energy". The term "lattice energy" is usually defined as the energy released when gaseous ions react to form a lattice; consequently, high lattice energy implies great stability.

The lattice energies of C_3S and β-C_2S were calculated in this laboratory. The reactions are

$$3Ca^{++}(g)+SiO_4^{4-}(g)+O^{--}(g)=Ca_3SiO_5(c) \quad (1)$$

$$2Ca^{++}(g)+SiO_4^{4-}(g)=Ca_2SiO_4(c) \quad (2)$$

and the lattice energies are $U_{C_3S}=-2570$ kcal and $U_{C_2S}=-1728$ kcal. The lattice energy of CaO, U_{CaO}, is reported to be -842 kcal [11]. The difference $U_{C_3S}-U_{C_2S}-U_{CaO}=-2570+1728+842=0$. Actually, this should be equal to the heat of formation of C_3S from C_2S and CaO, which is 2 kcal. The error in U_{C_3S} and U_{C_2S} may be 20 or even 200 kcal, but most of the error cancels on subtraction. Even so, the agreement is surprisingly close.

Stoichiometry of the Hydration of C_3S

A mixture of portland cement, C_3S, or C_2S with a limited amount of water is called a "paste". If the initially plastic paste is allowed to stand, in a few hours it "sets", then continues to harden for months, or possibly even for years. This type of hydration is called paste hydration. It attempts to simulate the hydration of portland cement, C_3S, and C_2S in concrete and mortar.

Brunauer, Copeland, and Bragg hydrated C_3S in two ways: in paste form, using a water/C_3S weight ratio of 0.7 [12], and in a small steel ball mill, using a water/C_3S weight ratio of 9.0 [13]. Brunauer, Kantro, and Copeland [14] further investigated the paste hydration of C_3S, and they also studied a third method of hydration. In this, a water/C_3S weight ratio of 9.0 was used, and the reaction was carried out in a polyethylene bottle rotated on a wheel at 30 rpm. Kantro, Brunauer, and Weise [15] reported further work on the ball-mill hydration of C_2S. All these reactions took place in a controlled temperature room, at 24±1 °C.

At complete hydration of C_3S, the stoichiometry of each of the three hydration reactions was represented by the equation:

$$2Ca_3SiO_5+6H_2O=Ca_3Si_2O_7\cdot 3H_2O+3Ca(OH)_2. \quad (3)$$

Nevertheless, the three reactions were not identical. The ball-mill hydration produced a calcium silicate hydrate that was identical in crystal structure with the natural mineral afwillite. The paste hydration, as well as the hydration in the rotating bottle, gave a calcium silicate hydrate related to the natural mineral tobermorite.

The paste and the bottle hydration, which gave similar hydration products, will be discussed first, the ball-mill hydration later.

Calcium Hydroxide and the Molar CaO/SiO_2 Ratio in the Hydrate

1. The amount of calcium hydroxide was determined by X-ray quantitative analysis, using the method of Copeland and Bragg [16]. In almost every instance, the amount determined was smaller than that indicated by eq (3). It would have been a simple matter to assign the missing lime to the calcium silicate hydrate. In that case the molar CaO/SiO_2 ratio in the tobermorite-like hydrate would not be 1.5, as shown in the equation, but a variable amount, ranging from 1.52 to 1.75. However, certain lime extraction experiments indicated that this was not the correct explanation.

Franke [17] proposed a method for the determination of uncombined CaO and $Ca(OH)_2$ in hydrated and unhydrated calcium silicates and portland cements. A solvent mixture, consisting of acetoacetic ester and isobutyl alcohol, was refluxed with the sample, and, according to Franke, a single extraction removed all the free lime. The experience of Pressler, Brunauer, and Kantro [18] was that a single extraction did not come even close to removing all of the free $Ca(OH)_2$ from hydrated calcium silicates and portland cements. Variation of the ratio of acetoacetic ester to isobutyl alcohol or the time of refluxing did not solve the problem. However, by repeated Franke extractions on the same sample, the free $Ca(OH)_2$ could be determined with good accuracy. In these extractions a small part of the lime was removed from the calcium silicate hydrate, but the rate of removal of this lime was only about one-fiftieth of the rate of removal of calcium hydroxide. On this basis, a correction could be made for the lime removed from the calcium silicate hydrate. The multiple extraction method (M.E.M.) led to a CaO/SiO_2 ratio of 1.51 in the hydrate, which is the same as that shown in eq (3), within experimental error.

Later, Pressler, Brunauer, Kantro, and Weise [19] developed another modification of the Franke method for the determination of free $Ca(OH)_2$. In this, aliquot samples of the same material were treated with varying amounts of Franke solvent. In the solvent variation method (S.V.M.), again some lime was removed from the hydrate, but again a correction could be made for this. The two different methods led to the same results. The theoretical bases of the methods and the corrections are discussed in the papers [18, 19].

2. Brunauer, Kantro, and Copeland [14] found that the "missing lime", i.e., the difference between the stoichiometric quantity of $Ca(OH)_2$ indicated by eq (3) and the $Ca(OH)_2$ determined by X-ray quantitative analysis, was more easily extractable than the rest of the $Ca(OH)_2$. By the time half of the $Ca(OH)_2$ was extracted, all the missing lime was removed from the system, and X-ray analysis for $Ca(OH)_2$, combined with chemical analysis, indicated a molar CaO/SiO_2 ratio of 1.5 in the calcium silicate hydrate.

In spite of the easy extractability of missing lime, it may be argued that the tobermorite-like calcium silicate hydrate does contain this lime in a very loosely bound form. Several investigators, among them Kalousek and Prebus [20], reported the loosely bound lime as a part of the tobermorite-like structure. However, there are two types of experiments which point very strongly in the other direction.

It was stated earlier that the stoichiometry of the ball-mill hydration of C_3S was also represented by eq (3), but the calcium silicate hydrate was afwillite. In this case, X-ray quantitative analysis again gave $Ca(OH)_2$ values lower than that required by the equation. The missing lime was variable in amount, just as in paste and in bottle hydration, and the range of variation was also the same. There is no possibility here to ascribe the missing lime to the calcium silicate hydrate. Afwillite has a definite composition of $Ca_3Si_2O_7\cdot 3H_2O$. The conclusion here is inevitable that the missing lime is $Ca(OH)_2$ in a noncrystalline form [15].

The second line of evidence is more direct. In the paste hydration of β-C_2S, as well as in the paste hydration of portland cements high in C_2S, at room temperature, tobermorite-like hydrates were obtained with molar CaO/SiO_2 ratios ranging up to 1.75. In the paste hydration of C_3S, at 50° and 80 °C, the molar CaO/SiO_2 ratios in the hydrate were 1.57 and 1.61, respectively. These results, as well as others, are shown in table 1. Henceforth, in this paper the tobermorite-like hydrates with CaO/SiO_2 ratios greater than 1.5 will be called high-lime tobermorites. In these high-lime tobermorites, the CaO in excess of the ratio 1.5 was just as firmly bound as the CaO below the ratio 1.5. It appears, therefore, that the missing lime is not a loosely bound part of a high-lime tobermorite, but $Ca(OH)_2$. Because it is not detected by X-rays, it must be noncrystalline.

3. Initially, it was thought that the missing lime was adsorbed on the surface of the calcium silicate hydrate [12]. This tobermorite-like hydrate has a very large specific surface area, able

to accommodate the missing lime. Nevertheless, later work [14] indicated that the adsorption of lime on the hydrate surface was small, probably because in the competition between $Ca(OH)_2$ and water for the surface, the latter is adsorbed preferentially. Kalousek and Prebus [20], in more quantitative experiments, also found that the adsorption of $Ca(OH)_2$ on tobermorite-like hydrates was small. Indirect evidence for the small adsorption of $Ca(OH)_2$ can be found in earlier work. Bessey [21], Taylor [22], and Greenberg [23] found that the CaO/SiO_2 ratio in tobermorite-like hydrates, prepared by the reaction of $Ca(OH)_2$ and silica, at or near lime saturation, was 1.5, within their experimental error. Although Greenberg alone measured surface areas, unquestionably, all three investigators obtained hydrates with large specific surface areas and, in all probability, the surface areas were different. Had the adsorption of $Ca(OH)_2$ been significant, the apparent CaO/SiO_2 ratios would have been variable and probably all greater than 1.5.

The only alternative that remained was to assume that the missing lime was amorphous calcium hydroxide [14]. The idea was not new. Heller and Taylor [24] found evidence of amorphous or poorly crystallized $Ca(OH)_2$ in the products of the reaction between $Ca(OH)_2$ and silica gel at 110 °C and higher. Grudemo suggested that a little dissolved silica may have entered the lattice of some of the $Ca(OH)_2$, disturbing or destroying the lattice.

Takashima [25] published a paper recently on amorphous calcium hydroxide. He prepared $Ca(OH)_2$ by the reaction of water with CaO; then he determined the total $Ca(OH)_2$ by one of the standard extraction methods and the crystalline $Ca(OH)_2$ by X-ray analysis. He found considerable differences between the two, depending on the kind of CaO used and on the temperature of slaking. The amount of crystalline $Ca(OH)_2$ ranged from 31 to 100 percent of the total. He attributed the difference to amorphous $Ca(OH)_2$. He also found that amorphous $Ca(OH)_2$ reacted with methanol, whereas crystalline $Ca(OH)_2$ did not. It is interesting to note the similarity of approach and results between Takashima's experiments and those performed in this laboratory. Neither side knew about the experiments of the other.

4. The conclusion from the above considerations is that eq (3) represents the stoichiometry of the hydration of C_3S at room temperature correctly, at least as far as the calcium hydroxide content and the molar CaO/SiO_2 ratio in the tobermorite-like hydrate are concerned. The same conclusion was reached by Graham, Spinks, and Thorvaldson [26] by a very different approach. They used C_3S labelled with radioactive Ca^{45}, and made it react with unlabelled saturated $Ca(OH)_2$ solutions. The rate of liberation of lime due to hydration and the rate of appearance of Ca^{45} in the solution indicated that the CaO/SiO_2 ratio in the calcium silicate hydrate was 1.5. A similar result was obtained when inactive C_3S was hydrated with active $Ca(OH)_2$ solutions.

A different conclusion was reached by van Bemst [27, 28], who reported that the calcium silicate hydrate produced in the hydration of C_3S had a variable CaO/SiO_2 ratio, ranging up to 2.0. He determined the $Ca(OH)_2$ released in the hydration by thermogravimetric analysis, but there is evidence that such a determination fails to account for the amorphous $Ca(OH)_2$. It was stated earlier that in the ball-mill hydration of C_3S the calcium silicate hydrate produced was afwillite, and the presence of noncrystalline $Ca(OH)_2$ was unquestionable. Greenberg analyzed the hydration products thermogravimetrically for $Ca(OH)_2$ and the analysis checked the X-ray analysis with remarkable accuracy. Thus, crystalline and amorphous $Ca(OH)_2$ appear to decompose in different temperature ranges.

Van Bemst [28] extracted the $Ca(OH)_2$ from a sample of C_3S hydrated at 60 °C. The maximum CaO/SiO_2 ratio that he reported for the extracted sample was 1.72. It was stated earlier that hydration of C_3S at higher temperatures leads to higher-lime tobermorites. In one preparation, a CaO/SiO_2 ratio of 1.63 was obtained at 80 °C in this laboratory (table 1). The error in this value and in van Bemst's value make the results not necessarily inconsistent.

5. In table 1, C–17 and C–18 represent a C_3S paste, 17-months old, dried under two different conditions. The paste contained no unhydrated C_3S. The molar CaO/SiO_2 ratio was determined for each, and the values 1.54 and 1.50 show the size of the maximum error in these determinations. In a similar manner, C–52 and C–53 represent another paste, 5-yr old, dried under the two different conditions. The ratios were 1.51 and 1.51. The average of the first two is 1.52, the average of the last two is 1.51. The excess over 1.50 may be experimental error, it may be a little adsorbed $Ca(OH)_2$, or it may be that the stoichiometry is not rigidly correct. Since one deals here with colloidal systems, as will be discussed later, such lack of accurate stoichiometry would not be surprising.

The four other C_3S pastes in table 1 indicate that the CaO/SiO_2 ratio increases slightly with increasing temperature of hydration.

Water of Hydration in the Hydrate

The water content of the calcium silicate hydrate depends on the drying conditions employed. Different investigators used different drying methods and reported different water contents.

The tobermorite-like hydrate has a very large specific surface area, of the order of 300 m^2/g. The surface is hydrophilic; the ions in the surface adsorb water readily. The water contents reported by most investigators consisted both of adsorbed water and of water of hydration, i.e., water which is part of the calcium silicate hydrate structure.

A complete physical separation of the two types of water is impossible. The hydrate is a colloid and, like other colloidal hydrates, it loses water from its structure continuously when equilibrated at lower and lower vapor pressures of water. The free energy of binding of the adsorbed water to the surface is variable, as in most adsorbent-adsorbate systems. Although the average free energy of binding of the combined water in the structure is greater than the average free energy of binding of the adsorbed water to the surface, the most firmly bound adsorbed water is held more strongly than the most loosely bound combined water. As a result, at lower vapor pressures some of the combined water is removed, while some of the adsorbed water is held by the hydrate.

When the products of the room temperature hydration of C_3S were dried at a water vapor pressure of 5×10^{-4} mm of mercury, which is the vapor pressure of ice at −78 °C, the molar H_2O/SiO_2 ratio in the tobermorite-like hydrate was always slightly greater than 1.0, averaging about 1.06 [14]. It is probable that part of the water in excess of 1.0 was adsorbed water. This method of drying will be referred to as (*D*)-drying, or dry-ice drying.

When the hydration products were dried at a water vapor pressure of 8×10^{-3} mm, which is the equilibrium pressure of $Mg(ClO_4)_2 \cdot 2H_2O$ and $Mg(ClO_4)_2 \cdot 4H_2O$, the H_2O/SiO_2 ratio in the hydrate was 1.40 [14]. This would correspond to a tobermorite of formula $Ca_3Si_2O_7 \cdot 2.80H_2O$. However, adsorption experiments showed that about 0.30 mole of water was adsorbed on the surface; thus, the corrected formula was $Ca_3Si_2O_7 \cdot 2.5H_2O$. This method of drying will be referred to as (*P*)-drying, or perchlorate drying.

It is obvious that at higher vapor pressures the tobermorite would contain more combined water and more adsorbed water. Such experiments were not performed to date, so the number of molecules of combined water in the hydrate at saturation pressure, or in liquid water, is somewhat conjectural. Bernal [29] proposed the structural formula $Ca_2[SiO_2(OH)_2]_2[Ca(OH)_2]$, indicating three molecules of water in a molecule of tobermorite, and experiments performed in this laboratory are consistent with his view.

Stoichiometry of the Hydration of β-C_2S

1. When β-C_2S was hydrated at room temperature in a small steel ball-mill, with a water/C_2S weight ratio of 9.0, at complete hydration the stoichiometry was represented by the equation

$$2Ca_2SiO_4 + 4H_2O = Ca_3Si_2O_7 \cdot 3H_2O + Ca(OH)_2. \quad (4)$$

The calcium silicate hydrate was identical with the tobermorite obtained in the paste hydration or bottle hydration of C_3S [14], discussed earlier.

When C_2S was hydrated at room temperature in a rotating polyethylene bottle, with a water/C_2S weight ratio of 9.0, in 162 days the products still contained 27.5 percent unhydrated C_2S, as determined by X-ray analysis (D–40 in table 1). The tobermorite had a molar CaO/SiO_2 ratio of 1.54, which is, within the experimental error, the same as that shown in eq (4). However, longer hydration at room temperature resulted in tobermorites of higher CaO/SiO_2 ratios (D–55, 56 and 69

TABLE 1. *Compositions of hydrated* C_3S *and* C_2S *preparations*

1	2	3	4	5	6	7	8	9	10	11	12
Preparation	Type of hydration	Material	Age	Temp.	Type of drying	$Ca(OH)_2$	$CaCO_3$	Minor constituents	Unhydrated material	CSH	Composition of CSH
				°C		%	%	%	%	%	
D–40	Bottle	C_2S	162 d	25	D	11.2	0.8	1.6	27.5	58.9	$C_{1.54}SH_{1.07}$
D–55	Bottle	C_2S	265 d	25	D	7.6	1.4	1.5	7.1	82.4	$C_{1.73}SH_{1.39}$
D–56	Bottle	C_2S	265 d	25	P	7.8	0.9	1.5	6.9	83.0	$C_{1.73}SH_{1.71}$
D–69	Bottle	C_2S	778 d	25	D	8.9	1.3	1.5	0.0	88.3	$C_{1.73}SH_{1.37}$
C–23	Paste	C_2S	17 m	25	D	9.1	0.5	1.6	27.5	61.3	$C_{1.65}SH_{1.15}$
C–24	Paste	C_2S	17 m	25	P	9.0	.6	1.6	27.0	61.8	$C_{1.65}SH_{1.43}$
C–51	Paste	C_2S	4¼ y	25	D	11.1	.9	1.6	12.9	73.4	$C_{1.63}SH_{1.09}$
C–29	Paste	C_2S	2 m 19 m	50 25	D	5.3	2.0	1.6	32.0	59.2	$C_{1.73}SH_{1.19}$
C–30	Paste	C_2S	2 m 19 m	50 25	P	6.2	1.6	1.6	31.5	59.1	$C_{1.70}SH_{1.44}$
C–57	Paste	C_2S	2 m 5 y	80 25	D	5.3	0.9	1.6	27.8	64.4	$C_{1.75}SH_{1.29}$
C–58	Paste	C_2S	2 m 5 y	80 25	P	5.8	.7	1.6	27.2	64.8	$C_{1.74}SH_{1.59}$
C–17	Paste	C_3S	17 m	25	D	38.5	.7	0.7	0.0	60.2	$C_{1.54}SH_{1.10}$
C–18	Paste	C_3S	17 m	25	P	38.6	.9	.6	.0	59.8	$C_{1.50}SH_{1.39}$
C–52	Paste	C_3S	5 y	25	D	38.8	1.2	.7	.0	59.3	$C_{1.51}SH_{1.09}$
C–53	Paste	C_3S	5 y	25	P	38.3	.8	.6	.0	60.3	$C_{1.51}SH_{1.45}$
C–27	Paste	C_3S	2 m 19 m	50 25	D	36.8	.8	.7	.0	61.8	$C_{1.58}SH_{1.13}$
C–28	Paste	C_3S	2 m 19 m	50 25	P	36.0	.9	.6	.0	62.5	$C_{1.57}SH_{1.46}$
C–55	Paste	C_3S	2 m 5 y	80 25	D	30.5	.5	.7	13.5	54.8	$C_{1.63}SH_{1.29}$
C–56	Paste	C_3S	2 m 5 y	80 25	P	31.1	.4	.7	13.2	54.6	$C_{1.59}SH_{1.61}$

in table 1). The ratio was 1.73 after 265 days, and it was the same after 778 days. These ratios are based on determination of $Ca(OH)_2$ by the two modifications of the Franke method, S.V.M. and M.E.M., discussed earlier. X-ray analysis always gave lower results for $Ca(OH)_2$ than Franke extractions, which indicates the presence of amorphous lime.

When C_2S was hydrated at room temperature in the paste form, with a water/C_2S weight ratio of 0.7, complete hydration was not obtained even in 4½ years. The CaO/SiO_2 ratio was 1.65 after 17 months (C–23 and 24), when the paste contained 27.5 percent unhydrated C_2S, and it was 1.63 after 4½ years (C–51), when the paste contained 12.9 percent unhydrated C_2S. These ratios are the same within experimental error. At higher temperatures, higher ratios were obtained, 1.72 at 50 °C (C–29 and 30) and 1.75 at 80 °C (C–57 and 58).

Funk [30], in the paste hydration of C_2S, with a water/C_2S ratio of 0.5, reported molar CaO/SiO_2 ratios averaging 1.77 at 50 °C, 1.88 at 100 °C, and 1.84 at 120 °C. He used a modification of the Franke method for the determination of $Ca(OH)_2$, which involved only a single extraction. The present authors wonder whether the $Ca(OH)_2$ was completely removed. Funk stated that the extraction results agreed with X-ray results. If there was amorphous $Ca(OH)_2$ in the hydration products, which seems likely, the X-ray results were also too low. It would be of interest to determine the $Ca(OH)_2$ in Funk's preparations by S.V.M. or M.E.M.

The reason for questioning Funk's ratios is found in a hypothesis of Taylor and Howison [31], which puts the upper limit of the ratios at 1.75. This hypothesis will be discussed in detail later. For all that, Funk's results may be entirely correct, and the reason for the small differences between his results and those obtained in this laboratory may possibly be found in the different water/C_2S ratios used.

2. The H_2O/SiO_2 ratio of the tobermorite of CaO/SiO_2 ratio 1.5, when subjected to (*D*)-drying, is close to 1.0, though usually somewhat higher. This is true whether the tobermorite comes from hydrated C_3S or C_2S.

For high-lime tobermorites, obtained in paste hydration and subjected to (*D*)-drying, the increase in CaO/SiO_2 ratio results in a corresponding increase in H_2O/SiO_2 ratio, i.e., adding a molecule of lime appears to be accompanied by the addition of a molecule of water. This is seen in table 1, column 12. For the eight (*D*)-dried pastes, four C_3S and four C_2S, the average excess of CaO over 1.5 was 0.13, and the average excess of water over 1.0 was 0.17. Funk [30] obtained similar results. He dried his hydrated C_2S preparations over P_2O_5 at 20 °C to constant weight. For 13 pastes, prepared at 50, 100, and 120 °C, the average of the excess for CaO was 0.33, and for H_2O, 0.36.

Tobermorite-Like Hydrates

When calcium hydroxide reacts with silica in water at room temperature, a calcium silicate hydrate of variable CaO/SiO_2 ratio is formed. The ratio, which depends on the concentration of lime in the solution, ranges from about 0.8 to 1.5. The same hydrates may be formed by other reactions, such as the reaction of calcium nitrate and sodium silicate, the hydration of C_3S or C_2S in large excess of water [22], and the reaction of ethyl orthosilicate with calcium hydroxide [32].

The hydrate system was studied by many investigators. Steinour [33], in an excellent review paper, reported the results of sixteen investigations. Although there is a vague general agreement between most of these results, they differ considerably in detail. The differences were probably caused, at least in part, by lack of adequate experimental techniques and lack of complete equilibration. However, probably there was a more subtle reason also, which will be discussed later.

The authors of this paper do not intend to present a full-scale discussion of the tobermorite-like hydrates. Nevertheless, a discussion of certain aspects of the system seems desirable in order to show how the tobermorites obtained in the hydration of C_3S and C_2S fit into the family of tobermorites.

Since the appearance of the above paper of Steinour, other investigations were published, by Taylor [22], by Kalousek [34] and by Grudemo [32]. The results of the first two are reproduced in figure 1. Again, there is a broad general agreement, but a disagreement in detail [35].

Taylor called the hydrate, ranging in CaO/SiO_2 ratio up to 1.5, calcium silicate hydrate (I) or CSH(I). It will be noted in figure 1 that the CaO/SiO_2 ratio in the hydrate rises sharply at lime saturation. Taylor called this high-lime hydrate calcium silicate hydrate (II) or C_2SH(II).

Claringbull and Hey [36] pointed out the similarity between Taylor's CSH(I) and the natural mineral tobermorite. There is no general agreement on nomenclature of calcium silicate hydrates as yet; some call the synthetic hydrates CSH(I) or hydrate I, others call them tobermorite minerals, tobermorite-like hydrates or simply tobermorites. The hydrates with CaO/SiO_2 ratios greater than 1.5 are called C_2SH(II), hydrate II, or high-lime tobermorites.

The most important difference between the curves of Taylor and Kalousek, from the point of view of the present discussion, is the difference in the vicinity of lime saturation. From a calcium ion concentration of about 11 millimoles per liter to lime saturation, Kalousek drew a flat curve, as shown in figure 1, corresponding to a CaO/SiO_2 ratio 1.33. Between a concentration of 15 millimoles per liter and lime saturation, Kalousek had three points on this curve and six points above

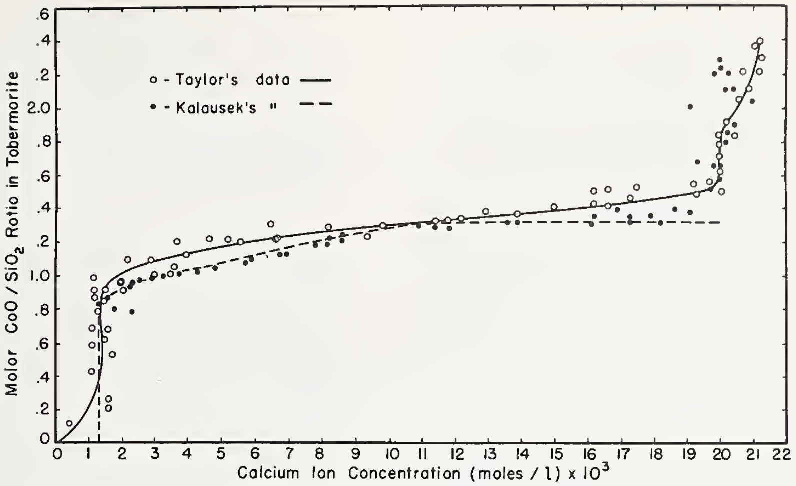

FIGURE 1. *Variation of the molar* CaO/SiO_2 *ratio in tobermorite with the calcium ion concentration in the solution.*

it. Taylor, on the other hand, obtained a continuous rise in CaO/SiO_2 ratio, reaching 1.5 at lime saturation. Grudemo [32], in one series of experiments, reached a maximum CaO/SiO_2 ratio of 1.45, in another, 1.56. Earlier work of Bessey [21] is in agreement with Taylor's curve, as well as later work of Greenberg [23], and as yet unpublished work performed in this laboratory.

Investigators for a long time debated the question whether the lime in excess of a CaO/SiO_2 ratio of 0.8 should be regarded as adsorbed or whether it is in solid solution. More recently, Brunauer, Copeland, and Bragg [12] pointed out that the extra lime cannot be regarded as physically adsorbed, and Taylor and Howison [31] advanced arguments for the extra lime being part of the crystal structure. Thus, the extra lime appears to be in solid solution—though it is a special type of solid solution, as will be seen later.

The high-lime end member of the tobermorite solid solution series, at lime saturation, has a CaO/SiO_2 ratio of 1.5, as Taylor's curve shows in figure 1. Beyond this point, one obtains the high-lime tobermorites, ranging in ratio up to 1.75, possibly higher. Kalousek and Prebus [20] contend that the tobermorite of ratio 1.5 should be regarded as the low-lime end member of the high-lime tobermorite series. There is considerable justification for this. The tobermorite obtained in the hydration of C_3S or C_2S, having a CaO/SiO_2 ratio of 1.5, resembles a high-lime tobermorite far more than the low-lime tobermorites. There seems to be a drastic change in morphology, in degree of crystallinity, as well as in other properties of the hydrate in the vicinity of lime saturation. This will be discussed later.

Crystal Structures and Densities of Tobermorites

1. The tobermorites are layer crystals. Their similarity to the clay minerals was pointed out by Taylor [22], to vermiculite by McConnell [37], and to montmorillonite by Grudemo [38].

The formula of the natural mineral tobermorite, found in Northern Ireland, is probably $Ca_4(Si_6O_{18}H_2) \cdot Ca \cdot 4H_2O$. Its crystal structure was determined by Megaw and Kelsey [39], who found that the layers were actually triple sheets, with some similarities to vermiculite. Taylor and Howison [31] describe the structure as follows.

"The central part of each layer, equivalent to the octahedral layer in a clay mineral, could be described as a distorted calcium hydroxide sheet divested of all its hydrogen atoms. This sheet is flanked on both sides by parallel rows of wollastonite-type chains, which are kinked in a plane perpendicular to that of the sheets. Only two-thirds of the tetrahedra in each chain are linked directly to the central CaO_2 sheet by sharing of oxygen atoms. The other third, which are held away from the CaO_2 sheet, will be called "bridging" tetrahedra. The composite 2:1 sheets so far described have the composition $Ca_4Si_6O_{18}$. Between them are the remaining or interlayer calcium atoms, and water molecules. The distribution of the hydrogen is uncertain. There may be more SiOH than is implied by the formula $Ca_4(Si_6O_{18}H_2) \cdot Ca \cdot 4H_2O$, with corresponding replacement of interlayer water by hydroxyl.

"To a good approximation, tobermorite from the above localities is orthorhombic with a—11.23, b—7.37, c—22.6 A, Z=4. The crystals are laths with length b (parallel to the chains) and cleavage (001) (the plane of the layers); a and b are both strongly pseudo-halved, and for many purposes a pseudo-cell with Z=1 may be used. This pseudo-cell is body centered. The longest observed basal spacing is therefore 002 (d=11.3 A), and corresponds to the thickness of a single 2:1 layer."

The CaO/SiO_2 ratio in the natural mineral is 0.83. In artificially prepared tobermorites, the ratio ranges up to 1.75, possibly higher. Throughout this wide variation in composition, such properties as density, index of refraction and X-ray diffraction pattern remain remarkably constant.

2. Taylor and Howison [31] measured the densities of tobermorites ranging in CaO/SiO_2 ratio from 0.81 to 1.50, and found no systematic trend to increase with the ratio. All of their density values were too low, as they themselves realized. They attributed the low densities to lack of complete penetration of the pore system by the liquid used for the measurements. This is doubtless correct, but there was another reason, too. Since their specimens were dried at a water vapor pressure of 6 mm, all of them contained adsorbed water. For example, the samples dried at 108 °C and 6 mm pressure probably had about half of their surface covered with adsorbed water. This is a considerable amount of water, because the specific surface of tobermorite is very large.

Taylor and Howison, nevertheless, believed that their conclusions as to the approximate constancy of the density was correct, and work in this laboratory confirms their conclusion [14]. The average density of five tobermorite preparations, having CaO/SiO_2 ratios of 1.50 and H_2O/SiO_2 ratios of 1.00, was 2.85 ± 0.02 g/cc. These were hydrated C_3S and C_2S preparations, dried at a water vapor pressure of 5×10^{-4} mm (*D*-drying). A tobermorite in a paste hydrated C_2S preparation, similarly dried, had a CaO/SiO_2 ratio of 1.65 and an H_2O/SiO_2 ratio of 1.15; its density was 2.85 g/cc. It is obvious that if in a given sized pseudo-cell molecules having compositions of $3CaO{\cdot}2SiO_2{\cdot}2H_2O$ are replaced by an equal number of molecules of composition $3.30CaO{\cdot}2SiO_2{\cdot}2.30H_2O$, the density must go up markedly. As the example shows, such molecule for molecule substitution does not happen.

The *a* and *b* dimensions of the pseudo-cell show a very slight shrinkage with decreasing water content [22]; but the change is so slight that for most purposes these dimensions can be considered constant. The *c* dimension, i.e., the distance between layers, shows a considerable variation, which will be discussed later. However, this alone cannot account for the constant density.

3. An ingenious hypothesis for the explanation of the constancy of density was advanced by Taylor and Howison. They suggest that as the CaO/SiO_2 ratio increases, calcium replaces silicon in the lattice. The "bridging" SiO_4 tetrahedra, which are not attached to the central CaO_2 sheet, are gradually removed or, more correctly, only SiO_2 is removed because two of the oxygen ions in each of the tetrahedra are common to adjacent groups. The removal of SiO_2 breaks the metasilicate chain. A calcium ion then enters the lattice, but not directly into the place of SiO_2, i.e., not into the layer, but between layers. Because the calcium ion has two positive charges and SiO_2 is neutral, to preserve charge balance, two hydrogen ions must also be removed. The overall replacement is SiO_2H_2 by Ca. Such a replacement would have a relatively small effect on the pseudo-cell weight, as table 2 shows.

In addition, some other features of the system would also be explained.

TABLE 2. *Replacement of* SiO_2H_2 *by* Ca

Pseudo-cell contents	$CaO:SiO_2:H_2O$	Pseudo-cell weight
I. $Ca_4Si_6O_{18}{\cdot}CaO_4H_{10}$	0.83:1:0.83	730
II. $Ca_4Si_{4.5}O_{15}{\cdot}Ca_{2.5}O_4H_7$	1.44:1:0.78	697
III. $Ca_4Si_4O_{14}{\cdot}Ca_3O_4H_6$	1.75:1:0.75	687

(a) The upper limit of the CaO/SiO_2 ratio would be 1.75, corresponding to the removal of all bridging tetrahedra. This is in complete agreement with findings in this laboratory. The highest-lime tobermorite, obtained in the paste hydration of β-C_2S, had a ratio of 1.75, as shown in table 1. The higher ratios of Funk [30] and van Bemst [28] were discussed earlier.

(b) The rate of equilibration between tobermorites and calcium hydroxide solutions is very slow. If increasing the lime content would involve merely uptake of lime between the layers, one would not expect such slow equilibration. However, according to the hypothesis, increasing the lime content would involve removal of SiO_2 from the layers, which may well be very slow.

Taylor and Howison realized that their hypothesis was probably an over-simplification of a very complex problem. This is true, as will be seen shortly. Nevertheless, the present authors believe that basically, though not in detail, the hypothesis of Taylor and Howison is correct. It is hard to visualize any other explanation for the constancy of density.

In several aspects, the hypothesis is not borne out by certain experimental findings.

(a) Taylor and Howison point out that the above described replacement would lead to gradual decrease in the crystallinity of the tobermorites. No such decrease was found by Grudemo [32] for synthetic tobermorites of ratios 0.98 to 1.36, nor in this laboratory for tobermorites of ratios 0.97 to 1.44. At least, as far as the layer spacings (*h k 0*) are concerned, the number, location and sharpness of the lines remains practically unchanged. There appears to occur, however, a sharp decrease in degree of crystallinity of the (*h k 0*) spacings around the ratio 1.5, which is associated with a change in morphology. From a ratio of 1.5 to 1.75 the morphology and the degree of crystallinity remain again constant. This will be further discussed later.

(b) The water contents indicated in table 2 for formulas II and III are much too low. For example, if 80 percent of the bridging tetrahedra would be removed, the tobermorite would have the formula $Ca_3Si_2O_7{\cdot}1.55H_2O$, which agrees with the formula in eqs (3) and (4), except for water.

The situation would be improved, if SiO_2H_2 were replaced not by Ca alone, but by Ca plus a water molecule. In this case, the formula of the above tobermorite would be $Ca_3Si_2O_7{\cdot}3.15\ H_2O$—close to that indicated by eq (3). There would be two other advantages in this addition to the hypothesis.

(1) The pseudo-cell weight would remain more nearly constant. The tobermorite obtained by 80 percent removal of the bridging tetrahedra would have a pseudo-cell weight of 724, and that obtained by 100 percent removal (formula III in table 2) would have a weight of 722. Such a high degree of constancy of density is indicated by the results obtained in this laboratory and cited earlier.

(2) Grudemo [32] showed that gradual increase in the CaO/SiO_2 ratio from 0.98 to 1.56 resulted in a gradual decrease in the *c* spacing from about 13.7 to about 10.4 A. Apparently, the calcium ions pull the layers closer to each other. Taylor [22], as well as many others, showed that increasing the water content resulted in an increase in the *c* spacing, ranging from 9.3 to more than 14 A. Brunauer, Kantro and, Copeland [14] pointed out that the decrease in *c* spacing caused by addition of a molecule of CaO is approximately equal to the increase in *c* spacing caused by the addition of a molecule of H_2O. It follows, therefore, that to keep the volume of the pseudo-cell constant, the addition of a calcium ion should be balanced by the addition of a water molecule.

Further evidence along these lines will be presented later.

(c) The removal of bridging tetrahedra would lead to a breaking up of the long metasilicate chains. This may be regarded as a partial depolymerization. When all bridging tetrahedra are removed, at $CaO/SiO_2=1.75$, all remaining silicon tetrahedra would be in the form of "dimers"; i.e., two tetrahedra joined at one corner (sharing one oxygen ion).

As a matter of fact, Greenberg and Pressler [40] found evidence of increasing depolymerization with increasing CaO/SiO_2 ratio. However, the depolymerization was far greater than that indicated by the Taylor-Howison hypothesis.

Various investigators [41] showed that most ortho and pyrosilicates readily dissolve in dilute HCl, whereas most chain, layer and three-dimensional structures of connected SiO_4 tetrahedra do not. Alexander [42] showed that one can distinguish between monomers, dimers and higher polymers in the solution by means of the rate of reaction of these species with molybdic acid. Using these techniques, Greenberg and Pressler obtained the results shown in table 3. In their experiments, 0.5 g. samples were dissolved in 200 ml. of 0.5 N hydrochloric acid at 0 °C. The percentage dissolved in 2 minutes is shown in column 2. The filtered solution was brought in contact with the molybdic acid reagent, and the extent of reaction in 2, 10, and 60 minutes is shown in columns 3, 4 and 5.

TABLE 3. *Solution properties of hydrated silicates*

1 Preparation	2 Percentage dissolved	3 Molybdic acid reaction 2 Min.	4 10 Min.	5 60 Min.
$Na_2H_2SiO_4·8H_2O$	100	69.2	79.2	100
Hydrated C_3S	100	57.9	82.3	97.3
Tobermorite, 1.5	85.5	42.2	64.1	83.6
Tobermorite, 1.0	72.0	15.0	27.9	55.0
Tobermorite, 0.8	37.8	9.6	18.9	33.6
β-wollastonite	12.4	4.3	6.6	10.9

First of all, it is clear that hydrated C_3S behaves very much like $Na_2H_2SiO_4·8H_2O$. Thilo [43] showed that the latter is an orthosilicate. At the other end, it is also clear that β-wollastonite behaves very differently, as one would expect for a metasilicate chain. The three tobermorites of table 3 were prepared by the reaction of calcium hydroxide and silica gel at 85 °C for 3 hr, with initial CaO/SiO_2 ratios of 1.5, 1.0, and 0.8. The solution behavior of these three tobermorites is intermediate between the two extremes.

It appears, therefore, that increasing depolymerization occurs with increasing CaO/SiO_2 ratio. The tobermorite of CaO/SiO_2 ratio 1.5, obtained in the hydration of C_3S, contains largely or wholly monomers, i.e., independent SiO_4 tetrahedra.

4. Whatever the genealogy of tobermorites may be, the tobermorite obtained in the room temperature hydration of C_3S or C_2S appears to contain no chains of SiO_3 but chains of SiO_4, very much like that postulated by Bernal [29]. The tetrahedra, very probably, are joined by hydrogen bonds. The hydrate itself is an orthosilicate, just as C_3S and C_2S are orthosilicates.

This particular tobermorite was called in all publications from this laboratory simply "tobermorite". Henceforth, to distinguish it from all other tobermorites, it will be called tobermorite (*G*). The name tobermorite gel was suggested by Taylor in private communication.

Tobermorite (*G*) is a very poorly crystallized hydration product. The natural mineral exhibits dozens of X-ray diffraction lines, as do the synthetic tobermorites prepared hydrothermally [24, 44]. Tobermorites, synthesized in suspensions at room temperature, show about a dozen diffraction lines. However, the tobermorites obtained in the room temperature hydration of C_3S and C_2S in this laboratory show only three diffraction lines. There is a very strong and very broad line with a maximum at 3.05 A, and two much weaker broad lines at 2.79 and 1.82 A. These spacings were obtained on samples dried at a vapor pressure of 5×10^{-4} mm. Heller and Taylor [44] found that these spacings have indices of (110), (200), and (020), respectively, and they reported the same spacings at 3.07, 2.81, and 1.83 A, on less strongly dried samples.

All three lines are (*h k 0*) spacings, i.e., spacings within the layer. Taylor [22] pointed out that drying results in a slight shrinkage of these spacings. The (020) spacing represents half the distance between Si atoms in the chain. Twice this distance, 3.64 A, is the *b* length of the orthorhombic pseudo-cell. Twice the (200) spacing, 5.59 A, is the *a* length of the pseudo-cell. The three lines in tobermorite (*G*) correspond to three of the strongest lines of all tobermorites.

Tobermorite (*G*) exhibits no basal spacing. In the first experiments performed in this laboratory, a paste-hydrated C_3S tobermorite sample, dried at 5×10^{-4} mm pressure, gave a *c* spacing of about 11 A and a density of 2.44 g/cc [12]. Never again was such a sample obtained. In dozens of preparations, obtained by hydration of C_3S and C_2S and dried at the same vapor pressure, the *c* spacing (002) was absent, and the average density was 2.86 g/cc [14].

Tobermorite (*G*), dried at 5×10^{-4} mm pressure, has the formula $Ca_3Si_2O_7 \cdot 2H_2O$. From the *a* and *b* lengths of the pseudo-cell and from the density, the *c* length can be obtained, and it is 9.3 A. Numerous investigators found this value for the *c* spacing of very strongly dried tobermorites; it appears to be the distance of closest approach of two layers.

Tobermorite (*G*), dried at 8×10^{-3} mm pressure, has the formula $Ca_3Si_2O_7 \cdot 2.8H_2O$. Calculation, using the density of 2.73 g/cc, leads to a layer-to-layer distance of 10.3 A. The extrapolated density of $Ca_3Si_2O_7 \cdot 3H_2O$ is 2.71 g/cc [15].

Even the three broad diffraction lines of tobermorite (*G*) do not represent the lowest limit of the degree of crystallinity of tobermorites. A tobermorite exhibiting a single broad diffraction band will be discussed in connection with the ball-mill hydration of C_3S.

5. It is seen in figure 1 that Taylor and Kalousek obtained tobermorites of different CaO/SiO_2 ratios at the same lime concentration in the solution. In earlier investigations, even greater variations were obtained [33]. To be sure, equilibrium is very slowly established for reasons discussed before. However, some investigators did approach equilibrium from both the high- and the low-lime directions, and still obtained somewhat different curves.

There are two factors that may cause such variations. One of these is difference in the structure and the degree of crystallinity of the tobermorite obtained in the reaction. For a given CaO/SiO_2 ratio, every recent investigator reports a somewhat different X-ray diffraction pattern; and even the same investigator reports somewhat different patterns for different methods of preparation. The formula SiO_2 does not define a chemical compound; quartz, crystobalite, and amorphous silicas have different free-energy contents and solubilities. Just so, the variations in the crystal structure of a tobermorite of a given CaO/SiO_2 ratio may cause variations in the free energy content and in solubility. Thus, it may happen, as figure 1 shows, that Taylor's tobermorite, with a ratio of 1.1, is in equilibrium with a calcium ion concentration of about 3 millimoles per liter, whereas Kalousek's is in equilibrium with a concentration of about 6 millimoles per liter.

A second factor is variation in the specific surface area of tobermorite. Very few investigators have measured surface areas; nevertheless, it is clear that considerable variations may be obtained. Two tobermorites, having the same CaO/SiO_2 ratio and the same crystal structure, would have different free energy contents and solubilities if they have different specific surface areas.

Water of Hydration in Tobermorites

1. When tobermorite (*G*), obtained in the hydration of C_3S or C_2S is (*D*)-dried, the CaO/SiO_2 ratio is 1.5 and the H_2O/SiO_2 ratio is slightly greater than 1.0. Part of the excess, as was stated before, is probably adsorbed water, held firmly on the most active part of the surface.

In agreement with Bernal's views [29], tobermorite (*G*) is an orthosilicate, with two hydrogens on two of the oxygen ions in the SiO_4 tetrahedra. According to his structural formula, $Ca_2[SiO_2(OH)_2]_2[Ca(OH)_2]$, two of the water molecules, in hydroxylic forms, are in the tobermorite layers—or in the $H_2SiO_4^{=}$ chains, constituting parts of the layers. The third water molecule, likewise in hydroxylic form, is between the layers.

On the basis of experiments performed in this laboratory, it appears more likely that the interlayer water is molecular; so Bernal's formula would be modified to $Ca_2[SiO_2(OH)_2]_2 \cdot CaO \cdot H_2O$. With drying of increasing severity, the interlayer water is lost continuously. At (*P*)-drying, the formula is approximately $Ca_2[SiO_2(OH)_2]_2 \cdot CaO \cdot \frac{1}{2}H_2O$, at (*D*)-drying, $Ca_2[SiO_2(OH)_2]_2CaO$. The density indicates that at (*P*)-drying the *c* spacing (interlayer distance) is 10.3 A, at (*D*)-drying 9.3 A. At (*D*)-drying all the interlayer water is removed, and the minimum distance between the layers is attained.

It was found in this laboratory [14] that tobermorite dried to this stage, even after soaking in water for a day, did not swell. Megaw and Kelsey [39] proposed that when a tobermorite having a *c* spacing of 11.3 A was dehydrated to a stage with a *c* spacing of 9.6 A, the metasilicate chains in one layer fitted into the grooves between those in the next adjacent layer. This would explain the strong attraction between adjacent layers, leading to the exclusion of water. Taylor and Howison [31] suggested that the packing would be similar in hydrates having *c* spacings of 10.3 A. Tobermorite (*G*), subjected to (*P*)-drying, gives a calculated *c*-spacing of 10.3 A. Upon soaking in water, it shows some swelling, but the swelling is very slow and very slight.

After (*D*)-drying, a tobermorite (*G*) molecule contains only the hydroxylic water attached to the SiO_4 tetrahedra in the layers, with the slight excess mentioned before. The water in the layers is far more firmly held than that between the layers. A tobermorite (*G*) preparation, dried over P_2O_5 for four weeks to constant weight, still had an H_2O/SiO_2 ratio of 0.95. Thus, at a vapor pressure of the order of 1/1000 of that used in (*D*)-drying, very little of the layer water was lost. The difference between 0.95 and 1.00 is only slightly greater than the experimental error.

It will be shown that tobermorite (*G*) is very finely divided in the *c* direction. This dimension of the crystallites—if one can call such poorly crystallized particles crystallites—is colloidal; it even verges on the molecular. On the other hand, the dimension of the particles in the *b* direction, i.e., along the silicate chains, is quite large, of the order of a micron or several microns. Thus, speaking with some license, tobermorite (*G*) is a colloid in the *c* direction but not a colloid in the *b* direction. It is interesting to note that interlayer water is lost continuously, as water is usually lost by colloids, but the water content of the orthosilicate chains remains almost constant over a wide range of vapor pressures.

2. It was shown earlier that in high-lime tobermorites the addition of lime to the structure always resulted in addition of water to the structure, in the approximate molar proportion of 1:1. If the modification of the Taylor-Howison hypothesis proposed in this paper is correct, the same should be valid for low-lime tobermorites as well. Experiments performed in this laboratory indicate that this is what happens. The results are shown in table 4.

TABLE 4. CaO/SiO_2 *and* H_2O/SiO_2 *molar ratios of low-lime tobermorites*

1	2	3	4	5	6	7	8
Preparation	Starting CaO/SiO_2	Reaction time (days)	Temp.	CaO/SiO_2	H_2O/SiO_2	ΔCaO	ΔH_2O
			°*C*				
F-29X	1.0	88	50	0.98	0.65	--------	--------
F-18X	1.0	165	23	.99	.67	0.01	0.02
F-20X	1.5	254	23	1.25	.90	.27	.25
F-27X	1.5	91	50	1.28	.93	.30	.28
F-23X	2.0	292	23	1.38	1.00	.40	.35
F-22X	2.0	75	50	1.44	1.07	.46	.42

Very pure lime and silica were used, in ratios 1.0, 1.5, and 2.0, and the reactions were carried out at 23 and 50 °C, for various lengths of time. One-half of the preparations were (*D*)-dried, the other (*P*)-dried. The results are given only for the (*D*)-dried samples; essentially the same results were obtained for the others. Ignition loss, CO_2, free SiO_2, and free CaO were determined for each preparation; thus, the ratios in columns 5 and 6 are quite accurate. The Δ values in the last two columns were obtained by comparison with F–29X which had the lowest CaO/SiO_2 and H_2O/SiO_2 ratios.

In contrast with these results, Taylor and Howison [31], confirming earlier work of Taylor [45], came to the conclusion that low-lime tobermorites, dried around 100 °C, have H_2O/SiO_2 ratios substantially independent of the CaO/SiO_2 ratios. Drying around 100 °C is not too different from (*D*)-drying. The present authors have no explanation for the very different results beyond what they stated earlier. The tobermorite system is a complicated one, to say the least. Differences in starting materials and experimental procedures lead to wide differences in the properties of the products. Much further work will be needed before this system will be, not fully, but adequately understood.

Morphology of Tobermorites

1. The first extensive electron optical studies of tobermorites prepared at room temperatures have been published by Grudemo [32]. The low-lime tobermorites consist predominantly of very thin crinkled foils; some of which are so thin that Grudemo estimated them to be of unit cell thickness. Some of these foils or sheets appear to roll, partially or completely, into tubes or fibers. Kalousek and Prebus [20] obtained similar electron micrographs and came to similar conclusions. Gaze and Robertson [46] obtained tobermorite foils from hydrated portland cement, and they estimated that these foils were of the order of two molecules in thickness.

At lime saturation, the micrographs show predominantly tubes or fibers. Grudemo states, "In saturated and supersaturated lime solutions, a fibrous or needle-like growth of the crystals seems to be promoted, probably caused by a degeneration of the sheets into lath-like structures and by twisting and rolling of the crystal sheets."

Figure 2 shows electron micrographs of hydrated C_3S and C_2S preparations, obtained by Copeland and Schulz in this laboratory. Figures 2a to 2c show tobermorite (*G*), as well as occasional $Ca(OH)_2$ crystals, obtained in the paste-hydration of C_3S, and figures 2d to 2f, those obtained in the paste-hydration of β-C_2S. The pastes were dispersed by an ultrasonic generator, using 1,1,1 trichloro-ethane as the liquid. Almost complete dispersion was always obtained, and tobermorite (*G*) always appeared as fibers. The undispersed part was less than 10 percent, and it is probable that most of this also consists of fibers.

The micrographs give clear indications that the fibers are rolled-up sheets. Although in the photographs much of the distinctness of the original micrographs is lost, still enough is seen to show the correctness of this conclusion. Many dozens of micrographs show the rolling of the sheets, in different stages. The fibers are long and straight, most of them longer than 1μ. The magnifications are shown in the figure; the length of the line is 1μ.

It was stated earlier that the X-ray diffraction pattern of tobermorite (*G*) consists of only three broad (*h k O*) lines and no (*O O l*) line. It seems reasonable to assume that the rolling of the sheets into fibers causes the great change in the degree of crystallinity of the substance. At any rate, the drastic change in morphology and in degree of crystallinity appear to be simultaneous.

2. Figures 2g and 2h show electron micrographs of C_2S hydrated in a polyethylene bottle rotated on a wheel for more than two years (*D*–69 of table 1). It will be noted that the particles look quite different from those obtained in the paste-hydration of C_3S and C_2S; instead of straight fibers, they are cigar-shaped. Again, almost all of the tobermorite was dispersed by ultrasonic treatment, and all dispersed material consisted of such cigar-shaped particles. The morphology of

FIGURE 2a. *Electron micrograph of hydration products of paste-hydrated* C_3S.

The length of the line in figures 2a to 2h is 1 micron.

FIGURE 2b. *Electron micrograph of hydration products of paste-hydrated* C_3S.

FIGURE 2c. *Electron micrograph of hydration products of paste-hydrated* C_3S.

FIGURE 2d. *Electron micrograph of hydration products of paste-hydrated* C_2S.

FIGURE 2e. *Electron micrograph of hydration products of paste-hydrated* C_2S.

FIGURE 2f. *Electron micrograph of hydration products of paste-hydrated* C_2S.

FIGURE 2g. *Electron micrograph of hydration products of bottle-hydrated* C_2S.

FIGURE 2h. *Electron micrograph of hydration products of bottle-hydrated* C_2S.

this preparation is identical with that of Taylor's $C_2SH(II)$, published by Grudemo [32].

As a matter of fact, the material is identical with Taylor's $C_2SH(II)$ in, probably, all respects. It is far better crystallized than the tobermorites obtained in the paste hydration of C_3S and C_2S; and, in fact, its X-ray pattern is the same as that of Taylor's $C_2SH(II)$ [22]. Although initially Taylor believed that the CaO/SiO_2 ratio in this hydrate was close to 2, later he estimated it to be 1.75; and, as table 1 shows, the hydrate in *D*–69 has a ratio of 1.73. The water content of the hydrate in *D*–69 is higher than that of similarly dried high-lime tobermorites.

Preparation *D*–40, in table 1, presents an interesting transition between tobermorite (*G*) and $C_2SH(II)$. The morphology of the hydrate in *D*–40 is the same as in *D*–69; nothing but cigar-shaped particles is in evidence. The composition, however, is the same as that of tobermorite (*G*), both with respect to CaO/SiO_2 ratio and H_2O/SiO_2 ratio. The X-ray diffraction pattern cannot be easily determined because of the 27.5 percent unhydrated C_2S in *D*–40; however, to the extent that it can be deciphered, it seems to be intermediate between that of tobermorite (*G*) and $C_2SH(II)$. The *c*-spacing of the hydrate in *D*–69 exhibits a strong reflection at 9.9 A, in agreement with Taylor's value of 10.0 A (22) for $C_2SH(II)$. Tobermorite (*G*) shows no *c*-spacing. The hydrate in *D*–40 gives such a weak line for the *c*-spacing that it is not quite certain that the line is there.

3. Hydrated C_3S and C_2S set and harden very much like hydrated portland cements; and, doubtless, the formation of tobermorite (*G*) is predominantly responsible for the setting and hardening of portland cements. Bernal [29] pointed out that the fibrous character of tobermorite presents a way for the reconciliation of the old Le Chatelier-Michaelis controversy on the nature of the setting of cement.

Le Chatelier emphasized the fibrous nature of the hydration products; Michaelis emphasized the gel-like characteristics. Bernal states, "We have long known from electron microscope results and the polymer systems that most of the things called gels were, in fact, very fine fibrous crystals; the characteristic gel of collagen (gelatin jelly) is simply a network of fine fibers holding water in between them . . . . One of the most important things to establish was that calcium silicate hydrate did form such a network . . .".

Bernal, Jeffery, and Taylor [7] state, "The rapid growth of long fibers might well lead to the production of interlocking crystals, similar in principle to those formed in gypsum plasters, but on a very much smaller scale."

The interlocking of tobermorite fibers may well explain the adhesion of the fibers to each other, but the adhesion of these fibers to the large $Ca(OH)_2$ crystals in C_3S, C_2S, and portland cement pastes, and to the much larger aggregate pieces in concrete probably requires a more detailed and more basic explanation. Nevertheless, the present authors do not doubt that Bernal's ideas constitute a good beginning toward the understanding of the strength of hardened paste and concrete.

4. Strength and dimensional stability are the two most important engineering properties of concrete, and both of these properties are probably strongly dependent on the properties of tobermorite.

Hardened portland cement paste swells when it imbibes water and shrinks when water leaves. Taylor and Bessey [47] showed that low-lime tobermorites can be hydrated and dehydrated reversibly up to about 100 °C, with a change in the interlayer spacing. Such reversible change in the interlayer spacing may occur in tobermorite (*G*) as well, though it cannot be demonstrated by X-rays since the *c*-spacing is absent.

The fibers of tobermorite are apparently rolled-up foils or sheets, and the sheet has a thickness of two or three layers, as will be shown later. Water can enter between these layers, with the result of swelling the fiber. Such a mechanism of swelling has been suggested by Bernal [29].

There are two other ways in which tobermorite may swell upon entry of water. Water may not only enter between the layers constituting a sheet, but it may also be adsorbed on the external surfaces of the sheet itself. Because the sheet is rolled up into a fiber, adsorption would also lead to swelling of the fiber. The third mechanism is entry of water into the spaces where fibers make contacts with each other, with the result of pushing the fibers away from each other. This mechanism would not involve swelling of the fibers.

It is quite likely that all three mechanisms contribute to the swelling of tobermorite, but much painstaking work must be performed before the relative importance of these mechanisms can be assessed.

Specific Surface Area and Particle Dimensions

1. It was stated earlier in this paper that tobermorites produced at room temperature were colloidal substances, with large specific surface areas. This large specific surface is one of the most important properties of tobermorite.

Powers and Brownyard [48] were the first who measured the specific surface areas and porosities of hardened portland cement pastes, and they were able to deduce highly significant correlations between these basic physical properties and such vitally important engineering properties as compressive strength, dimensional changes caused by changes in water content, permeability to water, and freezing and thawing of water in the pores. This work, as well as subsequent work performed in this laboratory along similar lines, is discussed by Powers in his review paper contributed to this symposium.

It was found in this laboratory that about 80 percent of the specific surface area of hardened portland cement paste is contributed by tobermorite. Although the other hydration products contribute the other 20 percent of the surface, it is clear that the surface dependent properties of hardened portland cement pastes are determined predominantly by the tobermorite surface.

Bogue and Lerch [49] showed that the compressive strengths of hardened C_3S and C_2S pastes increased progressively with increasing extent of hydration, as will be discussed later. The strength of hardened portland cement paste is about the same as that of hardened C_3S and C_2S pastes, and the strength of all three is essentially the strength of tobermorite.

Unquestionably, the other hydration products of portland cement make important contributions to the physical, chemical, and engineering properties of hardened portland cement paste. The present authors believe that it is also unquestionable that the contributions of none of the other hydration products, nor of all of them put together, equal in importance the contributions of tobermorite.

2. All investigators who published specific surface area values for tobermorites used the BET method [50]. Greenberg [23] used nitrogen adsorption, but nitrogen surface values for tobermorites are unreliable; in the great majority of instances they are too low. The incorrectness of the nitrogen surfaces was demonstrated by Brunauer, Kantro, and Weise [51], who showed that the nitrogen values frequently indicated negative surface energies, which is absurd. Apparently, the aggregation of the tobermorite sheets, or their rolling into fibers, or the aggregation of the fibers, or all these factors together create spaces inaccessible to nitrogen molecules, though accessible to water molecules.

Kalousek [52] used both nitrogen and water vapor for surface area determination, but he believed that nitrogen measured the external surfaces correctly. He attributed the difference between the two to the ability of water and the inability of nitrogen to penetrate between the layers of tobermorites. Originally, this opinion was shared by investigators in this laboratory [12], but later work necessitated the abandoning of this view [14]. As was stated earlier, strongly dried tobermorite (*G*) does not admit water between its layers even when soaked in water. In the adsorption experiments, the maximum relative humidity used was 33 percent.

The nitrogen surface values obtained in this laboratory ranged from 21 percent to 100 percent of the water surface values. The important fact is that the upper limit of the nitrogen surface values enables one to calculate the area occupied by an adsorbed water molecule on the surface of tobermorite.

The BET method gives a value for V_m, the weight of nitrogen or water that covers the surface with a complete adsorbed monolayer. In order to calculate the specific surface, one must know the area covered by a single adsorbed molecule. One can calculate the molecular area of nitrogen from the density of the liquid at −195.8 °C, the temperature at which the adsorption measurements are usually carried out. That the value thus obtained, 16.2 A^2, is really the correct area of an adsorbed nitrogen molecule has been confirmed by a great variety of experiments, among which the earliest, and still most impressive, is that of Harkins and Jura [53].

The molecular area of 16.2 A^2 for nitrogen has been adopted the world over, and because of the inert nature of nitrogen, the area applies to all adsorbents. The situation is not so simple, however, for water. The area calculated from the liquid density is 10.6 A^2, but this value cannot be applied to all adsorbents. Because of their strong dipole moments, the water molecules are oriented on ionic surfaces, with the result that the nature and the configuration of the ions of the surface influence the packing of the adsorbed molecules.

Naturally, it is easy to calibrate the water against nitrogen, when the nitrogen surface gives a correct area. Although this is the case for the great majority of adsorbent-adsorbate systems, it is not the case for tobermorites, as was shown above. Nevertheless, the upper limit of the nitrogen surface values can be used for such purpose. Using the largest nitrogen V_m value obtained for any tobermorite preparation, one calculates a molecular area of 11.4 A^2 for water adsorbed on the tobermorite surface.

There are three other comparisons that confirm this value.

(a) The molecular area of water adsorbed on a $Ca(OH)_2$ surface is 10.3 A^2 [54]; that adsorbed on a hydrous amorphous silica (silanol) surface is 12.5 A^2 [55]. The average of the two is 11.4 A^2. The surface of tobermorite is a sort of "chemical mixture" of the surfaces of the two others.

(b) The ball-mill hydration of C_3S produces the calcium silicate hydrate afwillite [13], as was stated before. Afwillite is a well crystallized product, with a specific surface area of about 16 m^2/g. Nitrogen and water give the same surface values for all afwillite preparations, if the molecular area of water is taken to be 11.4 A^2.

(c) Copeland determined the specific surface area of tobermorite by means of low angle X-ray scattering—entirely independently of adsorption. The water adsorption surface agrees with the value of Copeland, if the molecular area of water is taken to be 11.1 A^2. An uncertainty of 3 percent may arise in either set of experiments.

In the following discussion, all specific surface area values are based on water vapor adsorption, and the molecular area of water is taken to be 11.4 A^2.

3. Tobermorite (*G*), obtained in the hydration of C_3S and C_2S, consists of fibers, which are very probably rolled-up sheets. If the rolling of the sheets does not create spaces to which water cannot penetrate, the area measured by water adsorption for the fibers should be the same as that of the sheets prior to rolling. This area could be calculated from crystal structure data, if the thickness of the sheets were known.

Electron micrographs indicate that the sheets are very thin—of the order of a few layers, at most. Because the thickness is very small compared to the two other dimensions of the sheet, practically all of the surface area resides in the two sides of the sheet. The *a* and *b* dimensions of the orthorhombic pseudo-cell of tobermorite (*G*) are 5.59 and 3.64 A, respectively, when the composition is $Ca_3Si_2O_7 \cdot 2H_2O$ (in the (*D*)-dried state). If one places one molecule into the pseudo-cell and assumes that the sheet is one layer thick, the specific surface area is 755 m^2/g.

If the sheet is two layers thick, the specific surface area is 377 m^2/g. The largest specific surface area measured for any tobermorite (*G*) preparation made in this laboratory was 376 m^2/g [14]. Naturally, the almost exact agreement is somewhat fortuitous. Neglecting the edge areas makes the calculated specific surface a few percent less than the true surface. On the other hand, aggregation of the fibers, with possible bonding at the contact areas, may reduce the surface accessible to water molecules by a few percent. A third, and also small, factor will be considered shortly.

If the thickness of the sheet is three layers, the calculated specific surface, again neglecting edge areas, is 252 m^2/g. The smallest surface measured for any tobermorite (*G*) in this laboratory was 244 m^2/g [51]. Dozens of tobermorite (*G*) preparations gave specific surface area values between 244 and 376 m^2/g. Thus, the tobermorite (*G*) sheets always, or nearly always, consist of two or three layers. It was found in this laboratory that this conclusion is valid also for the tobermorite (*G*) in hydrated portland cements.

It is interesting to compare these results with those obtained for the low-lime tobermorites shown in table 4. Preparations F–29X, F–18X, F–27X, and F–22X had specific surface areas of 378, 249, 241, and 241 m^2/g, respectively. Apparently, the tobermorite sheets of the first one consisted of two layers, those of the last three, of three layers. However, the specific surface areas of F–20X and F–23X were 135 and 135 m^2/g, respectively, indicating sheets that are about 6 layers thick.

In contrast with tobermorite (*G*), each of the six preparations shows a *c*-spacing in the X-ray patterns. The lines are very broad for the first four preparations, but quite sharp for the last two. Apparently, 6 layers are sufficient to give a sharp diffraction line.

4. The above surface areas were measured on (*D*)-dried preparations. The surface areas obtained for (*P*)-dried preparations were always lower. The reason for this is that (*P*)-drying leaves a considerable amount of adsorbed water on the surface. If it is assumed that (*D*)-drying removes all adsorbed water, the amount of adsorbed water in (*P*)-dried samples can be calculated. Such a calculation leads to the result, reported earlier, that in $Ca_3Si_2O_7 \cdot 2.8H_2O$ about 2.5 H_2O is water of hydration and 0.3 H_2O is adsorbed water.

It was shown earlier that the H_2O/SiO_2 ratio in (*D*)-dried preparations is always greater than 1.0. The excess may be in part interlayer water not completely removed, and in part adsorbed water. It is quite likely that there is some adsorbed water in tobermorite (*G*) after (*D*)-drying, but judging from the amount adsorbed at (*P*)-drying, it must be small. Probably not more than 2 or 3 percent of the surface area is covered with water after (*D*)-drying.

This adsorbed water would make the specific surface areas determined by water vapor adsorption too small by a percent or two. It is clear that all three factors neglected in the basic calculations, preadsorption of water, adsorption on edge areas, and lack of adsorption on contact areas, are small, and they partly compensate for each other.

5. From the data given so far, certain conclusions can be drawn for the average dimensions of the tobermorite (*G*) sheets. If one calls the length of the average sized sheet in the direction of the silicate chains *B*, the length perpendicular to this *A*, and the thickness of the sheet *t*, the surface area per unit volume is given by

$$S=\frac{2(AB+At+Bt)}{ABt}. \tag{5}$$

S is the product of the specific surface area and the density, and *t* is about 20 A for the two-layer sheets and 30 A for the three layer sheets.

Solving for *B*, one obtains

$$B=\frac{At}{(S/2)At-(A+t)}. \tag{6}$$

It follows from eq (6) that

$$(S/2)At>A+t \tag{7}$$

and the lowest limit of *A* is given by

$$(S/2)At=A+t. \tag{8}$$

Because the fibers are rolled-up sheets, the average length of the fibers seen in electron micrographs gives the *B* dimension of the sheet. However, nothing can be said about the *A* dimension of the sheet on the basis of electron micrographs. Calculations based on eq (8) show that the *A* dimension of the average sheet cannot be less than 360 A for the two-layer tobermorite (*G*) and 515 A for the three-layer tobermorite (*G*).

If the average length of the fibers is 1 μ, the *A* dimension is 390 A for the two-layer sheet and 560 A for the three-layer sheet. If it is greater than 1 μ, as the electron micrographs seem to indicate, the *A* dimension is between 360 and 390 A for the two-layer sheets, and between 515 and 560 A for the three-layer sheets.

It can be seen from the above considerations that specific surface area, combined with other information, leads to reasonably good estimates of all three dimensions of the average tobermorite (*G*) particle.

Other Properties of Tobermorites

1. A most useful collection of X-ray powder data, as well as of a number of other properties of tobermorites, has been published by Heller and Taylor [56].

Extensive data on index of refraction are found in the papers of Taylor and Howison [31, 57]. The average index of refraction of tobermorite (*G*), obtained in the paste hydration of C_3S and C_2S, was 1.56 for each. Dr. L. S. Brown of this laboratory made the measurements.

2. Kalousek and Roy [58] and Kalousek and Prebus [20] reported infrared absorption data for tobermorites. Hydrothermally prepared and well-crystallized tobermorite absorbs infrared radiation at 2.9 and 6.2 μ; low-lime tobermorites of CaO/SiO_2 ratios 0.8 to 1.33 absorb at 2.9, 6.2, and 6.8 μ; and poorly crystallized high-lime tobermorites, with ratios 1.5 and higher, absorb at 2.9 and 6.8 to 7.0 μ. In addition, a broad band between 9 and 11 μ was present in all preparations. The 2.9 μ band was attributed to hydroxylic water, and the 6.2 μ band to molecular interlayer water.

In hydrated C_3S, van Bemst [28] found only a very broad infrared absorption band between 8.2 and 11.2 μ. A dissertation by Hunt [59], which includes infrared investigations of the hydration products of C_3S and C_2S, was not available to the present authors at the time of writing this paper.

3. Kalousek [34] applied differential thermal analysis in the study of the system lime-silica-water. Somewhat later, van Bemst published DTA curves for the hydration products of C_3S [28]. The method of hydration he used was very similar to that called "bottle" hydration in this paper. He obtained two endothermic peaks for the calcium silicate hydrate, a larger one at 150° and a smaller one at 335 °C. S. Gordon determined a DTA curve for preparation D–69 of table 1, and the curve was quite similar to that of van Bemst, with the large peak near 200° and the smaller one at 330 °C. It was shown earlier in this paper that the hydrate is probably identical with Taylor's $C_2SH(II)$. In contrast with this, Gordon's curves for paste-hydrated C_2S and C_3S (C–51 and C–52 of table 1) do not show the peak at 335 °C.

McConnell [37] obtained two distinct endothermic peaks for a natural mineral tobermorite at 128° and 249 °C. He attributed these peaks to "unbound" or interlayer water and "bound" water. The two peaks seem to fuse into a broad hump at or near 200 °C for D–69, C–51, and C–52.

The DTA curve of McConnell showed an exothermic peak at 851 °C, corresponding to the conversion of tobermorite to wollastonite. Van Bemst found that this peak shifted gradually from 840° to 920 °C, as the CaO/SiO_2 ratio in the tobermorite increased. He reported that lower-lime tobermorites converted into wollastonite, but high-lime tobermorites converted into β-C_2S.

4. A thermobalance was used by Greenberg [23], van Bemst [28], Nicol [60], and others for quantitative determination of the hydration products of C_3S and C_2S.

The differential thermobalance developed by DeKeyser [61] was employed by van Bemst [28] for the study of hydrated C_3S. He obtained endothermic peaks for the tobermorite at 70°, 250°, 310°, and 390 °C. He stated, "Differential thermogravimetric analysis indicates much better than thermal analysis the less important phenomena of thermolysis."

The present authors believe that infrared absorption, differential thermal analysis, thermogravimetry, and differential thermogravimetry may prove to be very valuable tools for the investigation of the properties of this complex system. However, much work will have to be done before all the infrared bands, and all the DTA peaks and differential thermobalance peaks will be definitely interpreted.

Aqueous Phase

1. The aqueous phase in contact with tobermorites of varying molar CaO/SiO_2 ratios has been studied by many investigators [33]. One of the often quoted investigations is that of Flint and Wells [62], who made silica sols react with $Ca(OH)_2$ at 30 °C. They plotted the amount of dissolved silicic acid as a function of the calcium ion concentration in the solution, and obtained a curve with an ascending branch at low calcium ion concentrations, followed by a sharp descent within a narrow calcium concentration range, and ending with a slowly descending, almost linear, curve at higher calcium concentrations. They found that the solid species in contact with the solution along the first branch was hydrated silica with some sorbed $Ca(OH)_2$; along the rest of the curve it was a calcium silicate hydrate with increasing molar CaO/SiO_2 ratios.

The first branch of the curve can be explained as increasing solubility of silica with increasing *p*H. Alexander, Heston, and Iler [63] found that the solubility of silica gel in NaOH solutions increased with increasing *p*H. They attributed the effect to the formation of $H_3SiO_4^-$ ions above *p*H 7. The equilibria can be expressed by the equations

$$SiO_2(s)+nH_2O(l)=H_4SiO_4aq. \tag{9}$$

$$H_4SiO_4aq.+nH_2O(l)=H^+aq.+H_3SiO_4^-aq. \tag{10}$$

The equilibrium constants are

$$K_1=a_{H_4SiO_4} \tag{11}$$

$$K_2=\frac{a_{H^+}a_{H_3SiO_4^-}}{a_{H_4SiO_4}} \tag{12}$$

where a refers to the activity of each species. The product of eqs (11) and (12) is

$$K_1K_2=K_3=a_{H^+}a_{H_3SiO_4^-}. \qquad (13)$$

As the pH increases, a_{H^+} decreases, and $a_{H_3SiO_4^-}$ must increase. Thus the solubility of silica increases by the formation of $H_3SiO_4^-$ ions. Greenberg and Price [64] obtained similar results when $Ca(OH)_2$ was used instead of NaOH.

2. Along most of the descending branch of the Flint and Wells curve, the solution is in equilibrium with tobermorites of increasing CaO/SiO_2 ratios. Greenberg, Chang, and Anderson [65] investigated the solubilities of tobermorites of CaO/SiO_2 ratios 0.8, 1.0, 1.2, and 1.5, prepared at 85 °C by the reaction of $Ca(OH)_2$ and silica gel. The pH, the calcium ion, and the silicic acid concentration were determined for the solutions in contact with the tobermorites. Using the known dissociation constants of silicic acid and the Debye-Hückel limiting law, the activities of the calcium and $H_3SiO_4^-$ ions were calculated. For the tobermorite of ratio 0.8, the product

$$K_{sp_1}=a_{Ca^{++}}a^2_{H_3SiO_4^-} \qquad (14)$$

was found constant and equal to $10^{-8.5}$ at 25 °C. For the tobermorites of higher ratios the product was not constant.

3. The relative amounts of H_4SiO_4, $H_3SiO_4^-$ and $H_2SiO_4^=$ species vary with pH in sodium and calcium silicate solutions. As the pH increases, H_4SiO_4 diminishes and $H_3SiO_4^-$ increases. At still higher pH values, $H_2SiO_4^=$ ions begin to appear in the solution, and their concentration increases with increasing pH. At a pH of 10.8 the $H_3SiO_4^-$ ion concentration is at its maximum, the H_4SiO_4 concentration is already small, and the $H_2SiO_4^=$ concentration is yet small. Beyond this pH, the $H_3SiO_4^-$ concentration diminishes and the $H_2SiO_4^=$ concentration increases, until eventually the latter ion takes over almost completely.

Greenberg, Chang, and Anderson [65] found that for their tobermorites of ratios 1.0, 1.2 and 1.5 the product

$$K_{sp_2}=a_{Ca^{++}}a_{H_2SiO_4^=} \qquad (15)$$

was constant. Their values for pK_{sp_2} (the negative of the logarithm of K_{sp_2}) at 25 °C for two preparations with ratio 1.0 were 6.9 and 7.0, and for the preparations with ratios 1.2 and 1.5 were 6.9 and 7.0, respectively. The uncertainty in their pK_{sp_2} values was 0.1, so the solubilities of tobermorites with ratios ranging from 1.0 to 1.5 are the same within experimental error. Greenberg, Chang, and Anderson obtained a pK_{sp_2} value of 7.0 for a tobermorite of ratio 1.0 at 40 °C. Thus, the solubility is approximately the same in the temperature range 25 to 40 °C.

4. Greenberg and his coworkers added 1.25- and 5.0-g samples of C_3S to 1,000 ml of water at 30 °C, and the mixtures were stirred. The K_{sp_2} values were determined as a function of reaction time. Initially, both samples indicated supersaturation with respect to tobermorite, but the supersaturation kept on decreasing. The 1.25-g sample gave a K_{sp_2} value of 10^{-7} after 20 hr. The 5-g sample reached a K_{sp_2} value of $10^{-6.9}$ after 200 minutes, and remained constant thereafter for the duration of the experiment (20 hr).

These experiments indicate that tobermorite (*G*) obtained in the hydration of C_3S, has the same solubility product, within the experimental error, as the synthetic low-lime tobermorites, with CaO/SiO_2 ratios 1.0 to 1.5.

It was noted that the solution in contact with the 5-g sample became supersaturated with respect to $Ca(OH)_2$ after 80 minutes of reaction time, and remained so for the duration of the experiment.

Energetics of the Hydration Process

Heats of Hydration of C_3S and β-C_2S

1. It is interesting that the first values for the heats of hydration of C_3S and β-C_2S were obtained by an indirect method. Woods, Steinour, and Starke [66] determined the heat evolved in the hydration of portland cements of different chemical compositions, and calculated by least squares analysis the heats assignable to the individual components. The values obtained were 136 cal/g for C_3S and 62 cal/g for C_2S. The cements were hydrated for one year.

Direct determinations were made by Lerch and Bogue [67]. They hydrated the compounds and obtained the values 120 and 62 cal/g for C_3S and C_2S, respectively. More recently, Verbeck and Foster [68], using the method of Woods, Steinour and Starke, obtained 117 and 53 cal/g for the heats of hydration of C_3S and C_2S, respectively. Their portland cements were hydrated for 6½ yr. The three sets of results are in reasonably good agreement, indicating that the heats of hydration of the two silicates in portland cements are approximately the same as the heats of hydration of the pure compounds.

Powers and Brownyard [48] pointed out that the calorimetrically determined heat of hydration of portland cement is a composite quantity. In the hydration process, a finely divided substance forms, called the "cement gel", and this gel adsorbs large amounts of water. The overall heat of hydration is the sum of the chemical heat of hydration and the heat of adsorption of water on the hydration products. Powers and Brownyard found that the heat of adsorption of water on two hydrated portland cements was about one-fourth of the overall heat of hydration.

All of the above heat determinations, as well as all others that will be reported in this paper, were made by a method proposed by Woods and Steinour [69]. Heats of solution of the unhydrated and the hydrated materials were measured in a calorimeter, and the heat of hydration was obtained as the difference.

All three sets of values given above for C_3S and C_2S are overall heats of hydration. Brunauer, Hayes, and Hass [2] determined the chemical heats of hydration by removing the adsorbed water from the hydration products prior to measuring their heats of solution. They did this by (*D*)-drying the preparations. The values obtained were 96.5 cal/g for the hydration of C_3S and 24.5 cal/g for C_2S. Lack of adequate knowledge of the system hampered these early determinations of the chemical heats of hydration. More accurate values are given in the present paper.

2. As a matter of fact, the overall heat of hydration of C_3S or C_2S is the sum of four terms, rather than two terms. For tobermorites of appreciable surface, the relation is

$$H_o = H_c - S + H_{H_2O} + H_{Ca(OH)_2} \qquad (16)$$

where H_o is the overall heat of hydration, H_c is the chemical heat of hydration when a tobermorite of negligible surface is produced in the reaction, S is the surface energy of tobermorite, H_{H_2O} is the heat of adsorption of water, and $H_{Ca(OH)_2}$ is the heat of adsorption of $Ca(OH)_2$. Because the adsorption of $Ca(OH)_2$ on tobermorite surfaces is small, the last term can be neglected. If the specific surface of a tobermorite is small, the last three terms on the right hand side can be neglected. If the specific surface of tobermorite is not small, the chemical heat of hydration is $H_c - S$.

The term S in eq (16) requires some elaboration. An atom, ion, or molecule in the surface layer of a substance has always greater energy than in the body of that substance. This excess energy is called surface energy. All solids and liquids have a part of their energies residing in their bodies, and a part residing in their surfaces. Ordinarily, substances have relatively small specific surface areas; consequently, the surface energy can be neglected. Only for colloids does surface energy constitute an appreciable fraction of the total energy.

The surface energy is usually expressed as ergs per cm^2 surface. The order of magnitude of the surface energy of a number of crystalline substances is 1,000 ergs/cm^2. If the specific surface area of a substance of this sort is 4 m^2/g, its surface energy is 1 cal/g. In most calorimetric work, the experimental error is far greater than 1 cal/g.

As was shown before, tobermorites prepared at room temperatures have large specific surfaces; so S can not be neglected. Furthermore, the specific surface areas are variable. The consequence of this is that the term "heat of hydration of C_3S" is indefinite, unless one specifies the surface area of the tobermorite (*G*) produced in the hydration.

The C_3S and C_2S used in this laboratory were very finely ground, with an average particle size of the order 10μ. Even so, the surfaces of C_3S and C_2S can be neglected without introducing an appreciable error. The specific surface area of tobermorite (*G*) is about 1,000 times greater than that of C_3S or C_2S. The surface area of the $Ca(OH)_2$ produced in the reaction can also be neglected. In the paste and the bottle hydration of C_3S and C_2S, $Ca(OH)_2$ separates out as large particles, some of which are even visible to the naked eye. Only in the ball-mill hydration of C_2S does $Ca(OH)_2$ acquire a sizable specific surface, but even there it contributes only about 2 percent of the surface of the hydration products [51].

Thus, in the hydration of the two calcium silicates, specification of the surface area of tobermorite is sufficient to define the energetics of the reaction. The specific surface area of tobermorite defines S and H_{H_2O} in eq (16).

In a reaction like that of silica gel with $Ca(OH)_2$, the situation is more complicated. Silica gels usually have even larger specific surface areas than tobermorites; so the specific surface area of the silica gel must also be specified.

3. The surface energy of tobermorite (*G*), with composition $Ca_3Si_2O_7 \cdot 2H_2O$, was determined by Brunauer, Kantro, and Weise [51], and it was found to be 386 ± 20 ergs/cm^2 at 23.5 °C. For a tobermorite of specific surface area of 300 m^2/g, the surface energy amounts to 27.7 cal/g. If one compares this with the heats of hydration of C_3S and C_2S given earlier, one realizes the magnitude of the surface energy contribution.

In earlier work in this laboratory, the surface energies of $Ca(OH)_2$ [54] and of hydrous amorphous silica [55] were found to be 1,180 and 129 ergs/cm^2, respectively. The surface energy of tobermorite (*G*) is very close to the geometric mean of these values. This was expected for two reasons: tobermorite (*G*) is chemically intermediate between $Ca(OH)_2$ and hydrous silica, and it is also intermediate structurally. The $Ca(OH)_2$ used in the experiments consisted of nearly perfect crystals, the hydrous silica was completely amorphous, and tobermorite (*G*) was very poorly crystallized.

In figure 3, the heat of solution of $Ca_3Si_2O_7 \cdot 2H_2O$ is plotted against the specific surface area of the tobermorite. The 14 points represent 14 preparations, 7 obtained from the hydration of C_3S and 7 from the hydration of C_2S. (The method of preparation is shown in table 5.) The slope of the straight line in figure 3 is the surface energy expressed in cal/m^2.

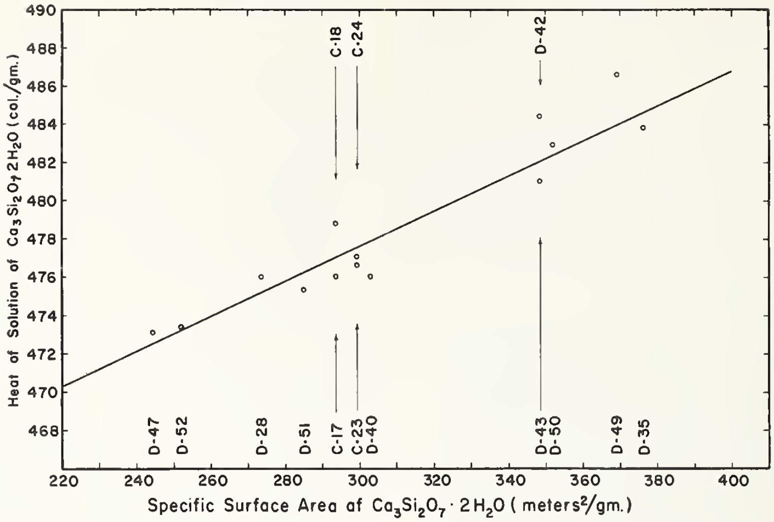

FIGURE 3. *Variation of the heat of solution of* $Ca_3Si_2O_7 \cdot 2H_2O$ *with specific surface area for 1.0-g samples.*

In the same investigations, the heat of the reaction

$$Ca_3Si_2O_7 \cdot 2H_2O(s) + H_2O(l) = Ca_3Si_2O_7 \cdot 3H_2O(s) \qquad (17)$$

was also determined. It was found to be −7,600 cal at 23.5 °C. The surface energy of $Ca_3Si_2O_7 \cdot 3H_2O$ was not determined, because of experimental difficulties, but it was estimated to be close to that of $Ca_3Si_2O_7 \cdot 2H_2O$.

4. Using the heats of solution obtained for the above 14 preparations, the heats of hydration of C_3S and C_2S were calculated.

The tobermorites in 12 of the 14 preparations had CaO/SiO_2 ratios of 1.5, within the experimental error. The two exceptions were the two C_2S pastes, C–23 and C–24, in table 5, which had CaO/SiO_2 ratios of 1.65.

For the 7 C_3S preparations the heats of hydration were first calculated on the basis of the equation

$$2Ca_3SiO_5 + 5H_2O = Ca_3Si_2O_7 \cdot 2H_2O + 3Ca(OH)_2 \qquad (18)$$

and for the 5 C_2S preparations, with tobermorites of CaO/SiO_2 ratio 1.5, on the basis of the equation

$$2Ca_2SiO_4 + 3H_2O = Ca_3Si_2O_7 \cdot 2H_2O + Ca(OH)_2. \qquad (19)$$

All of the tobermorites contained more than two molecules of water per molecule; consequently, corrections were made by using the enthalpy change in eq (17), 420 cal/g of water. The tobermorites also had different specific surface areas but, using the surface energy given before, they were all corrected to a specific surface area of 300 m²/g. The heats of hydrations thus obtained are shown in table 5.

TABLE 5. *Heats of hydration of* C_3S *and* C_2S

For reactions shown in equations 18, 19, and 20.

C_3S designation	Method of hydration	Heat of hydration, cal/g C_3S	C_2S designation	Method of hydration	Heat of hydration, cal/g C_2S
C–17	Paste	77.5	C–23	Paste	7.7
C–18	Paste	76.0	C–24	Paste	7.5
D–35	Bottle	78.7	D–40	Bottle	8.8
D–42	Bottle	76.4	D–28	Ball mill	7.8
D–43	Bottle	78.5	D–47	Ball mill	6.9
D–49	Bottle	76.0	D–51	Ball mill	8.3
D–50	Bottle	77.5	D–52	Ball mill	8.4

For the two C_2S pastes the equation was

$$2Ca_2SiO_4 + 3H_2O = Ca_{3.30}Si_2O_{7.30} \cdot 2.30H_2O + 0.7Ca(OH)_2 \qquad (20)$$

Corrections were made for specific surface area and for excess water in C–24, and the results are also shown in table 5.

It will be noted that the heat contents of the hydration products of C_3S are about the same, regardless of the method of preparation. The same is true for C_2S. More accurate determinations in the future may reveal differences, but for the time being the results may be averaged. The average heat of hydration for the C_3S preparations in table 5 is 77.2 cal/g C_3S, and for the C_2S preparations, 7.9 cal/g C_2S.

To obtain the heat of hydration for the reaction represented by eq (3), the enthalpy changes in the reactions shown in eqs (17) and (18) must be combined. The result is −42,850 cal at 23.5 °C, or 93.8 cal/g C_3S. A similar calculation for the heat of hydration of the reaction shown in eq (4) leads to a value of −10,320 cal at 23.5 °C, or 30.0 cal/g C_2S. These are the chemical heats of hydration of C_3S and C_2S, H_c-S in eq (16), when the tobermorite produced in the hydration has a specific surface area of 300 m^2/g. For a tobermorite with a different specific surface, correction can be made by using the surface energy of 386 $ergs/cm^2$.

5. No investigations were made to determine the heat of adsorption of water on the tobermorite surface, H_{H_2O}. A rough estimate can be made by comparing the H_c-S values with the H_o values of Lerch and Bogue [67], given earlier. Their H_o value for C_2S was 62 cal/g; subtracting 30.0 cal/g gives 32 cal/g C_2S for H_{H_2O}. A similar calculation for C_3S gives 26.2 cal/g C_3S for H_{H_2O}.

Comparison of eqs (3) and (4) shows that 1 g of C_2S gives 32.5 percent more tobermorite (*G*) than 1 g of C_3S. Thus, using 32 cal/g C_2S for H_{H_2O}, calculation would give 24.2 cal/g C_3S. The 2.0 cal/g C_3S difference between this and the value calculated above is well within the errors of the two sets of experiments.

The specific surface areas of the hydration products of C_3S and C_2S were not measured in the experiments of Lerch and Bogue. It is unlikely that the specific surface areas of their tobermorites were equal. If the tobermorite (*G*) in their hydrated C_3S had about 20 m^2/g greater specific surface than that in their hydrated C_2S, the 2-cal difference would be accounted for. It was shown before that the range of variation in the specific surface area of tobermorite (*G*) is about 6 times greater than this difference. Figure 3 indicates that the specific surface areas obtained in the hydration of C_2S tend to be smaller than those obtained in the hydration of C_3S.

Free Energies and Entropies of Hydration

1. No experimental determinations of the specific heats of tobermorite (*G*) have been made to date; consequently, the entropy change and the free energy change in the reactions represented by eqs (3) and (4) can not be accurately calculated. The best one can do at present is to make an educated guess at these quantities.

The difference between the free energies of hydration of C_3S and C_2S can be fairly accurately calculated.

It follows from eqs (3) and (4) that

$$2\Delta F_{C_3S}=F_T+3F_{Ca(OH)_2}-2F_{C_3S}-6F_{H_2O} \qquad (21)$$

and

$$2\Delta F_{C_2S}=F_T+F_{Ca(OH)_2}-2F_{C_2S}-4F_{H_2O} \qquad (22)$$

where ΔF_{C_3S} and ΔF_{C_2S} are the free energies of hydration of C_3S and C_2S per mole of C_3S and C_2S, respectively; and F_T, $F_{Ca(OH)_2}$, F_{C_3S}, F_{C_2S}, and F_{H_2O} are the free energies of formation of tobermorite (*G*), $Ca(OH)_2$, C_3S, C_2S, and H_2O, respectively. The difference is given by

$$\Delta F_{C_3S}-\Delta F_{C_2S}=F_{Ca(OH)_2}+F_{C_2S}-F_{C_3S}-F_{H_2O}. \qquad (23)$$

The values of $F_{Ca(OH)_2}$ and F_{H_2O} are -214.33 and -56.69 kcal, respectively [70], and those of F_{C_2S} and F_{C_3S} are -516.6 and -657.8 kcal, respectively. The last two values were calculated by using the heats of formation of C_2S and C_3S given by Barany, King, and Todd [71] and the entropy values of Todd [10]. The difference $\Delta F_{C_3S}-\Delta F_{C_2S}$ is -16.4 kcal. If one uses the value obtained by Brunauer, Kantro, and Weise [3] for the heat of decomposition of C_3S into C_2S and CaO, instead of King's value [9], $\Delta F_{C_3S}-\Delta F_{C_2S}$ becomes -15.3 kcal.

2. The entropies of $Ca(OH)_2$ and H_2O at 25 °C are 18.2 and 16.72 e.u., respectively [70], and the entropies of C_3S and C_2S are 40.3 and 30.5 e.u., respectively [10]. The entropy change in the hydration of C_3S and C_2S could be calculated, if the entropy of $Ca_3Si_2O_7 \cdot 3H_2O$ were known.

The entropy of tobermorite (*G*) can be estimated in the manner Latimer [72] estimates entropies. The entropies of CaO, SiO_2, hydroxylic water, and interlayer water in the tobermorite are estimated to be 9.8, 13.8, 8.7, and 10.4 e.u. per mole, respectively. These values lead to an estimate of 84.8 e.u. for $Ca_3Si_2O_7 \cdot 3H_2O$. To this, one may add 3.3 e.u. to account for the surface entropy of a tobermorite with a specific surface area of 300 m^2/g, and the figure may be rounded out to 90 e.u., to account for the low order of crystallinity of tobermorite (*G*). The estimate is probably good within ±5 e.u.

The entropy change in the reaction represented by eq (3), calculated from the above data, is -36.3 e.u., and that in the reaction represented by eq (4) is -19.7 e.u. It will be recalled that the equations refer to the hydration of two moles of C_3S and C_2S.

3. Using the ΔH values reported earlier, $-42,850$ cal for $2C_3S$ and $-10,320$ cal for $2C_2S$, the free-energy change in the hydration of $2C_3S$ at 23.5 °C is $-32,000$ cal, and in the hydration of $2C_2S$, $-4,400$ cal. The difference between ΔF_{C_3S} and ΔF_{C_2S} per mole is -13.8 kcal. This is to be compared with the more accurate value of -15.3 kcal, reported before. The agreement is not spectacular, but it is the best that the present authors can do with available data.

Rates and Mechanisms of Hydration

Rates of Hydration of C_3S and β-C_2S in Paste Form

1. Although there are sizable gaps in our understanding of the changes in matter and energy that occur in the hydration of C_3S and β-C_2S, there has been a steady and significant progress since 1952, the year of the Third International Symposium on the Chemistry of Cement. The situation is far less satisfactory in our understanding of the rates

and mechanisms of the hydration of C_3S and C_2S. Not enough work has been done, the results of different investigators do not agree, and few have attempted to interpret even their own results. A systematic and thoroughgoing investigation has been started in this laboratory, but the results will be available only in the future.

To be sure, the problem is not simple. The question immediately arises, how to measure the rate? The one direct method is to measure the amount of unhydrated C_3S or C_2S remaining in the system after various times by means of X-ray quantitative analysis, but only van Bemst [27, 28] and Kantro, Brunauer, and Weise [15] have used this method so far. The latter investigators used it in their study of the ball-mill hydration of C_3S. Van Bemst used the method extensively in studying what is called the "bottle" hydration of C_3S and C_2S in this paper, in which he employed a very large excess of water. By far the most important method of hydration is paste hydration, and the rates of hydration of C_3S and C_2S in the ball mill or in a bottle supply no information about the rates of paste hydration. Van Bemst published a few data on the paste hydration of C_3S [27]; these are the only rate data in the literature of paste hydration obtained by the direct method.

Other investigators have used indirect methods, such as the determination of the water of hydration, of the $Ca(OH)_2$ produced in the reaction, or of the heat evolved in the reaction. These methods would supply reliable information about the rate of disappearance of C_3S or C_2S only if the hydration products were the same throughout the entire reaction. It is easy to see, however, that the products in the early stages of the reaction may be different from those in the later stages. Reaction probably occurs both by direct contact of the surfaces of the anhydrous grains with water and by precipitation out of solution. The products of these reactions may be different, as van Bemst believes they are [28]. In different stages of the reaction, the relative amounts of the products forming by the two mechanisms may be different.

In the early stages, intermediate products may form on the surfaces of the grains, which differ in composition from the final products. Similarly, in the early stages, prior to the establishment of lime saturation in the solution, the tobermorite precipitating out of the solution may have a lower CaO/SiO_2 ratio than later. A C_2S paste, which hydrated for one day in this laboratory, had a CaO/SiO_2 ratio of 1.15 in the tobermorite. Lime saturation was established in much less than one day, but the tobermorite had not enough time to convert to the equilibrium product. The same C_2S hydrating for 17 months had a CaO/SiO_2 ratio of 1.65 in the tobermorite, as was shown earlier.

It is possible that changes in the hydration products may occur not merely for hours or days, but for months. Bogue and Lerch [49] found, for example, that microscopical examination of a C_3S paste hydrated for three months revealed complete absence of unhydrated C_3S grains, whereas the water of hydration indicated only about 80 percent hydration.

Practically all data in the literature on the rates of paste hydration of C_3S and C_2S were obtained by indirect methods. The foregoing considerations show that these data cannot be directly equated with the rate of hydration of C_3S or C_2S. When, at a certain age of paste, 30 percent of the ultimate amount of $Ca(OH)_2$ is liberated, it is possible that only 15 percent of the C_3S has reacted. On the other hand, it is also clear that a knowledge of the percentage hydration of C_3S by itself is not enough. Only if the unreacted C_3S, the water of hydration, the $Ca(OH)_2$, and the heat evolved at each stage of hydration are determined, can one acquire a real understanding of the process of hydration.

2. Ershov [73] summarized a part of the rate data in the literature by stating that C_3S hydrates to the extent of 15 to 20 percent in 1 day, 35 to 50 percent in 3 days, 45 to 70 percent in 7 days, 68 to 75 percent in 1 mo, and 85 to 94 percent in 6 mo; β-C_2S hydrates to the extent of 4 to 7 percent in 3 days, 8 to 10 percent in 7 days, 11 to 12 percent in 1 mo and up to 30 percent in 6 mo. Actually, the range of variation is far greater than these figures indicate. For example, the results of Bogue and Lerch [49] indicate 45 percent hydration of C_3S in 1 day, and the results of Knoblauch [74] indicate 86 percent hydration of C_2S in 4 mo.

Ershov did not attempt to analyze the causes of variation. Variations in the actual rates arise from different methods of preparation of the silicates, from differences in the fineness of grinding, differences in water/solid ratio employed and differences in the temperature of hydration. Variation in the results arise also from the different methods used for rate determination.

The effect of particle size on the rates of hydration was investigated by Anderegg and Hubbell [75]. For fractions with mean dimensions of 19, 22, and 25 μ for C_3S, and 18 and 22 μ for C_2S, the results indicated no difference in the rates of hydration, within their experimental error, from 3 hr to 28 days. Sloane, McCaughey, Foster, and Shreve [76] found no difference in the rates of hydration of three fractions of C_3S: 65 to 100 mesh, 100 to 200 mesh, and 200 to 300 mesh. In both sets of investigations, microscopical examination of the hydration products was used to determine the extent of hydration. In contrast with these results, Steinour [77] found a strong dependence of the rate of hydration of C_2S on particle size. A less than twofold increase in the specific surface led to a roughly twofold increase in the water of hydration at ages up to 42 days.

The most extensive work on the effect of water/solid ratio was done by Work and Lasseter [78]. Whereas most investigators used a single water/solid ratio, usually 0.50, or at best a narrow range, these investigators used a range from 0.06 to 1.00. They determined the rates by measuring the water of hydration and the $Ca(OH)_2$ evolved in the reaction. The rates of hydration of C_3S and C_2S increase markedly with water/solid ratio in the range of low water/solid ratios, but the increase is slight from 0.45 up. For 3-months-old C_3S pastes, they reported water of hydration values of 18.2, 19.0, and 20.4 percent for water/C_3S ratios of 0.45, 0.60, and 1.00, respectively. In this laboratory, for 72-days-old pastes, water of hydration values of 18.2, 19.0, and 19.3 percent were obtained for water/C_3S ratios of 0.45, 0.57, and 0.70, respectively.

The most extensive data on the effect of temperature were obtained by Schwiete and by Knoblauch [74, 79]. They found a slight increase in the rate of hydration of both C_3S and C_2S with increasing temperature from 20 to 65 °C. They calculated from their rate data energies of activation of 2.1 kcal for C_3S and 1.8 kcal for C_2S. Though these calculations are open to question, as will be seen later, there is no question about the positive temperature dependence of the rates of hydration. Schwiete and Knoblauch used a new method for the rate determinations, dynamic differential calorimetry.

Some data of van Bemst [27] indicate a slight negative temperature coefficient between 4 and 40 °C. For a C_3S paste, with water/solid ratio of 0.5, he obtained 52 and 65 percent hydration after 7 and 28 days at 4 °C, but only 40 and 47 percent hydration after the same periods at 40 °C. He measured the C_3S remaining by means of X-ray quantitative analysis.

From the foregoing, it seems probable that the large variations in the rates of hydration, pointed out earlier, are caused by differences in the methods of preparation of C_3S and C_2S. The nature of the raw materials used, the temperature of burning, the rate of cooling of the burn and, in the case of β-C_2S, the nature and the amount of stabilizer used, may have important effects on the rates of hydration. The effect of stabilizer was extensively investigated by Funk [30]. Steinour [77] investigated all of these effects for the rate of strength development of C_2S. He found that low temperature of burning and quick quenching were especially important in producing rapid strength development.

3. Among the data in the literature, probably those of Bogue and Lerch [49] and Work and Lasseter [78] illustrate the courses of the reactions best. They measured the rates by means of the water of hydration and the $Ca(OH)_2$ produced, but the results of Bogue and Lerch for $Ca(OH)_2$ are not reliable because they heated the hydration products to about 530 °C prior to the lime determination. It was found in this laboratory that such a heating resulted in a reaction between the lime and tobermorite (*G*). The fact that the free lime at complete hydration of C_3S indicated a CaO/SiO_2 ratio of 2.2 in the tobermorite of Bogue and Lerch is a clear evidence that free lime was removed from the products by heating prior to determination. Strangely enough, Work and Lasseter obtained the same values for free lime whether they heated the hydration products or not. This is another example that shows the complexity of the system. The free-lime values they obtained for C_3S after 6 mo of hydration indicated a tobermorite with CaO/SiO_2 ratio of 1.6, or somewhat less.

The "fixed water" of Bogue and Lerch for completely hydrated C_3S agrees well with the water of hydration obtained in this laboratory by (*D*)-drying. The 1-yr-old C_3S paste, with a water/C_3S ratio of 0.50, appears to be completely hydrated. If one uses the water of hydration as a measure of the percentage hydration, one obtains the values shown in table 6, row 1. In curve 1 of figure 4, the percentage hydration is plotted against the logarithm of time in days. The logarithmic scale is used just to be able to represent the data clearly from 1 day to 2 yr. The data of Bogue and Lerch indicate practically no hydration between 28 days

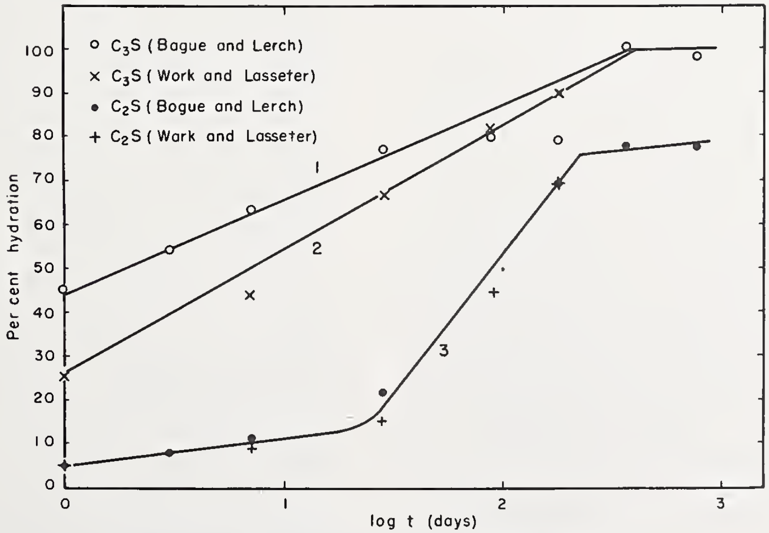

FIGURE 4. *Rates of hydration of* C_3S *and* C_2S.

Table 6. *Rates of hydration of* C_3S *and* β–C_2S

Water/solid ratio=0.50

	Substance	Investigators	Method of determination	Hydration, percent							
				1 day	3 days	7 days	28 days	3 mo.	6 mo.	1 yr	2 yr
1	C_3S	Bogue and Lerch	Water of hydration	45.3	54.2	63.2	76.8	80.0	78.9	100.0	97.9
2	C_3S	Bogue and Lerch	Strength	12.8	24.8	52.7	62.8	62.8	85.8	91.2	100.0
3	C_3S	Work and Lasseter	Water of hydration	24.2	----------	40.6	58.3	72.7	(90.0)	----------	----------
4	C_3S	Work and Lasseter	Calcium hydroxide	27.6	----------	47.8	75.8	90.0	(90.0)	----------	----------
5	β-C_2S	Bogue and Lerch	Water of hydration	5.0	7.7	10.8	21.6	56.6	68.8	(77.7)	77.0
6	β-C_2S	Bogue and Lerch	Strength	0.0	0.4	1.0	6.3	36.0	52.7	71.4	100.0
7	β-C_2S	Work and Lasseter	Water of hydration	5.3	----------	9.4	15.2	44.0	(68.8)	----------	----------

and 6 mo. Since no other data in the literature indicate such behavior, the curve was drawn by disregarding the 6-mo point. The 3-mo point is also somewhat too low.

Work and Lasseter obtained data only up to 6 mo. If it is assumed that their C_3S paste was 90 percent hydrated at that time, one obtains the percentage hydration values shown in table 6, rows 3 and 4. The first is based on water of hydration, the second on free $Ca(OH)_2$. It was shown above that the $Ca(OH)_2$ values of Work and Lasseter were fairly reliable. They did not use a water/C_3S ratio of 0.50, but interpolation between their ratios of 0.45 and 0.60 gave values for the ratio 0.50.

Plotting the average of the values shown in rows 3 and 4, table 6, gives curve 2 of figure 4. There are two notable differences between curves 1 and 2. The C_3S of Bogue and Lerch was 45 percent hydrated in 1 day; that of Work and Lasseter was only 26 percent hydrated. Both of these values are in agreement with values obtained by other investigators. A value of 41 percent hydration in 1 day was obtained by van Bemst [27] for one of his C_3S pastes, using X-ray analysis to determine the unhydrated C_3S. A value of 28 percent was obtained in this laboratory for a 1-day-old C_3S paste, using water of hydration and $Ca(OH)_2$ to measure the rate.

The second difference is that the C_3S of Work and Lasseter hydrates faster after 1 day than the C_3S of Bogue and Lerch. It is not certain that the former catches up with the latter in 1 yr—this is based on the somewhat uncertain assumption that the percentage hydration of the former was 90 percent in 6 mo. It is certain, however, that the slope of curve 2 is greater than that of curve 1.

4. The β–C_2S paste of Bogue and Lerch, likewise with water/solid ratio of 0.50, did not reach complete hydration in 2 yr. The extent of hydration after 1 yr was calculated on the basis of eq (19) of the present paper to be 77.7 percent, and the values in table 6, row 5, for other ages are based on this figure. It was assumed that the C_2S of Work and Lasseter, after 6 mo, was hydrated to the same extent as that of Bogue and Lerch, 68.8 percent, and the values in table 6, row 7, for other ages are based on this figure. As curve 3 of figure 4 shows, both sets of data can be represented by one curve.

It appears from the curves of figure 4 that the course of the hydration of C_2S is very different from that of C_3S. The initial hydration of C_2S is much slower; there is only 5 percent hydration in 1 day and 10 percent hydration in 7 days. The hydration appears to stop after about 1 yr, when about ¼ of the C_2S is still unhydrated. The most remarkable difference is in the time range from 3 days to 3 mo. In this period, the rate of hydration of C_3S diminishes strongly, whereas the rate of hydration of C_2S does not diminish at all.

In fact, both the data of Bogue and Lerch and those of Work and Lasseter indicate an increase in the rate of hydration of C_2S; the former a small increase, the latter a considerable increase. The average rates from the two sets of data are 0.40 percent C_2S per day from 7 to 28 days, and 0.51 percent C_2S per day from 28 days to 3 mo. Such an increase in rate is not unknown in reaction kinetics, and it is usually attributed to a catalytic effect of a hydration product.

The increase in rate appears to come about when 15 to 20 percent of the C_2S is hydrated. If a similar autocatalysis operates in the hydration of C_3S, it should occur in the course of the first day of hydration. Forbrich [80] actually found such an increase in rate for C_3S. Using a conduction calorimeter to measure the heat evolved, he obtained an initial heat evolution of about 1 cal/g C_3S per hour. The rate was still about the same after 4 hr, but then it began to climb, and it reached a maximum of about 3 cal/g C_3S per hour in 9 hr. The evolution of 1 cal/g C_3S corresponds to a hydration of about 0.8 percent.

As far as one can judge from the curves of Schwiete and Knoblauch [74, 79], their C_2S did not exhibit any autocatalysis.

5. Bogue and Lerch determined the compressive strengths of their hydrated C_3S and C_2S pastes. The strengths kept on increasing steadily from 1 day to 2 yr. Taking the compressive strength values at 2 yr as 100 percent, the percentages of the ultimate strength developed at different ages are shown in table 6, rows 2 and 6. The strength lags considerably behind the extent of hydration in the first 3 days for C_3S and in the first 3 mo for C_2S. Only when the hydration is about two-thirds complete, in 7 days for C_3S and in 6 mo for C_2S, does the percentage of the ultimate strength approach the percentage hydration. The

strength keeps on increasing after hydration stops; the increase between 1 and 2 yr is almost 10 percent for C_3S and about 40 percent for C_2S.

Steinour's results [77] for the early hydration and strength development of C_2S show that strength development lags behind extent of hydration up to 28 days, both for high and low surface C_2S.

Bernal, Jeffery, and Taylor [7] examined qualitatively, by means of X-rays, the hydration products of C_3S, and compared their results with the strength data of Bogue and Lerch. They came to the conclusion "that only a small amount of hydrate is needed in order to cement together the grains of the unchanged anhydrous compounds, and of the aggregate also, when this is present. Further reaction does not lead to any increase in strength and, indeed, could conceivably cause a decrease." The data of Bogue and Lerch, as well as those of Steinour, show that this conclusion is not correct.

The strength developed by a C_3S or C_2S paste at a given age shows as much variation from investigator to investigator as the extent of hydration, if not more. Ershov [73] finds, for example, that the ratio of the strength of C_3S to that of C_2S is "approximately 50 for specimens at the age of 3 days and about 5 for specimens aged 1 year." The results of Bogue and Lerch indicate that the ratio is about 50 at 3 days, but 1 rather than 5 at 1 yr. Ershov gives the ratios of the strengths at 28 days to those at 3 days the values 2 for C_3S and 6.7 for C_2S, whereas the values of Bogue and Lerch are 2.5 and 15, respectively.

Steinour's data [77] show especially well the magnitude of the effects of methods of preparation and fineness of grinding of C_2S on strength. Using a water/C_2S ratio of 0.40, he obtained compressive strengths ranging from 320 to 1,560 psi after 7 days, from 880 to 4,350 psi after 28 days, and from 2,270 to 11,250 psi after 6 mo.

Funk [30] hydrated C_2S with water vapor at 100 °C, and obtained a powder without any strength. He stated, "Electron micrographs show, in conformance with the loose structure of the preparations that water vapor action produces only loosely piled, acicular fibrous units. According to this, the high-lime tobermorite-like phase is not necessarily formed out of the solution phase. However, the aqueous solution phase must be present if hardening of the mass is to be produced."

Hydration in Excess Water

1. The most extensive data on the rates of hydration of C_3S with a large excess of water were obtained by van Bemst [28]. The ratio of water to silicate ranged from about 100 upward; in certain experiments saturated $Ca(OH)_2$ solution was used instead of water. The hydration was performed in polyethylene containers, constantly agitated in a thermostat. Temperatures of 25, 40, and 60 °C were employed. This method of hydration is similar to the "bottle" hydration used in this laboratory and described earlier in the present paper.

The course of the hydration of C_3S as observed by van Bemst may be summarized as follows. The silicate rapidly dissolves in water, and hydrate I, a low-lime tobermorite, is precipitated out of the solution. The CaO/SiO_2 ratio in the tobermorite is, presumably, the one that corresponds to the lime concentration in the solution according to figure 1 of the present paper; prior to lime saturation it is always less than 1.5. As the lime concentration in the solution increases, the solubility of C_3S diminishes, which results in a diminishing rate of hydration.

If at the time when saturation is reached the C_3S is less than half hydrated, the hydration virtually stops. There may be 30 or 40 percent unhydrated C_3S in the system, the solution may even be supersaturated with respect to $Ca(OH)_2$, and still there is no appreciable hydration between 28 and 56 days.

When the concentration exceeds 0.020 mole of CaO per liter, which corresponds to lime saturation at 25° and supersaturation at 40 °C, hydrate II appears as the hydration product of C_3S. At 60 °C this concentration was not reached in van Bemst's experiments, and only hydrate I was obtained. Van Bemst identified his hydrate II with Taylor's $C_2SH(II)$, and this is probably correct. It was shown earlier in this paper that the bottle hydration of C_2S in this laboratory resulted in a product that appeared to be identical with Taylor's $C_2SH(II)$.

When the hydration product is hydrate II, the rate is faster if less water is present. At a given temperature, the rate is fastest in a saturated lime solution. When water is used, lime saturation is reached faster if the amount of water is smaller; consequently, the rate is faster. Van Bemst concluded that the hydration was the fastest in the paste form, because of the very low water content.

Funk [30], investigating the hydration of C_2S at higher temperatures, also came to the conclusion that increasing the quantity of water diminished the rate. At 100 °C, with a water/C_2S ratio of 3, he obtained about 50 percent hydration in 10 days, and no appreciable further hydration took place in the next 20 to 30 days. On the other hand, with a water C_2S ratio of 0.5, complete hydration was obtained in 4 to 15 days.

In contrast with van Bemst and Funk, Brunauer, Kantro, and Copeland [14] found that bottle hydration, with a water/solid ratio of 9, was much faster than paste hydration, with a water/solid ratio of 0.7. Table 1 of the present paper shows that bottle-hydrated C_2S, D–40, reached the same extent of hydration in 162 days as paste-hydrated C_2S, C–23, did in 17 mo. Bottle-hydrated C_3S preparations reached 97 percent hydration in 48 days, whereas it takes more than 6 mo to reach that stage in the paste form.

Both van Bemst and Funk found that the rate of hydration increased with increasing temperature.

Van Bemst has advanced the hypothesis that hydrate I forms by precipitation out of solution, but hydrate II forms by reaction of the silicate surface with water. This may well be true, but further experiments are needed to test the hypothesis, as well as to explain the discrepancies in the experimental results discussed above.

2. The rate of hydration of C_3S in a small steel ball mill with a water/C_3S ratio of 9, was investigated by Kantro, Brunauer, and Weise [15]. Whereas the hydration of C_2S in the ball mill produces tobermorite (*G*) [14], the ultimate product of hydration of C_3S in the ball mill is afwillite [13].

The investigators used X-ray quantitative analysis to determine the amounts of C_3S and afwillite in the reacting system. In about 31 hr, the C_3S disappeared completely, but there was only about half as much afwillite produced as eq (3) of the present paper would indicate. The reason for this was that an intermediate compound formed first, which the investigators called hydrate III. It took about 25 days until the unstable hydrate III converted completely to afwillite.

The rate of disappearance of C_3S was found to be proportional to the surface area of the grains exposed to the steel balls. This indicated that hydrate III formed on the surfaces of the grains, and the rate determining step was the removal of the coating from the grains. The conversion of hydrate III to afwillite did not begin immediately upon the appearance of the former in the system. There was an induction period of about 6 hr which indicated an autocatalytic mechanism, i.e., a rate dependent on the concentrations of both afwillite and hydrate III.

The properties of hydrate III were found to be very similar to those of tobermorite (*G*) with respect to CaO/SiO_2 ratio, water content, heat of solution, heat of hydration, specific surface area, and surface energy. They differ only in two respects. Hydrate III shows only one very broad X-ray diffraction line, that corresponding to the strongest line of tobermorite (*G*), at about 3 A, whereas tobermorite (*G*) shows three diffraction lines. Hydrate III is unstable and converts to afwillite, whereas tobermorite (*G*) does not. A mixture of 50 percent C_2S and 50 percent C_3S by weight was completely hydrated in the ball mill. No X-ray quantitative analysis was performed on the hydration products, but inspection of the diffraction patterns indicated that tobermorite (*G*) and afwillite were present in the proportion corresponding to independent hydration of C_2S and C_3S.

Hydrate III appears to be a form of tobermorite with a structure so disordered that it exhibits only a single X-ray diffraction line. Just why it converts to afwillite rather than to a better crystallized tobermorite is not known at present.

Mechanisms of Hydration

1. When C_3S or C_2S is brought in contact with water, reaction may occur at the surfaces of the grains or in the solution phase. The surface of C_2S consists of Ca^{++} ions and SiO_4^{4-} groups, that of C_3S consists of these plus $O^{=}$ ions. These ions enter the solution as aqueous Ca^{++}, OH^- and hydrosilicate ions. When 0.25 g of C_3S was dissolved in 1 liter of water with vigorous stirring, in this laboratory, the electrical conductivity corresponded to the concentrations and mobilities of the Ca^{++}, OH^-, $H_3SiO_4^-$ and $H_2SiO_4^{=}$ ions for congruent solutions. Under other conditions, however, the different ions may dissolve at different rates.

In the solution mechanism, the hydrated ions form at the surface, diffuse away from the surface, react with each other to form tobermorite molecules, the molecules form nuclei, the nuclei grow, colloidal particles precipitate and flocculate. Practically nothing is known about the rates of these individual steps in the reaction.

Tobermorite may form directly on the surfaces of the silicate grains and may stay there. The hydrated grain surfaces may also serve as nuclei for the precipitation of tobermorite out of solution. In either case, a tobermorite gel coating would form on the surface, and the coating would grow in thickness with time. Whether further reaction proceeds on the surface or in solution, water and the ions must diffuse through this gel layer prior to reaction. Again, very little is known about the rates of the individual steps in this mechanism.

$Ca(OH)_2$ separates out of the solution as relatively large particles. These particles are overlaid by tobermorite gel and, not infrequently, they grow around and occlude tobermorite gel. When hydration is observed in a microscope, gel appears to form on the surfaces of the slide and the cover glass, at considerable distances from the grains. Such evidence shows clearly that a part of the tobermorite forms by precipitation from solution. On the other hand, hydration can also take place without the presence of liquid water. Funk [30] hydrated C_2S by water vapor at 100 °C and, in this laboratory, C_3S was hydrated by water vapor at room temperature. In these experiments, probably, the surface reaction mechanism is operative.

Not much is known about the relative importance of the two mechanisms in various stages of the reactions between the silicates and water. It is generally believed that, in the later stages of paste hydration, diffusion through the gel layer becomes the rate-controlling step, but it is not known when these stages are reached by C_3S and C_2S under different experimental conditions.

2. Le Chatelier [81] was the first to advance the solution and precipitation mechanism. Baikov [82] distinguished three steps in the hydration process. The first is the solution step, during which water becomes progressively saturated. The second is the "colloidization" step, during

which precipitation of colloidal particles takes place. This corresponds to the beginning of the setting process. The third is the "crystallization" step, during which the gels are transformed into crystalline aggregates. This is the period of hardening.

Though both Le Chatelier and Baikov advanced their hypotheses for the hydration of cements, subsequent investigators applied them to the hydration of calcium silicates as well. This is natural, since C_3S and portland cement are quite similar in their setting and hardening characteristics.

The Soviet investigators have adopted the Baikov hypothesis with various modifications and additions. A modern version of it is described by Rehbinder [83], who, on the basis of his own work and that of his coworkers, also distinguishes three stages in the hydration process. He states that "setting and hardening represent a complex of hydration processes developing in time, of a self-induced dispersion of cement particles (minerals of cement clinker), of a formation of coagulated thixotropic structures, and of the development on these as a base of a crystalline structure of new hydrated formations through crystallization out of a supersaturated water solution." These processes occur most rapidly in the hydration of C_3A, next comes C_4AF, then C_3S, and finally C_2S.

The first step in the hydration of C_3S or C_2S, accordingly, is the breaking up of the coarse grains into particles of colloidal dimensions. The grains have micro-cracks and other types of defects, and water and various ions, penetrating into the cracks and the weak spots of the lattice, produce dispersion. The surfaces of the dispersed colloidal particles are covered with hydration products. Rehbinder states, "The presence of a highly dispersed colloidal fraction appears, in this manner, as a necessary condition of the thixotropy of a coagulated structure." He identifies the setting process with the formation of a coagulating structure, which hardens reversibly, i.e., thixotropically.

The presence of the dispersed silicate particles and of the hydration products, which are very small, brings about a supersaturation of the solution. "A crystallization of new formations out of the supersaturated solution takes place as a result of the appearance and growth of surface nuclei of crystallization." Thus, on the coagulated structure as a base, at first a more or less open crystalline structure of the hydration products develops; however, as time passes, the crystalline structure becomes denser by the addition of further products of hydration. At this stage, the hydration progresses more slowly, because the unhydrated cores of the colloidal particles are covered by hydration products. This is the process of hardening which, in contrast with the setting process, develops an irreversible and much stronger crystalline structure.

The present authors are acquainted only with a small fraction of the literature on which the above conclusions of Rehbinder are based. Because of the shortness of time available for the writing of this paper and because the authors, unfortunately, do not read Russian, they have been handicapped in reporting the Soviet literature on the hydration of C_3S and C_2S. They hope that some of their Soviet colleagues will make up for this deficiency by attaching discussions or supplementary papers to the present paper. With respect to the above mechanism of hydration, they wish to make three comments, and they hope that Professor Rehbinder or one of his colleagues will clarify these points.

(a) In the paper cited [83], experiments are described showing that the surface of hydrating C_3A increases twenty-fold in the first 30–40 minutes. The present authors do not see that this reveals anything about the self-induced dispersion of C_3A particles; the growth of surface may be caused entirely by the larger specific surface of the hydration products. The specific surface area of tobermorite, for example, is about 1,000-fold greater than that of C_3S; 2 percent hydration, therefore, would cause a twenty-fold increase in the surface. This much hydration probably occurs in the first few minutes.

It is entirely reasonable to expect the kind of dispersion of grains described by Rehbinder, but it may be a relatively slow process. The autocatalytic processes in the hydration of C_3S and C_2S, described earlier, could be explained by such a splitting of the grains. Because the rate of hydration is proportional to the surface of the unreacted silicate in both the solution and surface reaction mechanisms, formation of new surfaces of the reactant would increase the rate. If grain splitting is the true explanation of autocatalysis, the rate of splitting becomes significant in hours for C_3S and in days for C_2S. This sort of splitting would have nothing to do with thixotropy, which is probably established in far shorter times.

(b) In general, the present authors do not see the connection between thixotropy and dispersion of the grains of the silicates. Thixotropy is caused by the appearance of tobermorite in the system. Lewis, Squires, and Broughton [84] point out that some clay suspensions in water, containing as little as 0.1 percent solids, exhibit thixotropy, and hydrating C_3S contains far more than this quantity of tobermorite immediately after mixing with water.

(c) Rehbinder seems to draw a clear-cut distinction between "coagulating structure" and "crystalline structure." As far as degree of crystallinity is concerned, tobermorite in the completely hydrated and hardened paste, i.e., in Rehbinder's "crystalline structure," is still very poorly crystallized; its X-ray diffraction pattern contains only three lines. The present authors wonder whether tobermorite in the early "coagulating structure" is any different in degree of crystallinity, or in any other respect, from the tobermorite obtained later.

3. Thixotropy, setting, and hardening are phenomena accompanying the formation of more and

more tobermorite in the hydrating system. According to current theory [85], thixotropic gels are made up of particles which are in contact at certain points only. The particles usually have the shapes of rods or plates; the rods probably form contacts at the ends, and the plates form contacts between oppositely charged edges and plane surfaces. The forces are van der Waals and electrostatic; they are sufficiently strong to hold the system together in a network structure at a low concentration of particles in the solution, but they are not so strong as to prevent breaking of the bonds between the particles by a small shearing stress. By changing the *p*H or the ionic strength of the solution in contact with the solid surfaces, Kruyt and his coworkers [86] were able to change the forces of attraction and repulsion between the particles in thixotropic gels.

Tobermorite consists of fibers or sheets; consequently, its morphology is suited for the formation of a thixotropic gel. Its surface is ionic, so both electrostatic and van der Waals forces are present. In some experiments performed in this laboratory, alite exhibited thixotropy by the time the first measurements could be made, which was 15 min after mixing with water. Tobermorite, obtained by the reaction of silica and $Ca(OH)_2$ in water at 85 °C, exhibited different degrees of thixotropy when the reaction was carried out with and without stirring. Also, when a thixotropic gel was obtained without stirring, shearing action transformed the gel into a sol, which on standing did not revert back completely to the original gel structure. This lack of complete reversibility in thixotropic properties may well be a characteristic of the tobermorite obtained in the paste hydration of C_3S as well.

One of the requirements for setting is that enough hydration products should form in the system, but this may not be the whole story. Bogue and Lerch [49] reported initial setting times of 3.7 and 4.7 hr for C_3S and C_2S, respectively, and final setting times of 6.0 and 24.0 hr, respectively. Although the extent of hydration was not determined by them for times less than 24 hr, it seems likely that more C_3S hydrated in 3.7 hr than C_2S in 4.7 hr. Another requirement for setting may or may not be the formation of chemical cross-links between tobermorite (*G*) fibers at the areas of contact. This may come about through calcium ions, or by hydrogen bonding, or by condensation of $Si(OH)_4$ groups, forming siloxane linkages. Even if such chemical linkages are present to a certain extent, the predominating forces must be electrostatic and van der Waals. That the binding between fibers is not very strong is indicated by the fact that Copeland was able to disperse completely hydrated and hardened C_3S and C_2S pastes by ultrasonic agitation.

A true understanding of the mechanisms of thixotropy, setting and hardening of C_3S and C_2S still lies in the future.

4. Hansen [87] has proposed that the hydration of the silicates occurs through diffusion of water into the solid and diffusion of lime out of it. The experiments of McConnell [88] and Nacken [89] appear to support this hypothesis. Jeffery [90] described McConnell's results as follows. "McConnell at Cambridge, in his investigations of Ballycraigy and Scawt-Hill minerals, has found bredigite (α-C_2S) and larnite (β-C_2S), hydrated to tobermorite (or plombierite, in his nomenclature). The hydrate occurs as pseudomorphs of the original C_2S crystals. In the case of larnite the characteristic delicate twinning is preserved in the hydrate, alternate lamellae extinguishing together under crossed nicols. . . . Much of the tobermorite occurs as a homogeneous flintlike sheath, up to five centimeters thick, round nodules of unaltered larnite. . . . McConnell concludes that detailed study of the gel so formed indicates that the process of hydration is a solid reaction which is effected by diffusion."

Nacken found similar evidence for the hydration of C_3S. He observed under the microscope that C_3S hydrated from the surface, then the reaction progressed inward. The product formed a pseudomorph of the original grain of C_3S.

A simple calculation shows that the tobermorite gel formed in the hydration of C_2S occupies considerably more space than C_2S itself. This is true, to a lesser extent, of C_3S also. This was pointed out by Powers [91]. It is clear, therefore, that the pseudomorphs observed by Nacken and McConnell could not contain all the tobermorite formed in the hydration of the particular C_3S and C_2S grains. It follows also that not only lime diffuses out of the solid, but silica as well.

5. Schwiete and Knoblauch [74, 79] found that the hydration of C_3S followed a reaction equation of the third order, and the order for C_2S was 1.5. They did not interpret the meanings of these orders. Plotting the logarithms of the rate constants against the reciprocals of the absolute temperatures, they obtained the energies of activation reported earlier in this paper. It is doubtful that the energies of activation thus obtained are energies of activation in the true sense of that term. The small positive temperature coefficients seem rather to indicate a diffusion controlled reaction mechanism.

Zur Strassen [92] interpreted the results of Schwiete and Knoblauch in terms of a diffusion mechanism. If the thickness of the gel layer is called *y*, one can make the simple assumption that

$$\frac{dy}{dt}=k \text{ and } y=kt. \qquad (24)$$

This may happen when the reaction at the water-solid interface is slower than the diffusion of water through the gel layer. If water in the reaction zone is used up more rapidly than it is supplied by diffusion through the gel, one may assume that the rate is inversely proportional to the thickness of the gel layer,

$$\frac{dy}{dt}=\frac{1}{y}k \text{ and } y=k't^{\frac{1}{2}}. \qquad (25)$$

Apart from an initial faster reaction in the first few days, the hydration of C_2S obeys equation 24 up to about 120 days. At that time about 80 percent of the C_2S is hydrated; after that time, the reaction slows down. On the other hand, the hydration of C_3S obeys equation 25, up to about 30 days. For C_3S also there is an initial higher rate and a final lower rate. The conclusion is that, throughout most of the hydration process, the reaction occurring at the interface is the rate controlling step in the hydration of C_2S, but diffusion through the tobermorite gel is the rate controlling step in the hydration of C_3S. The final slowing down in the hydration of C_2S is explained by the building up of the gel layer—when the layer becomes sufficiently thick, diffusion becomes the rate controlling step. However, the final slowing down in the hydration of C_3S is not explained.

Although zur Strassen's approach is undoubtedly an oversimplification of the problem, it constitutes a good beginning toward a quantitative treatment of the part of the hydration process which is diffusion controlled. However, much painstaking experimental and theoretical work must be performed before an adequate understanding of the mechanisms of the hydrations of C_3S and C_2S will be achieved.

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Paper III–2. Hydrothermal Reactions in the System $CaO–SiO_2–H_2O$ and the Steam Curing of Cement and Cement–Silica Products*

H. F. W. Taylor

Synopsis

The field is reviewed under the following headings: (I) Introduction and nomenclature; (II) Experimental methods; (III) Individual ternary phases; (IV) Some general considerations; (V) Hydration of C_3S, C_2S, and neat cement in pastes cured at elevated temperatures; (VI) Reactions occurring in lime-silica and cement-silica pastes cured at elevated temperatures. The aim of sections (I) to (IV) is to summarize existing knowledge and problems in the field of fundamental studies on the system $CaO–SiO_2–H_2O$ at or above 100 °C. These studies constitute the background for ones bearing more directly on technical practice which are reviewed in sections (V) and (VI). In section (V) the reactions in C_3S and β-C_2S pastes are chiefly considered; they serve as a model for the more complex ones occurring in neat cement pastes. In section (VI), reactions in lime-quartz pastes are similarly considered as a model for the case of cement-silica pastes.

The conditions under which poorly crystallized tobermorite minerals are formed hydrothermally are discussed, but not the constitution of these phases, as this is reviewed elsewhere in this symposium.

Résumé

La question est revue sous les titres suivants: (I) Introduction et nomenclature; (II) Méthodes expérimentales; (III) Phases ternaires individuelles; (IV) Considérations générales; (V) Hydratation de C_3S, de C_2S, et de ciment en pâte pure conservée à des températures élevées; (VI) Réactions qui se produisent dans les pâtes silice-chaux et silice-ciment conservées à des températures élevées. Les sections (I)–(IV) ont pour but de résumer les connaissances actuelles et les problèmes dans le domaine des études fondamentales sur le système $CaO–SiO_2–H_2O$ à 100 °C ou à une température plus élevée. Ces études constituent la base pour des études qui portent plus directement sur la pratique technique, et qui sont revues dans les sections (V) et (VI). Dans la section (V) ce sont surtout les réactions dans les pâtes de C_3S et de β–C_2S qui sont considérées; elles servent de modèle pour les réactions plus complexes qui se produisent dans les pâtes pures de ciment. Dans la section (VI) les réactions dans les pâtes quartz-chaux sont également examinées en tant qu'elles constituent un modèle pour l'étude des pâtes silice-ciment.

L'exposé examine les conditions sous lesquelles les minéraux tobermorites faiblement cristallisés sont formés hydrothermiquement, mais la constitution de ces phases n'est pas discutée puisqu'elle est revue dans une autre partie de ce symposium.

Zusammenfassung

Der Diskussionsgegenstand wird in den folgenden Kapiteln behandelt: (I) Einführung und Nomenklatur; (II) Experimentalmethoden; (III) Individuelle ternäre Phasen; (IV) Einige allgemeine Gesichtspunkte; (V) Hydratation des C_3S, des C_2S und der Purzementpasten, die bei höheren Temperaturen gelagert werden; (VI) Reaktionen, die sich in Kalk-Kieselerde und Zement-Kieselerde-Gemischen, die bei höheren Temperaturen gelagert werden, abspielen. Es ist der Zweck der Kapitel (I)–(IV), die vorhandenen Kenntnisse und die Probleme, die die Forschungen im System $CaO–SiO_2–H_2O$ bei und über 100 °C noch offengelassen haben, zusammenzufassen. Diese Forschungen haben große Bedeutung als das Grundwerk für andere, die den technischen Mann mehr interessieren, und die in Kapitel (V) und Kapitel (VI) besprochen werden. In Kapitel (V) werden überwiegend die Reaktionen in C_3S und in β–C_2S Pasten besprochen; sie sind Modelle für die komplizierteren Reaktionen, die in Purzementpasten auftreten. In Kapitel (VI) werden die Reaktionen in Kalk-Quarz-Gemischen in der gleichen Weise behandelt; sie dienen als das Modell für die Zement-Kieselerde-Gemische.

Die Bedingungen, unter welchen schlecht kristallisierende Tobermoritmineralien hydrothermisch gebildet werden, sind besprochen, aber auf den Phasenaufbau wird nicht näher eingegangen, weil dies in anderen Vorträgen dieses Symposiums behandelt wird.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Department of Chemistry, University of Aberdeen, Scotland.

Introduction and Nomenclature

TABLE 1. *The hydrated colcium silicates (excluding the tobermorite group)* [a]

Name used in this review [b]	Probable or approximate composition: C	S	H	Principal other names in the literature [b]
Nekoite	3	6	7 or 8	----------
Okenite	1	2	2	----------
Z-phase [1,2]	1	2	2	CS_2H_2 [3].
Gyrolite	2	3	2	Centrallassite.
Reyerite	6	10	3	Truscottite.
Xonotlite	6	6	1	----------
Foshagite	4	3	1	----------
Afwillite	3	2	3	----------
Phase Z [4]	3	2	[d] 0	1.5 C/S gamma-type hydrate [5].
$C_6S_4H_3$ [c]	6	4	3	----------
Foshallassite [7] [c]	3	2	3	----------
Phase F [8] [c]	5	3	2	----------
$C_2S\alpha$-hydrate	2	1	1	$C_{10}S_5H_6$ [6], $C_2SH(A)$ [9], dicalcium silicate hydrate (I)[10].
Hillebrandite	2	1	1	$C_2SH(n=1.60)$ [6], $C_2SH(\beta)$ [9], C_2S β-hydrate [11], dicalcium silicate hydrate (II) [10].
Phase Y [4]	6	3	1	$C_6S_3H_2$ [6], $C_2SH(D)$ [9], $C_2SH_{0.5}$ [12,13].
Calcio - chondrodite [14].	5	2	1	Phase X [4].
Tricalcium silicate hydrate.	6	2	3	----------

[a] So-called "C_2S γ-hydrate" (synonyms: $C_2SH(C)$ [9], dicalcium silicate hydrate (III) [10], C_2S aq. [6], Phase X* [4], $C_2SH(CI)$, and $C_2SH(CII)$[13] is probably a mixture of calcio-chondrodite and Phase Z. So-called "CSH(A)" [9] is probably a quaternary phase containing CO_2, substantially identical with the mineral scawtite.

[b] References are given only where necessary to avoid confusion

[c] Phases described by only one investigator.

[d] Phase probably varies in composition, perhaps over the range C_3S_2—$C_6S_3H_2 \cdot$ aq.

TABLE 2. *The tobermorite group. Tentative system of classification and nomenclature*

C/S ratio	Degree of crystallinity: High	Low	Very low
	Complete X-ray powder pattern with *hkl* reflections.	Poor X-ray powder pattern with (mainly) basal and *hk* or *hkO* reflections.	Very poor X-ray powder pattern consisting of one or more *hk* lines or bands. No basal reflections.
Below 1.5 (near 0.83 when fully crystalline).	14-A tobermorite [a] 11.3-A tobermorite or tobermorite [b] 9.35-A tobermorite or riversideite	CSH(I) [d]	Plombierite.[e]
1.5 and over (probably 1.5–1.75 when fully crystalline).	"12.6-A tobermorite"[c] "10-A tobermorite"[c]	CSH(II) [f]	CSH gel.[g]

Notes and synonyms.

[a] Syn. plombierite [15].

[b] Syn. $C_4S_5H_5$ [6], well-crystallized calcium silicate hydrate (I) [16].

[c] The assumption that these species have C/S>1.5 is purely tentative.

[d] Crumpled foils. CSH(I) is here short for "calcium silicate hydrate (I)" and does not imply CSH composition. Syn. CSH(B) [9], 0.8–1.33 C/S hydrate [17], etc.

[e] Gelatinous natural mineral of composition $C_{0.8}SH_2$ [18].

[f] Fibrous. CSH(II) is here short for "calcium silicate hydrate (II)" and does not imply CSH composition. Syn. $C_2SH(II)$ [19], C_2SH_2 [9], 1.5–2.0 C/S hydrate [17], etc.

[g] Short for "calcium silicate hydrate gel," the phase formed in C_3S pastes at room temperature; or any other similarly ill-crystallized material of similar composition. Syn. tobermorite (G) [20], Hydrate (III) [21], etc.

An understanding of the chemistry of cement hydration at elevated temperatures rests first and foremost on a knowledge of the conditions of formation, crystal structures, and properties of the hydrated calcium silicates. The number of these phases is quite large, and it is not surprising that different investigators have evolved their own systems of nomenclature. Tables 1 and 2 show the names that will be used in this paper, together with the probable or approximate compositions of the phases, and the principal other names that have been used for them. The naming of the phases structurally related to tobermorite (table 2) is particularly difficult because some of them are badly crystallized and continuous variations in both composition and degree of crystallinity appear to exist. Any system of classification or nomenclature must therefore contain a large arbitrary element. That proposed in table 2 has been kept as simple as possible, and as knowledge increases further subdivisions will probably be needed. Thus there are indications of more than one variety of 11.3-A tobermorite, and the same is true of CSH(II) and perhaps of other cases. For certain purposes a more detailed terminology will thus eventually be needed. On the other hand, there is also an evident need for broader terms usable where it is impossible or undesirable to be more specific. Terms such as "tobermorite minerals," "tobermorite-like phases," and "tobermoritic material" have been used; some workers use the name "tobermorite" to include the entire group. In this paper the name "tobermorite" will (unless qualified) be restricted to the well crystallized phase with a basal spacing of about 11.3 A. The following broader terms will be used:

Tobermorite mineral: any phase or mixture of phases from the entire group.

CSH (short for "calcium silicate hydrate"): any phase or mixture of phases with a degree of crystallinity defined in table 2 as "low" or "very low." Assarsson [1, 2][1] used the term "phase B" in a roughly similar context; some workers refer to some or all such phases as "gels."

The name "crestmoreite" is used for the oriented intergrowths of tobermorite and apatite minerals which occur at Crestmore, Calif.

No attempt will be made in this review to discuss in detail all the earlier work on the $CaO-SiO_2-H_2O$ system under hydrothermal conditions; for this purpose, earlier reviews [11,19,28] may be consulted.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Experimental Methods

Hydrothermal synthesis and stabilities of phases. The early literature contains several reports of the hydrothermal synthesis of hydrated calcium silicates, but accurate identification of the products was impossible before the introduction of X-ray methods. Among the first significant studies were those of Thorvaldson and his co-workers [10, 22–24], Nagai [25–27], and Bessey [29]. Since then, many investigations have been reported. Flint, McMurdie, and Wells [6] made a notable advance in 1938 with the first systematic study covering a wide range of Ca:Si ratio. Starting materials that have been used include CSH made at or slightly above room temperature, anhydrous C_3S or C_2S, lime-silica mixtures, glasses, and other crystalline hydrated calcium silicates found as minerals or previously made hydrothermally. An important addition was made recently by Roy [30], who used CSH prepared below 100 °C and afterwards gently ignited. The crystallinity of CSH(I) and CSH(II) is reduced by heating at 400 to 600 °C, though it begins to increase again at 600 to 700 °C, when anhydrous crystalline phases begin to form [31]. Gels dried at 400 to 600 °C are probably particularly good starting materials for equilibrium studies because of their high reactivity and homogeneity and relative absence of pre-existing structure.

Most investigators until recently used closed bombs or autoclaves in which the pressure is generated internally. Stainless steel vessels have generally been used, though for the important temperature range below 200 °C sealed glass test tubes with silver inserts are equally satisfactory [39]. Where two fluid phases are present, the pressure is approximately defined by the saturated steam curve; where there is only one fluid phase it can be estimated from the degree of filling of the bomb [32].

Closed bomb techniques are simple, but have serious limitations. Except where saturated steam conditions exist, the pressure is often uncertain and sometimes uncontrollable. During a single run, the pressure and temperature cannot be varied independently. Combinations of high pressure and low temperature are not conveniently obtainable; below about 350 °C pressures higher than that of saturated steam cannot safely be obtained. These weaknesses have been largely overcome by the development of the Tuttle or cold-seal apparatus [33, 34], in which the pressure is externally applied, and can be controlled independently of the temperature. Pressures up to 70,000 psi and temperatures up to 900 °C are readily obtained.

Hydrothermal investigations can be divided broadly into equilibrium and nonequilibrium studies. The object of the first is to define the conditions of stability of the various phases. Two main types of equilibrium study have been made. Firstly, investigators using cold-seal apparatus have established stability relations between different solid phases in terms of P–T curves. Secondly, studies have been made of the compositions of solutions that exist in stable or metastable equilibrium with particular solid phases. Such studies are difficult because of the low solubilities involved, and have so far been made only at relatively low temperatures under saturated steam conditions [6, 35].

Nonequilibrium studies are particularly important in the range below 200 °C which is of direct technical importance. At these temperatures the approach towards equilibrium is slow, and often proceeds through formation of one or more intermediate phases [2, 36, 37]. The sequence of these phases is often markedly affected by small variations in experimental conditions; even minor variations such as the nature of the stabilizer in β-C_2S used as starting material can affect the phases produced under otherwise identical conditions [13, 38]. A given starting material may behave differently in pastes and in suspensions [39]. There are many other variable factors, some of which have been discussed by Kalousek [37].

Both equilibrium and nonequilibrium studies are important for understanding the processes of cement hydration. The equilibrium studies provide invaluable background material, but give little direct indication of the reactions likely to occur in pastes below 200 °C. These reactions show many complexities that could hardly be predicted by attempting to extrapolate P–T curves or other equilibrium data obtained at higher pressures and temperatures.

X-ray powder and optical studies. Since the last symposium, diffractometer methods have been widely introduced. They have clear advantages over film methods in speed and convenience, and, under favorable circumstances, in resolution and in precision of measurement of both spacings and intensities. It must, however, be stressed that they have disadvantages which should cause them to supplement and not supersede film methods. Diffractometer methods have so far proved less satisfactory for observing weak or diffuse reflections, especially at high angles. The surest method of indexing a powder pattern is direct comparison of powder and single crystal films made on the same camera. Occurrence of preferred orientation is more readily detected with suitable film methods. Lastly, where two or more phases occur and differ markedly in crystal size, assignment of lines to phases can often be based on the different textures of the lines when film is used, as the coarser particles give spottier lines. This ability is particularly valuable for studies of preparations made using quartz or β-C_2S, residual traces of which often give rough or spotty lines.

The specific gravity of an anhydrous or hydrated calcium silicate can usually be calculated to ±2 percent from the mean refractive index, using the

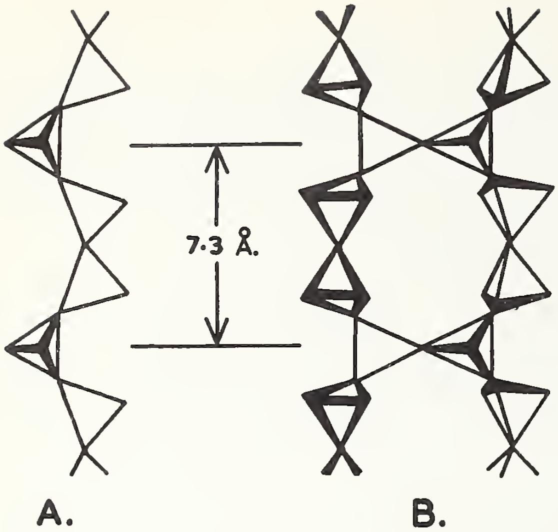

Figure 1. *Silicon-oxygen chains found in hydrated calcium silicates.*

A. Single Dreierkette. B. Double Dreierkette.

Lorentz-Lorenz equation [40]. This procedure has been used as an aid in determining composition [41], and to estimate the specific gravity where direct determination was impracticable [42].

Crystal-structure determinations. Major advances have been made since the London symposium in 1952. At that time, the only hydrated calcium silicates of which the structures were known were afwillite [43] and dicalcium silicate α-hydrate [44], both of which contain isolated $HSiO_4^{3-}$ groups. It was known that a group of hydrated calcium silicates had a repeat distance of about 7.3 A in one direction [19, 45], but the significance of this was not understood. Table 3 lists the compounds with this repeat distance. Anhydrous β-$CaSiO_3$ is included as it is the parent structure from which those of the hydrated compounds are derived. Its structure was established in 1954 by the work of Dornberger-Schiff, Liebau, and Thilo [46] on the isostructural compound $NaAsO_3$. Their results have since been confirmed by direct studies on β-$CaSiO_3$ [47–50]. These investigations disprove an earlier conclusion [51] that $Si_3O_9^{6-}$ rings were present.

Table 3. *Calcium silicates with a repeat distance of about 7.3 A*

Wollastonite	β-$CaSiO_3$
Parawollastonite	
Nekoite	$Ca_3Si_6O_{15}\cdot 7$ or $8\ H_2O$
Okenite	$Ca_3Si_6O_{15}\cdot 6H_2O$
Xonotlite	$Ca_6Si_6O_{17}(OH)_2$
Foshagite	$Ca_4Si_3O_9(OH)_2$
Hillebrandite	$Ca_2SiO_3(OH)_2$
Tricalcium silicate hydrate	$Ca_6Si_2O_7(OH)_6$
Tobermorite minerals:	
Tobermorite (11.3 A)	$5CaO\cdot 6SiO_2\cdot 5H_2O$
14-A tobermorite	$5CaO\cdot 6SiO_2\cdot 9H_2O$ (?)
9.35-A tobermorite (riversideite)	$5CaO\cdot 6SiO_2\cdot 0\text{-}2H_2O$
CSH(I)	$0.8\text{–}1.33^{a}CaO\cdot SiO_2\cdot aq.$
Plombierite	$0.8CaO\cdot SiO_2\cdot 2H_2O$
CSH(II)	$1.5\text{–}2.0CaO\cdot SiO_2\cdot aq.$
CSH gel	

[a] Or 1.5 (?).

An essential feature of the structure of β-$CaSiO_3$ is the occurrence of metasilicate chains kinked so as to repeat at intervals of three tetrahedra (fig. 1a). This gives the characteristic 7.3 A repeat distance. Such chains have been called "Dreierketten" to distinguish them from metasilicate chains kinked in other ways, as for instance the "Zweierketten" of pyroxenes [52]. The German words are provisionally retained as they are not conveniently translatable. Kinking of silicon-oxygen chains in calcium silicates into Dreierketten, rather than into some other form, occurs because this gives a good fit with the dimensions of the CaO_6 polyhedron [52, 53].

Dreierketten have been proved to exist in tobermorite [54] and foshagite [55, 56], while xonotlite contains double Dreierketten (fig. 1b) analogous to the double Zweierketten of the amphiboles [57, 58]. It is reasonable to attribute the 7.3 A repeat distance in the other compounds of this group to the presence of Dreierketten or related structural groupings. Mamedov and Belov [59–63] have discussed theoretically the possible modes of condensation of Dreierketten with each other and with CaO_6 polyhedra, and on this basis have suggested structures for okenite, nekoite, tobermorite, foshagite, hillebrandite, and (in collaboration with Klebtsova) for tricalcium silicate hydrate. Although reasonable, these structures are not based on any direct experimental evidence from X-ray intensities; that proposed for foshagite does not satisfactorily explain the intensity data [56].

No further crystal-structure determinations of the hydrated calcium silicates have been made, but the structure of calcio-chondrodite [14] may be inferred by analogy with the known structure of chondrodite [64]. The latter mineral, which has the composition $(Mg,Fe)_5(SiO_4)_2(OH,F)_2$, is closely related structurally to olivine ($(Mg,Fe)_2SiO_4$), and a calcium analog of olivine exists in γ-C_2S [65]. Olivine and chondrodite are the only magnesium or iron silicates that are known to have exact calcium analogs. The reason for this is probably that they contain separate SiO_4^{4-} tetrahedra, which can be separated more widely to accommodate the larger calcium ion. The other typical magnesium or iron silicate structures, such as the pyroxenes, amphiboles, and micas, contain condensed anions of the Zweierkette or derived types. These cannot be expanded to accommodate calcium, which therefore plays only a limited role in these structures.

Electron microscopy and diffraction. Several early attempts were made to study hydrated C_3S or cement pastes by electron microscopy, but the results seem to have been vitiated by carbonation or other disturbing factors. Grudemo [66, 67] made the first systematic study of pure, hydrated calcium silicate phases using this method; subsequently several others have been made [17, 31, 38, 39, 41, 68–73, 76]. The method of selected-area electron diffraction has also been developed and applied to the study of hydrated calcium silicates

[31, 41, 70–74]. General surveys of this method have geen given [74–75]. More recent applications of electron microscopy and diffraction to the study of the hydrated calcium silicates are described by other contributors to this symposium.

Infrared absorption. Application of this method to studies on hydrated calcium silicates is recent, and the results appear promising. Data have been reported prior to this symposium for tobermorite and related phases [76–78], xonotlite [77, 79], calcio-chondrodite, Phase Y and Phase Z [4], afwillite [80], and $C_2S\alpha$-hydrate [76, 81]. It is too early to assess the significance of the results, or even to interpret them with certainty, but there seem to be distinct possibilities of using the method to determine the form in which constitutional water is present, and other structural features. Two promising extensions of the method are the study of single crystals using polarized beams (applied to afwillite [80]) and investigation of the effect of substituting deuterium for hydrogen (applied to $C_2S\alpha$-hydrate [81]).

Weight-loss curves and differential thermal analysis. Weight-loss curves of hydrated calcium silicates have been determined using dynamic or thermobalance methods [76, 78, 82, 83], and using quasi-static methods in which the temperature is maintained for lengthy periods at successively higher values. Buckle [84] has recently reviewed the theory and practice of the quasi-static method, and has compared its merits with those of the dynamic method. The latter is much faster and therefore alone suitable for most routine work, but the quasistatic method is probably better for most fundamental studies.

Mackenzie [85] has reviewed the technique of differential thermal analysis and its application to clay mineralogy. The method has been applied to the study of hydrated calcium silicates, especially by Kalousek and collaborators [5, 37, 86–91].

The value of both weight-loss and DTA studies is increased if they are supplemented by X-ray studies made either with high-temperature cameras, or on cooled material. It is important to control the atmosphere, and essential to exclude CO_2, in all of these studies.

Oriented transformations. This term will be used to describe reactions in which crystals of one substance are formed out of those of another in such a way that crystallographic orientation is substantially preserved. Heller [92] reported the first, exploratory studies in the $CaO\text{-}SiO_2\text{-}H_2O$ system; the reactions she studied were mostly dehydrations effected by heating at ordinary pressures. Since then more such studies have been made [70–72, 93–97], and it has also been shown that some hydrothermal changes, such as that of tobermorite into xonotlite, occur or can occur in this way [98]. New experimental methods for the study of both thermal and hydrothermal transformations have been described [98–100]. Studies on oriented transformations provide a powerful means of linking crystal-structural information with chemical or phase-equilibrium data. From one such study it was concluded that the dehydration of a number of hydrated calcium silicates at about 700 °C involves rupture of Si-O rather than Ca-O bonds, with consequent migrations of silicon atoms or ions [94]. This conclusion enabled the prediction of the essential features of the crystal structure of foshagite, which were afterwards tested by classical X-ray methods [55, 56, 72].

Chemical extraction methods. There have been recent developments in methods for extracting uncombined $Ca(OH)_2$ [20, 101–103]. Some workers have also used methods for extracting uncombined silica, but the difficulties inherent in this procedure have been emphasized [104].

Individual Ternary Phases

Optical, X-ray powder, unit cell, specific-gravity, and other crystallographic data will not be listed as they were tabulated for most of the phases by Heller and Taylor [105] in 1956. Table 4 gives references to the principal additions or corrections to these data. Several new sets of powder data for other compounds have been published, but none differ significantly from the earlier data. The phases will be described roughly in order of increasing Ca:Si ratio, but this principle is sometimes departed from in order to group together related phases.

Okenite (CS_2H_2?) *and nekoite* ($C_3S_6H_{7\ or\ 8}$). These are the only two hydrated calcium silicates which are known to occur as well-defined natural minerals, but which have not yet been synthesized. Hydrothermal runs at low Ca:Si ratios little above 100 °C, which might be expected to yield them, appear to give instead compounds of the tobermorite or gyrolite groups together with hydrous silica. There has been one recent report of the

TABLE 4. *Crystallographic data for the hydrated calcium silicates. Principal additions or corrections to the compilation by Heller and Taylor [105]*

Phase	Nature of new data	References
Z-phase	X-ray powder data for new phase	[2,3]
	Sp. gr., refractive index	[3]
11.3-A tobermorite	Crystal structure	[54]
	Indexing of X-ray powder data	[71]
9.35-A tobermorite (riversideite).	Indexing of X-ray powder data, unit cell	[95]
Foshagite	Revised composition, unit cell, indexing of X-ray powder data	[72]
	Crystal structure	[55,56]
Phase F	X-ray powder data for new phase	[8]
Phase Z	X-ray powder data and optical properties of new phase	[4]
	Unit cell	See text.
Phase Y	X-ray powder data and optical properties of new phase	[4]
	Unit cell, specific gravity, indexing of X-ray powder data	[42]
C_2S γ-hydrate	Probably not a single phase	See text.
Calcio-chondrodite (Phase X).	X-ray powder data (indexed), unit cell, specific gravity, crystal structure (by analogy)	[14]
	Optical and X-ray powder data	[4]
Tricalcium silicate hydrate.	Indexing of X-ray powder data, unit cell, specific gravity	[41]

synthesis of nekoite [106], but it is based solely on optical evidence and cannot be considered established.

Okenite has been known as a mineral for over a century [70,107]. Nekoite is known only from one locality. It was originally described as okenite [108], but recent work has shown that it is a distinct species. It nevertheless resembles okenite in many ways and there is almost certainly a close structural relationship [70].

Published analyses indicate the formula CS_2H_2 for both minerals. A new analysis of nekoite suggests a higher water content, giving $C_3S_6H_7$ or $C_3S_6H_8$; the water is mostly lost by 200 °C, and there is infrared evidence to support the inference that it probably occurs in molecular form [109]. Synthesis is therefore most likely to be effected at low temperatures, possibly around 100 °C; prolonged reaction may be needed. This conclusion probably applies also to okenite.

Both okenite and nekoite form fibrous or markedly acicular crystals with one good cleavage in the prism zone and a 7.3 A repeat in the fiber direction [70]. On being heated at 800 °C, both minerals undergo oriented transformation giving β-$CaSiO_3$ [70,92]. Assuming the water to occur as molecules, the formulae of both minerals can be written $CaSi_2O_5 \cdot xH_2O$. These results strongly indicate the presence of Dreierketten condensed together to give infinite sheets of empirical composition $Si_2O_5^{2-}$. Mamedov and Belov [59] suggested a way of doing this which would explain the observed cell dimensions.

Gyrolite ($C_2S_3H_2$), *reyerite or truscottite* ($C_6S_{10}H_3$?) *and Z-phase* (CS_2H_2?). These three phases are structurally related; all form lamellar crystals with micaceous (0001) cleavage and are hexagonal or pseudohexagonal with a 9.73 A. They are most readily distinguished by their basal spacings, which are approximately 22.1 A for gyrolite [97,110], 18.7 A for reyerite [110,111], and 15.3 A for Z-phase [2]. Gyrolite and reyerite occur naturally [112–114]. Z-phase has not been found pure in nature, though some specimens of gyrolite probably contain minor amounts of it intergrown in parallel orientation [115]. The reported mineral centrallassite is identical with gyrolite, while truscottite is the same as reyerite [110]. The name reyerite has priority.

Doubts exist regarding the exact compositions of all three phases. Analyses of natural and synthetic gyrolites mostly agree reasonably well with the formula $C_2S_3H_2$ [112–115a], but Strunz and Micheelsen [110] have recently proposed the formula $C_3S_4H_3$. Analyses of natural reyerite or truscottite are hard to interpret because both of the known specimens are contaminated by other minerals which are difficult to separate. The formulae C_2S_4H and $2(CaO, MgO) \cdot 3SiO_2 \cdot 2H_2O$ have been suggested for truscottite (reyerite from Sumatra) while C_3S_4H has recently been proposed for reyerite from Greenland [110]. Harker [115a] recently found the composition of synthetic reyerite to be $C_6S_{10}H_3$. As will be seen later, reyerite is formed at relatively high temperatures, and the H_2O:Si ratio is therefore more likely to be 1:4 than 2:3. The Ca:Si ratio must be considered uncertain, though it appears definitely to be between 0.5 and 0.75. Harker's formula is perhaps the most probable.

Funk and Thilo [3] described a new phase in 1955, which they considered to have the formula CS_2H_2. Shortly afterwards, Assarsson [1,2] reported a new compound of uncertain but probably similar composition which he called Z-phase. Comparison of the X-ray powder patterns reported for these phases suggests that they are identical. Preliminary X-ray powder studies have been made in this laboratory of a specimen kindly provided by Funk. The powder data reported by Funk and Thilo were confirmed, but the patterns gave also a strong spacing of about 15 A, which was considered by Assarsson to be characteristic of Z-phase. The identity of the two preparations is thus confirmed. The similarity of the X-ray powder pattern to that of gyrolite suggests a structural resemblance, and the unit-cell or structural element is therefore probably hexagonal or pseudohexagonal with a 9.73, c 15.3 A, approx. The orthorhombic cell suggested by Funk and Thilo seems unlikely to be correct. It was based only on indexing of powder data.

Most of the data relating to the conditions of formation of these phases relate to saturated steam conditions, but Harker [115a] has briefly reported P-T curves defining the stabilities of gyrolite and reyerite, while Assarsson [116] made some runs in superheated steam. Gyrolite was first synthesized by Flint, McMurdie, and Wells [6] from gels and glasses with Ca:Si ratios in the range 0.5 and 0.66, at 150 to 400 °C. At 450 to 500 °C α-$CaSiO_3$ was obtained. They did not, however, distinguish gyrolite from reyerite; subsequent evidence suggests that the latter was probably formed at the higher temperatures. Subsequently, a number of workers have confirmed the formation of gyrolite, as distinct from reyerite or Z-phase, at temperatures mostly between 120 and 240 °C [1, 2, 8, 37, 79, 97, 104, 115a]. It appears to form very slowly at 120 °C, and more rapidly at 150 °C or above from gels or mixtures of lime with amorphous silica. The upper limit is at least 240 °C, though Harker's results show that gyrolite becomes unstable relative to reyerite and xonotlite above 220 °C; in the presence of excess silica, it becomes unstable relative to reyerite above 190 °C. Harker also found that formation of gyrolite was favored by the presence of up to 2 percent of alkali fluoride.

Buckner, Roy, and Roy [79] reported the formation of reyerite and gyrolite, together with other products, at 295 °C and 30,500 psi. This is the earliest report of the synthesis of reyerite. The inference that the phase is stable relative to gyrolite under these conditions was confirmed by Harker [115a], who showed that reyerite becomes unstable relative to xonotlite and silica above 355 °C at saturated steam pressure.

Jander and Franke [12] and Funk and Thilo [3] obtained products at 300 to 350 and 250 °C respectively, which could have been reyerite.

Peppler [35] determined the solubility relations at 180 °C for a preparation which he had identified as gyrolite; he found this compound to be metastable relative to xonotlite and hydrous silica at this temperature. This result seems to be incompatible with Harker's. Peppler had made his preparation by autoclaving an oxide mixture at 350° C, and it may therefore have consisted wholly or partly of reyerite.

Assarsson [1,2] obtained Z-phase by autoclaving mixtures of lime and amorphous silica at 140 to 240 °C. He could not prepare it at 120 °C, but his longest runs were only of 21 days' duration. He considered that it was an intermediate product in the sequence lime+silica gel→CSH(I)→Z-phase→gyrolite, and believed that it might have a stable field of existence at 130 to 150 °C. This is almost certainly too high, as gyrolite can be made at 120 °C. Funk and Thilo [3] obtained their product by autoclaving gels at 180 °C for 1 to 2 days; these conditions are comparable with those used by Assarsson.

These results indicate that Z-phase is the least, and reyerite the most, thermally stable of the three phases. The structural and compositional relations between the three compounds are not clear. The relationship does not appear to be simply one of varying numbers of water molecules between otherwise identical layers, since Z-phase has the shortest basal spacing but is formed at the lowest temperatures and is therefore presumably the most hydrous. Further studies on the compositions of all three phases are clearly needed.

Gyrolite loses three-quarters of its water below 450 °C; the structure undergoes relatively minor changes. The rest of the water is lost at 500 to 850 °C when oriented transformation occurs giving α-$CaSiO_3$ [97]. The principal water loss in reyerite probably also occurs around 800 °C [111]. A loss was also observed in a lower temperature range, but no change was detectable by X-rays, and this loss may have been caused by impurity. Z-phase loses one-half of its water by 100 °C, and the rest in two stages between 100 and 900 °C [3].

At present nothing is known about the crystal structures of these phases, but the oriented transformation of gyrolite to α-$CaSiO_3$ provides a possible clue, as the structure of the latter compound is known from work on the isostructural $SrGeO_3$ [117]. Another possible structural relation is with zeophyllite ($Ca_4Si_3O_{12}F_2H_6$) [96]. This mineral has also micaceous cleavage and is pseudohexagonal, with an a-axis not far from that of gyrolite.

Tobermorite ($C_5S_6H_5$). Crystalline tobermorite with a basal spacing of about 11.3 A occurs naturally in a pure form in Scotland [71,118] and N. Ireland [15], and in crestmoreite intergrowths at Crestmore, Calif. [108,119]. It is the essential constituent of most high-pressure steam-cured concrete and lime-silica products [37,120].

The first clearly described synthesis was made by Flint, McMurdie, and Wells [6]. They considered their product to be $C_4S_5H_5$ and remarked on its possible identity with the natural mineral. The next reported syntheses were by Heller and Taylor [16] and by Kalousek [37]. Heller and Taylor called their product "well crystallized CSH(I)." Taylor [119] showed that this preparation was essentially similar to the silicate constituent of crestmoreite, and Claringbull and Hey [118] showed that it was substantially identical with the pure, natural tobermorite from the type locality. These investigations established definitely the relationship between the natural and synthetic materials. Tobermorite has since been prepared by many other investigators [2, 68, 73, 76, 79, 82, 120, 121].

Among the more important of possible starting materials may be mentioned CSH(I), and mixtures of lime or cement with either quartz or amorphous silica. In the latter case, as is discussed later, reaction proceeds through intermediate formation of CSH(II) and CSH(I), or of phases similar to these. Formation of tobermorite under saturated steam conditions has been reported at temperatures varying between 110 [16] and 275 °C [6]. In the author's experience, it is most reproducibly formed by autoclaving a CSH(I) gel of appropriate Ca:Si ratio at 110 to 140 °C. Transformation to tobermorite at these temperatures is slow, periods of a month or longer usually being needed to complete the process, but a pure product can be obtained. It appears to persist indefinitely under these conditions, though whether it is truly stable is not known. It can be obtained more rapidly at higher temperatures, but is then definitely only an intermediate phase, and much care is needed to avoid partial or complete conversion into xonotlite or other phases. In pastes, it is reproducibly formed at 170 to 180 °C, though again only as an intermediate phase and probably rarely, if ever, free from other phases.

A broader view of the conditions of formation of tobermorite is obtained by considering the entire P–T field and not merely the curve defined by the pressure of saturated steam. Buckner, Roy, and Roy [79] showed that, at 12,000 to 25,000 psi, the equilibrium curve for the transformation of tobermorite to xonotlite, water, and possibly reyerite, lies at about 285 °C. This result points to the possibility of preparing pure samples of tobermorite both quickly and reproducibly by working at considerably higher pressures and temperatures than those commonly used hitherto. Under saturated-steam conditions, tobermorite begins to change to xonotlite at about 150 °C (75 psig). The same minimum temperature for the formation of xonotlite, to within ±10 °C., has been reported by several investigators. It is uncertain whether this temperature represents a point on the equilibrium P–T curve, or whether it is rate determined.

Electron micrographs of typical, synthetic preparations show well-defined flakes up to several microns across and possibly 200 A thick [17, 31, 68, 73]. The cleavage is (001) and there is in varying degrees a tendency to elongation parallel to *b*. Edges parallel in projection to (110) are often also developed. The selected-area electron-diffraction pattern is characteristic [31, 71, 73]. It shows the weak reflections indexable only in terms of the C-centered unit cell with *a* 11.3, *b* 7.3A approx, as well as the strong ones corresponding to the body centered pseudocell with halved *a* and *b*. The weak reflections are characteristic of tobermorite, but the strong ones are given by any sufficiently well-crystallized tobermorite mineral, including CSH(II), lying on (001) [31]. From selected-area electron-diffraction studies, Gard, Howison, and Taylor [31] found that tobermorite crystals sometimes lie superimposed one on the other in a relative orientation which suggested that their surfaces are derived from the Ca—O and not the Si—O part of the structure.

The main features of the crystal structure were established by Megaw and Kelsey [54], though some details are still uncertain. These investigators confirmed earlier suggestions of a layer structure in some respects analogous to that of vermiculite. They showed that each layer consists of a central Ca—O sheet covered on each side by rows of Dreierketten that form ribs. They likened the resulting complex layer to double-sided corrugated cardboard. Between these complex layers are more calcium atoms, and water molecules. The structure explains the observed morphology, and also the existence of higher and lower hydrates differing in *c*-spacing. Mamedov and Belov [60] suggested a modification of this structure involving the existence of Si—O—Si links between neighboring layers. It is not yet clear to what extent this modification is compatible with Megaw and Kelsey's experimental data. The question of the occurrence of such links is considered again later.

Infrared absorption data [76, 77] have been considered to support the view that both water molecules and bonded hydroxyl are present. Assuming Megaw and Kelsey's structure to be correct, the constitutional formula may be written as $Ca_4(Si_3O_9H)_2 \cdot Ca \cdot 4H_2O$. The hydroxyl is thus attached to silicon: the final $Ca \cdot 4H_2O$ denotes the interlayer material.

Most specimens of tobermorite change to 9.35-A tobermorite (riversideite) when heated to 300 °C at atmospheric humidity [15, 77, 95]. Taylor and co-workers [31, 71, 122], and Greenberg [82] obtained weight loss curves that were almost continuous, but McConnell [15] obtained a markedly stepped curve. More work is needed to decide the extent to which these differences can be explained by variation in experimental technique. On differential thermal analysis, Al-free tobermorite gives only a small exothermic peak or none at all at 800 to 850 °C [15, 68, 76, 91]. Al-substituted tobermorite, and also CSH(I), give a strong exothermic peak in this region [91].

Hydrothermal treatment of tobermorite with water causes oriented transformation to xonotlite without intermediate formation of riversideite [98].

Modified or anomalous forms of 11.3–A tobermorite. Kalousek [91] described the synthesis of tobermorite in the presence of reactive aluminous materials; he found that up to 4 or 5 percent of Al_2O_3 could enter the structure, the Al possibly substituting for Si. Al-bearing tobermorite differed from the pure compound in its thermal behavior, as mentioned above. At high Al-contents, there were also minor changes in the X-ray pattern, and the crystal size was reduced. Formation of tobermorite was accelerated, and conversion to xonotlite retarded by the presence of alumina.

Some other tobermorite specimens, both of synthetic and of natural origin, are anomalous in various ways. A natural specimen from Loch Eynort, Scotland, had a distinctly more fibrous form than is usual, with principal cleavage (100) [71]. The basal spacing of 11.3–A persisted right up to 800 °C, when β-$CaSiO_3$ was formed, even though all the water was lost below this temperature. The weaker electron-diffraction reflections, not indexable in terms of the pseudocell, differed from those of normal specimens. Some synthetic specimens free from alumina are also anomalous in that the 11.3–A spacing persists up to 800 °C [8]. In others, electron micrographs show, not the usual plates with conchoidal fracture, but plates that are composed of parallel laths imperfectly joined together [17,31]. These have been interpreted as CSH(II) fibres in course of forming into tobermorite [31] and, alternatively, as CSH(I) sheets showing incipient cleavage or breakdown [17]. There seems to be no evidence as to whether this morphology is correlated with persistence of the 11.3–A spacing except in the case of the Loch Eynort material.

Recent work shows that the Ca:Si ratio of tobermorite, as opposed to CSH(I), is not capable of wide variation, but it apparently can rise as high as 1.0 without any marked effect on the properties [17].

More work is needed before these anomalies can be explained. Clearly, however, the structure of tobermorite is capable of minor variations, which are difficult or impossible to detect by X-ray powder methods, but which markedly influence the morphology and behavior on dehydration. These variations can be caused by Al-substitution, but are not always due to this. It is tempting to speculate that they can be correlated with the formation of Si—O—Si links between the layers, possibly in the way suggested by Mamedov and Belov [60]. This correlation could account for the ability to undergo complete dehydration without shrinkage in *c*-spacing, and possibly also for the fibrous habit and the otherwise puzzling (100) cleavage of the Loch Eynort material.

9.35–A tobermorite (riversideite). $5CaO \cdot 6SiO_2 \cdot 0\text{-}2H_2O$. This is formed when "normal" specimens of tobermorite are heated to 300 °C or above at ordinary humidity. The change in basal spacing is discontinuous [95]. The 9.35–A tobermorite also occurs naturally in some specimens of crestmoreite intergrowth; these were originally called riversideite [108], and this name has since been transferred to their hydrated calcium silicate constituent [15].

X-ray studies [95] confirm Megaw and Kelsey's suggestion [54] that the stacking of the layers differs from that in 11.3–A tobermorite; the ribs on the surface of one layer pack into the grooves on that of the next, whereas in 11.3–A tobermorite the layers pack rib against rib. They show also that formation of riversideite from tobermorite is accompanied by marked reduction in the degree of crystallinity.

When riversideite is formed at the minimum temperature of about 300 °C [95] the H_2O:Si ratio is about 0.3 according to McConnell's data [15] or below 0.2 according to data from this laboratory [31, 122]. All the water is expelled by 700 °C but the X-ray pattern shows little or no change between 300 and 700 °C. It has been concluded from this observation that interlayer Si—O—Si links are formed [95]. There is some evidence that part or all of the water is present as molecules [77, 95]. Riversideite has not been made hydrothermally. It should possibly be regarded as a metaphase, with no field of true stability.

14–A tobermorite. $C_5S_6H_9$ (?). This occurs in nature as the main constituent of many specimens of crestmoreite [119]. McConnell [15] suggested the name plombierite, but later [18] used this for a gelatinous phase of approximate composition $C_5S_6H_{12}$ which was of much lower crystallinity. Historical evidence favors its use for the gelatinous mineral, and it seems preferable not to use it also for the very different crystalline one.

The 14–A tobermorite has been synthesized from lime-silica slurries at 60 °C [77]. It probably consists of layers of tobermorite stacked rib against rib, as in the 11.3–A form, but separated by a further layer of water molecules. There cannot, therefore, be any interlayer Si—O—Si links. The H_2O:Si ratio of 1.5 suggested above is based not on experimental evidence, but on a plausible density of packing of the extra water molecules. Infrared absorption data have been reported [77]. Dehydration to the 11.3–A form occurs at 100 °C [122]; McConnell found the process to be reversible [15], but attempts by the author to rehydrate 11.3–A tobermorite have been unsuccessful.

10–A and 12.6–A tobermorites. Well-crystallized tobermorite minerals with these basal spacings occur in some specimens of crestmoreite [105]. The basal spacings suggest that the 10–A form may be a well-crystallized form of CSH(II) and that the 12.6–A form is a more highly hydrated form of this, but there is no proof.

Ill-crystallized tobermorite minerals. These phases, which are classified in table 2, are characteristically formed below 100 °C, and are therefore discussed elsewhere in this symposium. They have also been reviewed recently by the present author [123]. Some reference to them is nevertheless needed because they are also formed as intermediate products in hydrothermal processes. As such, they play an important part in the steam curing of cement.

CHS(I) is characterized by a low Ca:Si ratio, which can be anything from 0.8 to 1.33 or possibly 1.5, and by its morphology of thin, crumpled foils. It gives a strong differential-thermal-analysis peak at 800 to 850 °C. The basal spacing of material dried at 6 mm varies between about 10 and 14A, depending on Ca:Si and H_2O:Si ratios and on other factors not properly understood. The reasons for the variable composition are still uncertain; the material is in many ways a typical, semicrystalline basic salt and is possibly inherently inhomogenous.

CHS(I) is very easily formed and appears to persist indefinitely at room temperatures. Under hydrothermal conditions it seems to be a short-lived intermediate product, which recrystallizes rapidly to tobermorite or other phases. Thus, Kalousek and Prebus [17] showed electron micrographs of typical crinkly foils of CSH(I) made in 2 hr reaction of lime and diatomite at 175 °C; in contrast, Gard, Taylor, and Howison [31] obtained no evidence of CSH(I) in the products of 7 day reactions at 140 °C. They found only CSH(II) and tobermorite.

Plombierite is a natural mineral showing some resemblance to CSH(I), although there are distinct differences [18].

CSH(II) is characterized by a high Ca:Si ratio, which probably always lies within the range 1.5–1.75. The morphology is characteristically fibrous but varies with the mode of preparation; cigar-shaped bundles of fibres [20, 38, 66, 67], long, thin fibres [17, 31], and tubular forms [17] have all been observed. The basal spacing of material dried at 6 mm is about 10.5A. The degree of crystallinity, as evidenced by the X-ray pattern, tends to be lower than that of CSH(I), though the samples consisting of cigar-shaped bundles are better crystallized than the others. The crystal structure is unknown, but is clearly related to that of tobermorite. The possibility of a 1:1 layer structure, in contrast to the 2:1 layer structure of tobermorite, has recently been suggested [31]. If this structure is correct, CSH(II) stands in something like the same relation to the hydrated form of halloysite as does tobermorite to vermiculite.

CSH(II) is probably the initial product of reaction between lime and silica, under hydrothermal conditions as well as at room temperature. It seems to be more persistent than CSH(I), but is nevertheless only an intermediate phase, even at 100 °C. Various, more stable phases can crystallize directly or indirectly from it at 100 to 180 °C and the factors determining which of them will appear in any given case are not fully understood. Afwillite is probably the stable product below about 140 °C, and hillebrandite above this temperature, but neither forms readily and $C_2S\alpha$-hydrate is the most usual product over the whole temperature range. Other possible products include $C_6S_4H_3$ and "Phase F."

CSH gel is the product formed in β-C_2S or C_3S pastes cured at room temperatures. It is also formed as the first product in such pastes at higher temperatures, up to at least 180 °C [38,39]. It resembles CSH(II) closely in composition, and in some other respects, but differs so much in degree of crystallinity, and possibly also in morphology, that it seems wiser to distinguish between them. The phases crystallizing from CSH gel are similar to those formed from CSH(II). In neat cement or C_3S pastes, where a sufficient excess of $Ca(OH)_2$ is also present, tricalcium silicate hydrate is a further recrystallization product.

A natural mineral recently described by McConnell [124], and the sythentic "Hydrate III" described by Kantro, Brunauer, and Weise [21] each appear to be roughly similar in composition and crystallinity to CSH gel.

Xonotlite. (C_6S_6H). This phase occurs as a natural mineral in many localities. It is also one of the easiest of the hydrated calcium silicates to make in the laboratory. The first well established synthesis was by Nagai [27]; syntheses up to 1950 were reviewed by Taylor and Bessey [11]. Since then many more have been reported. Xonotlite is formed reproducibly from any sufficiently reactive starting materials of its own Ca:Si ratio at 150 to 400 °C under pressures of saturated steam. Its formation from lime and silica proceeds through intermediate formation of CSH(II), CSH(I), and tobermorite [2,16]. The equilibrium P–T relations between xonotlite and tobermorite have already been discussed. Figure 2 shows the P–T curve for the equilibrium between xonotlite and β-$CaSiO_3$ [79]. Peppler [35] studied solid-liquid equilibria for xonotlite at 180 °C under a pressure of saturated steam. He concluded that it was a stable ternary phase in the system under these conditions.

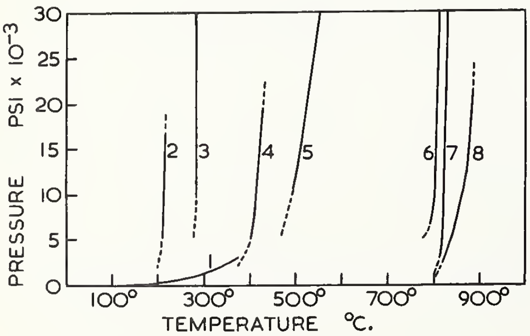

FIGURE 2. *P–T curves for some phase transformations in the* CaO-SiO_2-H_2O *system, obtained by Roy* [4] *and Buckner, Roy, and Roy* [79].

(1) H_2O liq.$\rightleftharpoons H_2O$ gas. (2) Afwillite$\rightleftharpoons$Phase Z$+H_2O$. (3) Tobermorite$\rightleftharpoons$xonotlite$+H_2O+$(?) reyerite. (4) Xonotlite$\rightleftharpoons\beta$-$CaSiO_3+H_2O$. (5) Tricalcium silicate hydrate$\rightleftharpoons$Ca-chondrodite$+Ca(OH)_2+H_2O$. (6) Phase Y$\rightleftharpoons\alpha'$-$C_2S+H_2O$. (7) Phase Z$\rightleftharpoons$Rankinite$+H_2O$. (8) Ca-chondrodite$\rightleftharpoons\alpha'$-$C_2S+CaO+H_2O$.

Xonotlite forms markedly fibrous or acicular crystals with a repeat distance of 7.3 A in the fiber direction. Synthetic crystals have a characteristically lath-like appearance in the optical or electron microscope [6,73]. These properties are satisfactorily explained in terms of the crystal structure, which was found by Mamedov and Belov [57,58] to contain double Dreierketten, of empirical formula $Si_6O_{17}{}^{10-}$ (fig. 1b) together with calcium and hydroxyl ions.

Published analyses of natural and synthetic xonotlites nearly all show higher water contents than that demanded by the formula $Ca_6Si_6O_{17}$-$(OH)_2$ which is indicated by the X-ray structure determination; many indicate a composition of about C_5S_5H. Weight-loss curves [8,79] show approximately the theoretical loss of 1/6 H_2O:Si over the range 650 to 750 °C in which conversion to β-$CaSiO_3$ occurs, together with additional water that is lost gradually at lower temperatures. This circumstance suggests that the formula $Ca_6Si_6O_{17}$-$(OH)_2$ is fundamentally correct, but that additional, more loosely bound water is usually or always present. The way in which this water is held is uncertain, although differential thermal analysis [79] and infrared absorption [77,79] constitute promising lines of approach. The question has also been discussed recently by Buckner, Roy, and Roy [79], and by Aitken and Taylor [8]. The dehydration reaction occurs by an oriented transformation, whether on heating at ordinary humidity [94] or under hydrothermal conditions [98].

Foshagite. (C_4S_3H). This phase was discovered as a natural mineral, and was originally believed to have the composition $C_5S_3H_3$ [125]. Its individuality as a species was at one time disputed, but was later established beyond doubt [6,72]. The original formula is, however, incorrect. Foshagite was first synthesized by Flint, McMurdie, and Wells [6] from glasses at 300 to 350 °C. under pressures of saturated steam. The synthesis has since been confirmed; Jander and Franke [12] made a product at 300 to 350 °C which was probably foshagite, while Gard and Taylor [72] prepared it at 500 °C and 6,000 psi, and Roy [4] at 450 °C and 15,000 to 30,000 psi. No P-T curves defining its stability range have been reported.

The crystals are markedly acicular, and the natural mineral forms long fibers [125]. There is a 7.3-A repeat distance along the fiber direction. The approximate crystal structure has been determined from X-ray fiber rotation photographs, and shows the presence of single Dreierketten together with calcium and hydroxyl ions [55, 56]. An alternative structure, involving double Dreierketten as in xonotlite [61], does not satisfactorily explain the X-ray intensities and other experimental data [56]. Foshagite is dehydrated at 650 to 750 °C, when it undergoes oriented transformation giving β-$CaSiO_3$ [92, 72]. There is also a tendency for β-Ca_2SiO_4 to crystallize, but the lime-rich product of this disproportionation is probably largely amorphous [56].

Afwillite. ($C_3S_2H_3$). This phase occurs as a natural mineral [126]. It forms short, prismatic crystals, and is remarkable among hydrated calcium silicates for its good crystallinity. Afwillite is a low-temperature product, which forms under pressures of saturated steam below about 160 °C. It was first synthesized by Bessey [11] at 98 °C. It has since been obtained by ball-milling of C_3S with water at room temperature [21, 127] and from lime-silica mixtures or β- or γ-C_2S at 110 to 160 °C [36, 128]. Its formation seems always to be slow. Heller and Taylor [36, 128] concluded from runs of 13 to 151 days' duration that afwillite was a stable phase at 110 to 160 °C, while Long and McConnell [124] obtained geological evidence that afwillite can exist in stable equilibrium with $Ca(OH)_2$ and solution at relatively low temperatures.

Although afwillite is probably a stable product, it is not readily prepared. Its formation from lime-silica mixtures, β-C_2S, or C_3S probably involves the intermediate formation of CSH(II) or similar material. As has already been noted, this compound changes more readily into other metastable but highly persistent phases, especially $C_2S\alpha$-hydrate. Under a pressure of saturated steam, afwillite probably becomes unstable relative to xonotlite and hillebrandite at about 140 °C. At higher pressures (fig. 2) it apparently remains stable until above 200 °C; the immediate decomposition products were unidentified, but at 300 °C and above Phase Z was obtained [4].

When afwillite is heated at atmospheric pressure, dehydration takes place at 275 to 285 °C [126, 129]. An oriented transformation occurs, giving γ-C_2S [92, 93, 129]. A preliminary discussion of the mechanism of this transformation has been given [93], but the question is complicated by the formation of one or more unstable, intermediate phases, a full explanation of which is not yet available [129]. On heating further to about 650 °C, a further oriented transformation occurs, giving an anhydrous, poorly crystalline form of Phase Z [4, 129]. This product was called "Phase Y" by Heller [92] (not the same as Roy's Phase Y!). At about 1,000 °C, rankinite is obtained [92]. The dehydration of afwillite has also been followed by differential thermal analysis [129].

Megaw [43] determined the crystal structure of afwillite; it is built from Ca^{2+} ions, H_2O molecules, and separate $HSiO_4{}^{3-}$ tetrahedra. Afwillite is structurally related to bultfonteinite ($Ca_4Si_2O_{10}H_6F_2$ [130]), but not closely to any other of the ternary phases. Infrared studies [80] support the results of the X-ray structure determination.

Phase Z. (C_3S_2—$C_6S_3H_2$ (?)). This phase was first described by Roy [4, 131], and must be distinguished from Z-phase (of Assarsson). It has not yet been reported as a natural mineral. Roy believed it to be C_9S_6H, but subsequent work suggests a variable composition, one end of the presumed solid-solution series being anhydrous. Roy made Phase Z from gels, and from afwillite, in runs of 1 to 14 days' duration (mostly 1 to 3 days) at about 300 to 830 °C and 2,000 to 20,000 psi. As already mentioned, an anhydrous variety of Phase Z is also produced when afwillite is heated in air at 650 °C. Work in this laboratory, on a specimen kindly provided by Roy, which had been made hydrothermally at 715 °C and 16,500 psi, showed that this specimen lost no weight in the range 100 to 1,400 °C. The material formed under such conditions is therefore anhydrous. In contrast, specimens made at lower temperatures and pressures appear to have higher Ca:Si ratios and to be hydrated. This result can possibly be attributed to hydrogarnet-type replacement of Si by 4H, which would give compositions trending towards $C_6S_3H_2$; further work is in progress to test this hypothesis. The so-called "C_2S γ-hydrate" or "$C_2SH(C)$" is probably a mixture containing the lime-rich, hydrated form of Phase Z as one constituent; this is discussed later.

The stability relations of Phase Z are not fully established. Roy obtained curves (fig. 2) for the upper stability limits of afwillite and of Phase Z, and it might be inferred that the latter was stable in the intervening field. However, longer runs appeared to give different products [132], and Phase Z may be unstable relative to Phase Y and other compounds, such as wollastonite or foshagite, over part or all of this range.

Roy [4] gave optical, X-ray powder, and infrared absorption data for Phase Z. The approximate unit-cell parameters have been determined in this laboratory from a combination of selected-area electron diffraction and X-ray work; the cell is orthorhombic or pseudoorthorhombic, body centered, with *a* 5.07, *b* 11.3, *c* 23A approx; the crystals are flaky with (001) cleavage. The unit-cell contents, for the anhydrous form of the phase, are 8 [C_3S_2]. The *a* and *b* dimensions are about the same as the corresponding ones for γ-C_2S and calciochondrodite, and Phase Z is evidently related structurally to these two compounds.

Incompletely characterized phases with Ca:Si near 1.5. Three apparently different phases of roughly similar compositions have each been reported only once. "$C_6S_4H_3$" was described by Flint, McMurdie, and Wells [6], who made it from glasses and from CSH(II) at 150 to 200 °C. They gave optical data, and the X-ray powder pattern was later reported [133]. "Phase F," of possible composition $C_5S_3H_2$, was reported by Aitken and Taylor [8] as a product formed in lime-quartz pastes cured at about 165 °C. Its formation was irreproducible, some specimens of lime giving it and others not. "Foshallassite," of approximate composition $C_3S_2H_3$, was reported as a natural mineral by Tschirwinsky [7]. The sum of the analysis was only 97.15 percent and the mineral was possibly zeophyllite.

Dicalcium silicate α-hydrate. (C_2SH). This phase is not known as a natural mineral; it was first isolated by Thorvaldson and Shelton [22] from steam-cured cement mortars. Early preparations are reviewed by Taylor and Bessey [11]. The compound has since been obtained by many investigators at temperatures usually between 100 and 200 °C under pressures of saturated steam [2, 5, 13, 36, 76]. The most usual starting materials have been lime-silica mixtures, gels, β- or γ-C_2S, or C_3S; in the last case, $Ca(OH)_2$ is also obtained. C_2S α-hydrate is readily formed from any of these starting materials; crystallization is further assisted by seeding [13]. Its formation is probably always preceded by that of CSH(II) or similar poorly crystallized material, and it is thus one of the several phases that can form from this below about 200 °C. Under most conditions it seems to be the most readily formed, and it is a common if not universal phase in steam-cured cement or lime-silica pastes of sufficiently high overall Ca:Si ratio. Its presence in steam-cured products is undesirable; this is considered later. Although C_2S α-hydrate crystallizes so readily, it does not seem ever to be produced as a stable phase. Below about 140 °C under saturated steam conditions, it is probably unstable relative to afwillite and $Ca(OH)_2$, while above 140 °C it is probably unstable relative to hillebrandite [2, 36]. Its transformation to these phases is slow.

The crystal structure has been determined [44] and indicates the constitution $Ca_2(HSiO_4)OH$. Infrared studies have been made of normal and deuterium substituted material [76,81]. Under favorable conditions, C_2S α-hydrate crystallizes well; Vigfusson, Bates, and Thorvaldson [23] made crystals up to 0.5 mm in size by treating quartz or silica glass plates with lime water in silver vessels at 170 °C. It forms orthorhombic tablets or plates of characteristic appearance. When formed in pastes, it is sometimes poorly crystallized. Buckle and Taylor [39] reported that its crystallization in autoclaved C_3S or β-C_2S pastes was gradual, cryptocrystalline material being initially formed. There is evidence of variable composition [2,5]. This seems unlikely to occur in fully crystalline material if Heller's structure is correct, but might occur in imperfectly crystalline material. Dehydration of C_2S α-hydrate occurs on heating in air of ordinary humidity at about 450 °C; weight-loss [76,84] and differential thermal analysis [5,76] studies have been made. The product is unoriented β-C_2S [92].

Hillebrandite. (C_2SH). This occurs as a natural mineral. The first established synthesis was by Nagai [27] in 1932. Hillebrandite has since been prepared by many investigators [2,5,6,11,23,35,73]. For a time there was doubt as to whether the natural and synthetic products were identical; but it was shown [11] that this was because the early powder data for the natural mineral were incorrect. Later work [36] revealed slight differences between the powder patterns of natural and synthetic materials. These have never been explained, but there can be no doubt that the two relate to essentially the same species.

Hillebrandite is one of the more troublesome of the hydrated calcium silicates to prepare. It has been obtained starting from lime-silica mixtures, gels, and β-C_2S, but there seems to be no record of its having been made from γ-C_2S or from C_3S. All of the preparations have been made at saturated steam pressures, usually in the range 150 to 250 °C. As has already been stated, the initial product of such reactions is probably CSH(II). Hillebrandite seems to crystallize from this not as an immediate product, but through intermediate formation of C_2S α-hydrate [2,5,36]. It forms slowly at 140 °C [36], and more rapidly at higher temperatures; but above about 160 °C "C_2S γ-hydrate" is often more readily formed. Kalousek, Logiudice, and Dodson [5], commenting on the difficulty of preparing hillebrandite reproducibly, believed that the physical state and reactivity of the silicic acid were important factors. One recent careful investigation [13] did not yield hillebrandite, even though its formation might have been expected under the conditions used. There is some evidence that hillebrandite is the stable phase in contact with water and saturated steam at about 140 to 180 °C. Heller and Taylor [36] obtained an apparently pure specimen by a 166-day treatment of β-C_2S at 140 °C. Peppler [35] determined its solubility relations at 180 °C, and from experiments of 6 months' duration concluded that it was a stable ternary phase at this temperature.

Hillebrandite forms fibrous crystals with a 7.3-A repeat distance, and almost certainly contains Dreierketten. The ionic formula is therefore possibly $Ca_2(SiO_3)(OH)_2$. Mamedov and Belov [62] suggested that double Dreierketten occur, giving $Ca_{12}(Si_6O_{17})(OH)_{14}$, or $C_{12}S_6H_7$. Further work is needed to test these two hypotheses. Dehydration occurs at 520 to 540 °C giving unoriented β-C_2S; Toropov, Nikogosyan, and Boikova [134] showed that there was an intermediate, amorphous stage, and believed that this supported Mamedov and Belov's suggested structure. Differential-thermal-analysis data have been obtained [5,134]. Kalousek, Logiudice, and Dodson [5] considered that variable Ca:Si ratio occurs, and further suggested the possibility of a solid-solution series embracing also foshagite and tricalcium silicate hydrate. Subsequent unit-cell determinations [41, 72, 135] show, however, that the three species are quite distinct. The possibility of limited variability of composition can nevertheless not be ruled out, at least for badly crystallized material.

Phase Y. (C_6S_3H). This phase is not known in nature. It was described by Roy [4, 131]; unit-cell and dehydration data were afterwards given [42]. It has since been shown [136] that several preparations of earlier workers were probably substantially identical with phase Y. These are $C_2SH_{0.5}$ of Jander and Franke [12], $C_6S_3H_2$ of Flint, McMurdie, and Wells [6] and van Valkenburg and Rynders [137], also called $C_2SH(D)$ [9], $C_2SH_{0.5}$ of Funk [13], and $C_2SH(D)$ of Buckle [84]. The evidence for this statement is based on: (1) optical data, which are substantially the same for all, apart from the preparation of Flint *et al*, which was a pseudomorph and might well be anomalous; (2) comparison of X-ray single crystal photographs for the actual preparations made by Roy, Funk, and Buckle; (3) comparisons of new X-ray powder photographs for these preparations, along with the published data of Jander and Franke and of Flint, McMurdie, and Wells. The X-ray powder data published previously for these preparations seem to have been inaccurate in varying degrees, and new data will be reported elsewhere. Other properties are well described by Roy [4] and Dent Glasser and Roy [42]. They obtained good evidence for the H_2O:Si ratio 1:3; other recent results are compatible with this ratio [13, 84].

Roy [4] obtained her preparation at high temperatures and pressures, typically at about 790 °C and 10,000 to 25,000 psi. The other workers used lower temperatures and pressures. Jander and Franke, Funk, and Buckle all worked at about 350 °C under pressures of saturated steam (2,450 psi) while Flint, McMurdie, and Wells worked at 450° C and 6,000 psi. Roy used as starting materials β- and γ-C_2S and gels; Jander and Franke used mixtures of lime and quartz; Buckle used β-C_2S; Flint, McMurdie, and Wells used C_2S α-hydrate; Funk found that his product was formed irreproducibly from α- or α'-C_2S, rarely from β-C_2S, and never from γ-C_2S. At high temperatures under hydrothermal conditions, Phase Y is decomposed giving α'-C_2S. Roy [4] obtained a P–T curve (fig. 2) for this transformation, which occurs at about 810 °C at 20,000 psi. Phase Y is also dehydrated giving β-C_2S when heated at about 700 °C under atmospheric humidity; weight-loss curves have been reported [42, 84].

Phase Y forms short, prismatic crystals, which often show simple twinning across a plane in the prism zone. The crystal structure is unknown. The repeat distance of 6.73 A in the prism direction suggests a resemblance to β-C_2S, but the transformation is unoriented [42]. The high dehydration temperature of 640 to 700 °C [42, 84] suggests that the hydroxyl is ionically bound, giving $Ca_6(SiO_4)(Si_2O_7)(OH)_2$. Roy [4] obtained infrared data, but these have not been interpreted in detail.

Calcio-chondrodite (*Phase X*). (C_5S_2H). This is not known as a natural mineral. It was first described by Roy [4, 131] and, somewhat later, by Buckle and Taylor [14]. Funk's "$C_2SH(CII)$" [13], discussed in the next section, also seems to have consisted largely of this phase. Roy called her product "Phase X," and considered it to be $C_8S_3H_3$; Buckle and Taylor called theirs calcio-chondrodite, with the formula C_5S_2H. They showed from a unit-cell determination that it was structurally analogous to the well established mineral, chondrodite ($(Mg,Fe)_5(SiO_4)_2(OH,F)_2$) and their formula was based on this analogy and supported also by other data. Comparison of the reported X-ray powder and optical data shows that the two preparations are substantially identical. There is, however, an error in the optical data given by Buckle and Taylor; the sign of elongation should be negative (as stated by Roy) and not positive.

Roy obtained calcio-chondrodite from various starting materials mainly at 400 to 800 C° and pressures above 5,000 psi. She obtained P-T curves (fig. 2) defining its stability relative to tricalcium silicate hydrate and to α'-C_2S. At lower pressures, it is formed at considerably lower temperatures; if, as seems likely, "C_2S γ-hydrate" is a mixture containing calcio-chondrodite, the latter can be obtained from β- or γ-C_2S at temperatures as low as 180 °C.

Calcio-chondrodite forms prismatic crystals which resemble those of olivine in appearance. They often show twinning across a plane in the prism zone. Roy [4] reported infrared data. Buckle and Taylor [14] reported a weight-loss curve and showed the dehydration products to be γ-C_2S and CaO. The formation of γ- and not β-C_2S, considered along with the structural similarity, suggests the probable occurrence of an oriented transformation, but this was not experimentally verified.

"C_2S γ-hydrate." ($C_2SH_{0.2-1}$). This name is used for the product most often obtained when β- or γ-C_2S or lime-silica mixtures with Ca:Si=2, are autoclaved at 200 to 300 °C under saturated steam pressures. It has been reported by many investigators [5, 6, 11, 24, 36, 76]. Recently, Roy [4] has described an essentially similar "Phase X*," and Funk [13] a "$C_2SH(CI)$" and "$C_2SH(CII)$." The material crystallizes badly, and the only recorded crystallographic data are a mean refractive index and an X-ray powder pattern. Both of these, and also the H_2O:Si ratio, vary slightly from one sample to another. Weight-loss [84] and differential-thermal-analysis [5, 76] data have been obtained, and also infrared data [76].

The X-ray pattern resembles that of calcio-chondrodite. Both Roy [4] and Buckle and Taylor [14] considered the possibility that the two substances were related. The general formula for the calcium chondrodite series is $2\frac{1}{n}CaO\cdot SiO_2\cdot\frac{1}{n}H_2O$ and the lower limit of Ca:Si ratio is thus provided by γ-C_2S. C_2S γ-hydrate cannot therefore be simply a member of this series. It is, however, so badly defined a substance that there is no convincing reason to believe that it is a single phase. The fact that its X-ray powder pattern is approximately reproducible proves nothing, because almost all the preparations have been made from starting materials of the same Ca:Si ratio. Indeed, when this ratio is lowered [5], there is an apparently gradual change to a pattern now identified as belonging to Phase Z.

It thus seems possible, as Roy [4] suggested, that C_2S γ-hydrate or "Phase X*" is a member of the calcium-chondrodite series mixed with a phase having $Ca:Si<2$. She suggested that hydrous silica might be present. It seems more probable to the author that these and similar products are mixtures of calcio-chondrodite and Phase Z. With increasing temperature of preparation, the Phase Z would become poorer in lime, and the proportion of calcio-chondrodite would therefore increase. In agreement with this hypothesis, Funk's C_2SH(CII), made at 250 to 350 °C, gave an X-ray pattern close to that of calcio-chondrodite, whereas his C_2SH(CI), made at 200 °C, gave a pattern resembling that of Phase Z.

C_2S γ-hydrate seems to form particularly readily from γ-C_2S. This is understandable if it is a mixture of two phases, both of which are structurally related to γ-C_2S, and which could thus be formed by oriented transformation. The difficulty of making hillebrandite from γ-C_2S can probably be explained by the fact that C_2S γ-hydrate forms more easily, and is not decomposed until temperatures well above those at which hillebrandite can be formed.

Tricalcium silicate hydrate. ($C_6S_2H_3$). This phase does not occur as a natural mineral but is reproducibly prepared by hydrothermal treatment at 200 to 450 °C of C_3S, or other starting materials of similar Ca:Si ratio [4,6,10,24,29,41]. Below 200 °C, C_2S α-hydrate and $Ca(OH)_2$ usually are formed, although tricalcium silicate hydrate has been made from C_3S in freshly mixed pastes as low as 75 °C [39]. Above about 450 °C, calcio-chondrodite is formed; Roy [4] determined a P-T curve defining the upper stability limit of tricalcium silicate hydrate (fig. 2). Under saturated-steam conditions, tricalcium silicate hydrate is not easily obtained free from C_2S α-hydrate or calcio-chondrodite. Curve 5 (fig. 2), on extrapolation downwards, may roughly coincide with the saturated-steam curve. If this is so, pure samples could better be obtained by working at pressures above this curve.

There has been considerable doubt about the $H_2O:Si$ ratio of this compound, and the value 2 has often been assumed. Recent work [41] supports earlier indications that the true value is 1.5. Tricalcium silicate hydrate forms long, fibrous crystals [6,41]. The repeat distance of 7.48 A in the fiber direction [41] is similar to that of wollastonite and other calcium silicates containing Dreierketten. Buckle, Gard, and Taylor [41] suggested that the relatively high dehydration temperature of 420 to 550 °C indicates ionic binding of the hydroxyl, giving the constitutional formula $Ca_6(Si_2O_7)(OH)_6$. The $Si_2O_7^{6-}$ groups could be placed with their long axes parallel to the fiber direction, giving Dreierketten with one tetrahedron in three missing, as is known to occur in cuspidine [138] and tilleyite [139]. Mamedov, Klebtsova, and Belov [63] developed this hypothesis further and postulated a complete crystal structure, but this has not been experimentally tested.

The weight-loss curve [41] suggests that the water is lost in two stages; this has not been explained. The products of dehydration are γ–C_2S and CaO; the formation of γ–C_2S could be taken to indicate a structural relationship, as with calcio-chondrodite. Further study of the mechanism of this transformation is needed.

Some General Considerations

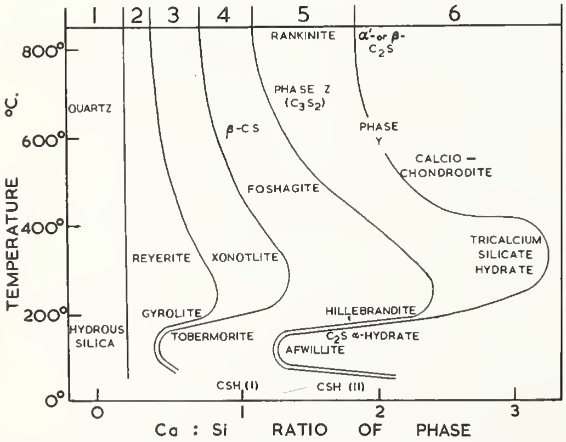

FIGURE 3. *Approximate temperatures of formation of the better established hydrated or anhydrous calcium silicates under hydrothermal conditions.*

Saturated steam conditions are assumed below 374 °C.; for other reaction conditions, see text. Curves group phases according to known or probable degree of condensation of anion. (1) Frameworks. (2) Sheets. (3) Double chains. (4) Single chains or rings. (5) Si_2O_7 groups. (6) Isolated tetrahedra.

The relationships between structure and the conditions of formation and of dehydration. Available knowledge of the CaO–SiO_2–H_2O system is quite inadequate to permit the drawing of anything approaching a true phase equilibrium diagram for the system as a whole. The results most important to cement chemistry can, however, be summarized by plotting the Ca:Si ratio of each phase against the temperature at which it is most readily formed (fig. 3). For this purpose it was assumed that: (1) below 374 °C the pressure is that of saturated steam, and above 374 °C it is about 5,000 psi, (2) reactive starting materials are used, such as CSH(I), β-C_2S, or C_3S, (3) reactions are carried out in aqueous suspension, and (4) sufficient time is allowed for the formation of *apparently* stable products (a few months below 150 °C, falling to a few days at 800 °C).

The curves in figure 3 group the phases according to the known or probable degree of condensation of the anion. They are necessarily somewhat speculative, mainly because many of the crystal structures are unknown. Certain trends nevertheless seem clear. Above about 200 °C, a low degree of condensation is favored by increase in Ca:Si ratio and increase in temperature. This trend is a consequence of the fact that, in these relatively high-temperature phases, water when present occurs as ionically bound hydroxyl, the proportion of which tends to decrease as the temperature is raised. The dislocation of the curves below 150 to 200 °C is explained by the fact that in low temperature products, water can also occur as Si–O–H or H_2O.

A relation between structure and temperature is also apparent in the conditions of dehydration at ordinary humidity under quasi-static conditions. Where the water occurs partly or wholly as H_2O or Si–O–H (tobermorite, nekoite, gyrolite, afwillite, C_2S α-hydrate), dehydration occurs below about 450 °C. In some cases, it begins below 100 °C. Where the water occurs entirely as ionic OH^-, dehydration occurs at higher temperatures. The dehydration temperature tends to increase as the water content decreases; in $Ca(OH)_2$, with the highest water content, it is about 400 °C [84], while in reyerite, xonotlite, foshagite, Phase Y, and calcio-chondrodite, which have low water contents, it is around 700 to 800 °C. Hillebrandite and tricalcium silicate hydrate are intermediate cases. A rough correlation between temperatures of hydrothermal formation and of dehydration at ordinary humidity is to be expected, as the dehydration of a hydrous phase under the two types of conditions is essentially the same process. In general, it occurs at considerably higher temperatures when atmospheric humidity is used; the dehydration of xonotlite to β-$CaSiO_3$, for instance, occurs at about 700 °C under these conditions but about 400 °C under hydrothermal conditions. This relationship is the opposite of what would be expected from extrapolation of P-T curves (fig. 2) to very low water-vapor pressures. It must be concluded that dehydration temperatures at ordinary humidity are usually determined by kinetic and not equilibrium considerations, and that the dehydration process is strongly catalyzed by water or steam under hydrothermal conditions.

The influence of CO_2 *contamination in hydrothermal studies on the* CaO-SiO_2-H_2O *system.* It is difficult entirely to avoid contamination of hydrated calcium silicate preparations by CO_2, and under technical conditions this is often virtually impossible. A knowledge of the influence of CO_2 on the system is therefore important. In principle, there appear to be three possible effects as regards the phases formed:

(1) *The* CO_2 *is present entirely as* $CaCO_3$.—Where more than a few percent of CO_2 is found by chemical analysis, the lines of calcite, or vaterite, or both can nearly always be found in the X-ray pattern. Crystallization in the form of vaterite seems to occur particularly readily in the presence of hydrated calcium silicates.

(2) *The* CO_2 *enters into the structure of a hydrated calcium silicate.*—This possibility is suggested by analogy with the hydrated calcium aluminates, some of which can accommodate CO_3^{2-} ions with relatively minor changes in structure, apparently through replacement of $2OH^-$ by CO_3^{2-} together with adjustment in the number of water molecules [140]. This replacement is thus most likely to occur in tobermorite minerals and other low-temperature phases. Gaze and Robertson [68] suggested that CO_3^{2-} could enter into the structure of tobermorite, but more recent evidence [141] indicates that all the CO_2 in tobermorite preparations can be attributed to calcite, aragonite, or vaterite.

(3) *New phases are formed, in which* CO_2 *is an essential constituent.*—There are three known phases of this type: spurrite, tilleyite, and scawtite.

Scawtite was originally found as a natural mineral and has been considered to have the formula $Ca_7(Si_6O_{18})CO_3{\cdot}2H_2O$. More recently, other specimens have been found with somewhat different compositions. McConnell and Murdoch [142], in a review of the subject, concluded that these variations in composition could best be explained by assuming replacement of tetrahedrally coordinated Si by C in triangular coordination; they proposed the general formula $Ca_{14}(OH)_4(Si_{16-x-y}C_{4x/3}H_{4y})O_{44}$. This cannot be right, as it implies that the carbon is trivalent; confusion has arisen between coordination number and oxidation state. The formula can also be criticized on the ground that it presupposes a structural relation to the amphiboles, which, as already seen, is unlikely for a calcium silicate. The unit cell [143, 144] suggests the presence of Dreierketten rather than Zweierketten. The correct formulation of scawtite thus awaits further work. The hypothesis of replacement of Si by C, in a broad sense, nevertheless appears highly probable, and the possibility thus exists of finding or preparing a scawtite low in CO_2.

Flint, McMurdie, and Wells [6] prepared a phase which they considered to be $CaO{\cdot}SiO_2{\cdot}H_2O$ under saturated steam conditions at 150 °C. Other workers have since obtained the phase under comparable conditions [16, 76, 79]; it appears to form from tobermorite at or just below the transition temperature to xonotlite. Bogue [9] called it CSH(A). Its X-ray pattern is very like that of scawtite [143, 144]. Buckner, Roy, and Roy [79] suggested that it was in fact identical with scawtite. This identity appears probable in view of the results for the natural mineral described above. The nonreproducibility of formation of CSH(A) further accords with the hypothesis that its synthesis depends on CO_2 contamination.

Tilleyite ($Ca_5(Si_2O_7)(CO_3)_2$) and spurrite ($Ca_5(SiO_4)_2(CO_3)$) are anhydrous phases and form at higher temperatures. Both occur naturally and have also been synthesized. In a series of studies [145–146], Tuttle and Harker obtained P_{CO_2}-T curves for phase transformations in the anhydrous ternary system CaO-SiO_2-CO_2. They synthesized both spurrite and tilleyite at high temperatures and pressures of CO_2. McConnell [147] showed that they could also be made at somewhat lower temperatures in the absence of excess CO_2 but with water at high pressures also present.

Hydrothermal Reactions in C_3S, β–C_2S, and Cement Pastes

All the studies discussed in the remaining sections of this review relate to saturated steam pressures.

The immediate products of hydration of C_3S *and* β-C_2S *in pastes.* When pastes of C_3S or β-C_2S are cured at 100 to 200 °C, the immediate products do not seem to differ greatly from those formed at ordinary temperatures. With most specimens of β-C_2S, and probably all specimens of C_3S, these products are CSH gel and $Ca(OH)_2$. The constitution and composition of the CSH gel is discussed elsewhere in this symposium [20], and will not be considered in detail here. Interpretations still differ, but it seems certain that Ca : Si is always between 1.5 and 2.0; there is evidence that it rises within this range as the curing temperature is increased [20, 38]. With this qualification, CSH gel formed at 100 to 200 °C seems to differ little from the corresponding product formed at room temperature.

Funk [38] has recently shown that the behavior of β-C_2S on hydration in pastes at 20 to 120 °C depends on the stabilizer present. With some stabilizers, including the commonly used 0.5 percent B_2O_3, CSH gel and $Ca(OH)_2$ were formed. Funk described β-C_2S made using these stabilizers as "completely stabilized." It seems probable that the β-C_2S in cement clinker is normally of this type. When certain other stabilizers were used, such as 0.2 percent Na_2O, the β-C_2S inverted on curing to give a modified form of γ-C_2S. These samples of β-C_2S were called "insufficiently stabilized." These effects were substantially independent of temperature within the range stated. Later work [13] showed the γ-C_2S to be anomalous in several respects. It had a composition, after drying over P_2O_5 at 20 °C, of 1.8 to 2.0 $CaO{\cdot}SiO_2{\cdot}$0.5–1.0 H_2O, showed minor abnormalities in its X-ray pattern, and tended, more readily than did normal γ-C_2S, to change further giving CSH gel.

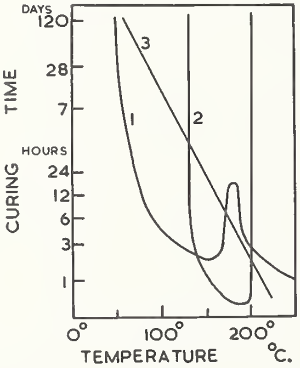

FIGURE 4. *Phases detected in* C_3S *pastes cured at 20 to 250 °C.*

(1) Lower limit of formation of tricalcium silicate hydrate. (2) Lower limit of formation of C_2S α-hydrate. (3) Upper limit of occurrence of unreacted C_3S. $Ca(OH)_2$ was nearly always found for temperatures below 200 °C. $Ca(OH)_2$ and CSH gel were the only hydrated phases detected below and to the left of curves 1 and 2.

Subsequent reactions in β-C_2S *pastes.* When "fully stabilized" β-C_2S is hydrated at ordinary temperatures in pastes to give CSH gel and $Ca(OH)_2$, no further reactions occur at any detectable rate. This is still true at 100 °C. Above about 120 °C, however, C_2S α-hydrate crystallizes from the gel. Buckle and Taylor [39] were able to detect this phase by X-ray methods after 5 days at 120 °C. It formed increasingly rapidly as the temperature was raised and was found after 12 hours at 180 °C. The β-C_2S used was rather coarsely ground, and C_2S α-hydrate might be expected to form more rapidly if the particle size was similar to that of the β-C_2S in cement. No other phases were detected in the products of runs at or below 180 °C, with curing times up to 28 days. Unchanged β-C_2S was found in all these products, and CSH gel and $Ca(OH)_2$ were also probably always present. These reactions show that hydration of β-C_2S in pastes at 100 to 180 °C proceeds in the way that might be expected from the fundamental studies discussed previously in this review. CSH gel and $Ca(OH)_2$ are the initial products. and above 120 °C C_2S α-hydrate crystallizes from them. Both processes occur more slowly than in suspensions, and the subsequent changes to give equilibrium products such as afwillite or hillebrandite do not occur in the times used in practice.

Subsequent reactions in C_3S *pastes.* Buckle and Taylor [39] studied the phases formed in C_3S pastes cured at 20 to 200 °C; they also made a few runs at higher temperatures. X-ray, optical, and weight-loss methods were used. They confirmed that CSH gel and $Ca(OH)_2$ were the immediate products, at least up to 200 °C. They were the only products for times up to 5 hr at 100 °C, or 30 min at 170 °C. With longer curing times, C_2S α-hydrate, or tricalcium silicate hydrate (TSH), or both were formed, as shown in figure 4. The exact positions of the curves in figure 4 apply only to the particular sample of C_3S used in the investigation. Other samples would possibly behave somewhat differently.

Figure 4 shows that C_2S α-hydrate is formed at 130 to 200 °C, and TSH in two ranges above and below 180 °C. These results do not differ appreciably from those found with suspensions except for the existence of the low-temperature range of formation of TSH at 50 to 170 °C. This range is not found with suspensions; Buckle and Taylor showed, in addition, that it did not occur with aged C_3S pastes that had already been cured for several years at room temperature. They concluded that TSH was formed at these temperatures as a nonequilibrium product. The only other investigators who have reported the formation of TSH below 180 to 200 °C appear to be Keevil and Thorvaldson [24], who were able to prepare it at temperatures as low as 110 °C by autoclaving initially dry C_3S powder in saturated steam. These conditions thus appear to resemble those existing in a paste.

Buckle and Taylor also made optical studies on C_3S pastes. In general, pastes cured below 200 °C consisted of a gelatinous or cryptocrystalline matrix in which were embedded crystals of unreacted C_3S and of hydrated phases. In pastes cured under sufficiently mild conditions of time and temperature, this matrix consisted of CSH gel together probably with cryptocrystalline $Ca(OH)_2$; under more severe conditions, it probably also contained cryptocrystalline C_2S α-hydrate or TSH, or both. These phases, and also $Ca(OH)_2$, segregated gradually from the matrix as curing proceeded. In pastes cured above 200 °C, the matrix had largely or completely disappeared and only crystalline phases were observed.

The reactions occurring in C_3S pastes can be summarized as follows. The initial products are CSH gel and $Ca(OH)_2$; at first they are so intimately mixed as to be barely distinct phases, but crystals of $Ca(OH)_2$ gradually separate. Two further processes can then occur under appropriate conditions. Firstly, at 130 to 200 °C, the CSH gel is transformed into C_2S α-hydrate. Crystallization of this phase is probably a gradual process. It is probably cryptocrystalline at first and, when in this state, can possibly have a nonstoichiometric composition, as was suggested by Kalousek, Logiudice, and Dodson [5]. The formation of C_2S α-hydrate probably occurs through an internal rearrangement within the CSH gel and does not depend much, if at all, on reaction with the $Ca(OH)_2$ crystals. It therefore occurs readily, even in aged pastes. Secondly, TSH can be formed. Because TSH has a high Ca:Si ratio, this process depends on reaction between the CSH gel and $Ca(OH)_2$. It therefore does not occur below 180 to 200 °C, except in fresh pastes where the $Ca(OH)_2$ crystals are still small, and which are thus still relatively homogeneous. Above 180 to 200 °C complete recrystallization of the material occurs within a few days. This results in the formation of TSH, or at higher temperatures, of calcio-chondrodite and $Ca(OH)_2$; these phases are probably then formed as equilibrium products.

The compressive strengths of autoclaved C_3S *and* β-C_2S *pastes.* Assuming typical curing times of 12 to 24 hr, the strengths of β-C_2S pastes increase continuously with curing temperature up to at least 200 °C; those of C_3S pastes, in contrast, decrease markedly when the curing temperature exceeds 180 to 200 °C. C_3S pastes cured below 180 to 200 °C are stronger than β-C_2S pastes, but for higher curing temperatures the reverse is true [39, 148]. This phenomenon is readily explained. Development of strength in C_3S or β-C_2S pastes without added silica seems to depend on the formation of an adequate proportion of the matrix. With either compound, the sequence of reactions is one in which the matrix is first formed and afterwards destroyed. β-C_2S reacts so slowly that the first process is still the dominant one, even after many hours' curing at 200 °C; strengths at this temperature are therefore greater for typical curing times of 12 to 24 hr than at lower temperatures. C_3S reacts more rapidly, so that the second process occurs extensively after a few hours at 180 to 200 °C. This causes the strengths of C_3S pastes cured for typical periods at 200 °C to be much lower than those of pastes cured for similar times at lower temperatures.

Hydrothermal curing of neat cement pastes. The first systematic study of the hydrated phases produced in neat cement pastes cured hydrothermally was made by Kalousek and co-workers [86–88]. They based their conclusions principally on the results of differential-thermal-analysis studies. With cements cured at 100 °C and above, any separate hydrated aluminate or sulfoaluminate phases that were initially formed were quickly decomposed. There was evidence that at 100 °C, ettringite persisted for up to 30 min; a C_4AH_{13}—$C_3A{\cdot}CaSO_4{\cdot}12H_2O$ solid solution was then formed, and was at a maximum in 2 hr, but this also had disappeared within 4 hr. The product of this reaction, which Kalousek called "Phase X," was a gel containing all the oxide components of the cement. At curing temperatures above 100 °C, no separate hydrated aluminate or ferrite phases at all were found. A particularly careful search was made for C_3AH_6 or hydrogarnet solid solutions, but these were not found, although a number of different cements were examined after differing curing times at temperatures between 120 and 175 °C. C_2S α-hydrate was, however, detected in cements cured at these temperatures.

Kalousek believed that Phase X formed at or above 100 °C differed from the corresponding phase formed at lower temperatures, though perhaps only in porosity. It seems to be essentially the same as CSH gel, modified by the incorporation of Al_2O_3 and the other minor components of the cement.

Kalousek [37] and Kalousek and Prebus [17] afterwards reported X-ray and electron microscope studies on neat cement pastes cured at 50 to 120 °C. With one cement, cured according to a plant cycle at 50 to 80 °C, they obtained evidence of the formation of CSH gel, fibrous CSH(II), $Ca(OH)_2$, hillebrandite, and, possibly, C_2S α-hydrate. An oil-well cement cured at 120 °C also appeared to yield hillebrandite. The reported formation of this phase can be compared with that of TSH from pure C_3S under similar conditions [39]. It is tempting to suppose that the phase formed in the cements may in reality have been TSH, as the X-ray patterns of TSH and hillebrandite are difficult to distinguish in a complex mixture. On the other hand, cements may very well differ from pure C_3S in their behavior. In either case, Kalousek's observation seems to provide further evidence that certain hydrated phases are sometimes formed in pastes at temperatures much lower than those at which they are formed in suspensions.

Sanders and Smothers [120] made X-ray studies on a neat cement paste cured for 24 hr at 182 °C.

They found CSH gel, $Ca(OH)_2$, C_2S α-hydrate, and unreacted C_3S and β-C_2S.

These results suggest that the behavior of neat cements in the autoclave is not too different from that of β-C_2S or C_3S; the successive formation of a modified form of CSH gel and of C_2S α-hydrate, together with $Ca(OH)_2$ in each case, seems established. More work is clearly needed to establish definitely whether, and if so in what form, the Al_2O_3 and other minor constituents are incorporated in the CSH gel. It would also be interesting to know whether separate aluminate phases, such as C_3AH_6, hydrogarnets, or $C_4A_3H_3$ can be detected if curing temperatures above 200 °C are used.

Hydrothermal Reactions in Lime-Silica and Cement-Silica Pastes

Introduction. The studies on neat cement, C_3S, and β-C_2S pastes described in the previous section are of direct technical interest only up to temperatures little above 100 °C. When higher curing temperatures are used, low strengths are obtained unless finely divided quartz or other reactive forms of silica are added to the cement. Small additions of silica cause a decrease in strength, but larger additions, of 40 to 70 percent on the weight of the cement, cause a marked increase [149]. These variations in strength can be compared with the overall Ca:Si ratio of the mix. For most neat cements, this ratio is around 3. Minimum strengths are obtained when it is around 2, and maximum strengths at 0.8–1.0. Comparable results for lime-quartz pastes have recently been obtained [150]. These results indicate that the bonding material in autoclaved products has a lower Ca:Si ratio than the CSH gel which serves this purpose in products cured at lower temperatures. As will be shown, it is also much more crystalline. This fact accounts for the lower drying shrinkages that are found with autoclaved products.

Autoclaved lime-silica pastes. These are of direct technical importance because they include sand-lime bricks, lightweight heat-insulating materials, and other commercial products. They are also of interest because they provide a means of studying the most important of the processes that occur in cement-silica pastes while avoiding the complications inherent in a multicomponent system.

Bessey [151] reported optical studies on sand-lime bricks, and also made estimates of the Ca:Si ratios of the bonding material based on soluble silica determinations. He found that the bonding material was sometimes gelatinous, sometimes crystalline, and that its Ca:Si ratio varied from 0.97–1.77. The gelatinous material was probably CSH gel, while the appearance of the crystalline one suggests that it may have consisted of xonotlite. Taylor [152] showed from X-ray and chemical studies that a tobermorite mineral was present in a commercial lightweight sand-lime block. The X-ray data can be reinterpreted in the light of present day knowledge as indicating the presence of crystalline 11.3-Å tobermorite. The overall Ca:Si ratio of the bonding material was shown from soluble silica determinations to be 1.28. A poorly crystallized tobermorite mineral of higher Ca:Si ratio than tobermorite itself was therefore probably also present and undetected by the X-ray determination.

A more systematic investigation was made by Kalousek [90] who prepared blocks from lime and silica, and also from other starting materials; he examined the products mainly by X-rays, differential thermal analysis, and soluble-silica determinations. His X-ray results confirmed that crystalline tobermorite was a frequent constituent of autoclaved pastes in which the bonding material had a Ca:Si ratio below 1.3. His differential-thermal-analysis results showed that CSH(I) was also present, as there was a strong exothermic peak at 840 to 860 °C. Where the Ca:Si ratio of the bonding material exceeded 1.3, the differential-thermal-analysis results showed the presence of C_2S α-hydrate.

Kalousek [37] later showed that the reaction between lime and silica involved the intermediate formation of CSH(II) and CSH(I), or of phases similar in composition to these. The reactions of $Ca(OH)_2$ with quartz and with silicic acid were followed using X-rays, differential thermal analysis, soluble-silica determinations, specific-surface measurements and electron microscopy. The reactions were studied in slurries with a water-to-solids weight ratio of 3.5, but it seems probable that the results are in general applicable also to pastes. For mixes of Ca:Si mole ratio 0.8, using either quartz or silicic acid, the initial product had the approximate composition $C_{1.75}SH_n$. Kalousek considered that this was usually CSH(II), but that in some cases where quartz was used, a poorly crystallized form of C_2S α-hydrate was formed instead. In either case, this lime-rich phase then reacted with more silica, giving in succession compounds of the compositions $C_{1.25}SH_n$, CSH_n, and $C_{0.8}SH_n$, followed by tobermorite. The specific surface rose to a maximum with the formation of $C_{0.8}SH_n$, and afterwards fell sharply with the crystallization of tobermorite. At first, Kalousek considered that the compositions $C_{1.25}SH_n$, CSH_n, and $C_{0.8}SH_n$ corresponded to distinct compounds, but later [17] he regarded these as being all essentially the same phase, with a Ca:Si ratio variable between 0.8 and 1.33. This is the phase called CSH(I) in this review.

Kalousek found that the rates of these successive transformations depended on the exact nature of the starting material. In particular, the transformation of CSH(I) into tobermorite was more rapid with quartz than with silicic acid. He attributed this difference to the higher silica concentrations in solution likely to be obtained with silicic acid, which he believed would make the

CSH(I) more stable relative to tobermorite. He found also that the presence of reactive Al_2O_3 favored the formation of tobermorite.

In the main, these results have been amply confirmed by the work of later investigators. It may, however, be doubted whether C_2S α-hydrate is ever an initial product in the lime-silica reaction. Other workers have considered that the initial product is always a poorly crystallized tobermorite mineral, and that C_2S α-hydrate forms from this as a second-stage product [2, 8, 36]. As stated previously, Kalousek's results, though obtained on slurries, probably apply in other respects to pastes. Rates of reaction may be somewhat different, and the intermediate products may be less well crystallized in pastes. The high-lime tobermorite mineral, in particular, is probably CSH gel rather than CSH(II) when formed in pastes.

Neese and associates [106, 121] studied the phases produced in lime-quartz pastes, using chemical, X-ray, and optical methods, as well as differential thermal analysis, weight-loss curves, and dilatometry. They prepared pastes with molar Ca:Si ratios of about 0.33 and 0.66, as well as ones using cement, which are discussed later. Typical results are shown in figure 5. They confirm Kalousek's views on the intermediate formation of CSH(II) and CSH(I).

Aitken and Taylor [8] also studied the phases produced in lime-quartz pastes. They investigated a wider range of Ca:Si ratios than did Neese, and also extended the autoclaving periods to longer times, but did not attempt to distinguish between different, poorly crystallized tobermorite minerals, which were collectively called CSH. Other products obtained were tobermorite, xonotlite, gyrolite, C_2S α-hydrate, hillebrandite, and "Phase F." From the results of this study, together with those already described, the principal features of the lime-quartz reaction in pastes autoclaved under saturated steam pressures at 100 to 200 °C can be summarized as follows:

(1) The initial reaction gives CSH(II) or CSH gel, with a Ca:Si ratio of at least 1.5. In pastes of low overall Ca:Si ratio (e.g., 0.8–1.0), the lime therefore disappears before the quartz.

(2) At low overall Ca:Si ratios, the CSH(II) reacts with more silica to give CSH(I). When first formed, this probably has a Ca:Si ratio of 1.25. The value drops gradually to 0.8 as reaction proceeds.

(3) The CSH(I) recrystallizes to tobermorite. The rate of this process depends greatly on the temperature. At 175 °C tobermorite can be detected within 12 hr, but at 125 °C (the lowest temperature at which it has been found in a paste) several days' reaction is needed. This process occurs more quickly if reactive aluminous materials are present, but more slowly if silica gel is substituted for the quartz.

(4) If the temperature is high enough, the tobermorite is changed into xonotlite. This phase has been detected in pastes cured at 165 °C, but its formation under these conditions is slow. It is not formed to a detectable extent in less than 24 hr below 180 to 190 °C.

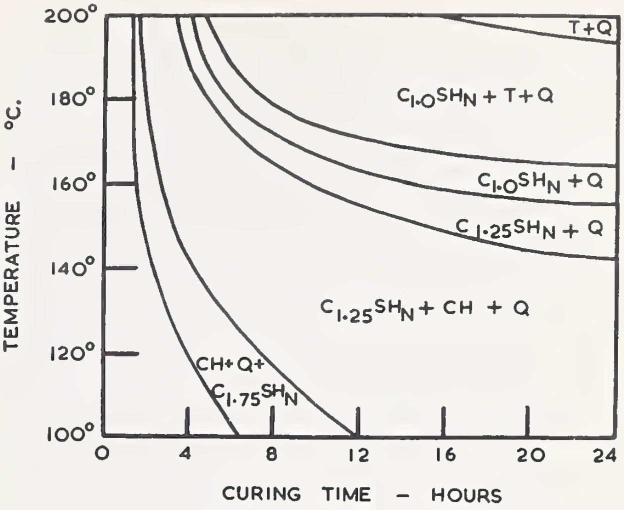

Figure 5. *Phases detected in lime-quartz pastes* (*Neese* [*121*]).

Ca:Si molar ratio 0.33, specific surface of quartz 4514 cm^2/g. Q=quartz, T=tobermorite, CH=$Ca(OH)_2$.

(5) At overall Ca:Si ratios below 0.83, unreacted quartz remains after all the CSH(II) and CSH(I) have been converted into tobermorite. Reaction of tobermorite or CSH(I) with residual quartz can occur, giving gyrolite. This reaction, however, is very slow, probably because it can only take place at the interface of the quartz and the tobermorite. Gyrolite can nevertheless sometimes be detected in pastes with Ca:Si$\leq$0.67 after one or more days' autoclaving at 165 to 200 °C. Its formation under these conditions is not very reproducible. Xonotlite is sometimes formed when gyrolite might be expected, presumably because the tobermorite alters to xonotlite more quickly than it can react with the quartz.

(6) If overall Ca:Si exceeds 1.2–1.3, there is not enough quartz to convert all the CSH(II) into CSH(I). A different set of reactions thus occurs, which begins with recrystallization of the CSH(II). The usual product of this recrystallization is C_2S α-hydrate which is formed slowly at 125 °C and more quickly at higher temperatures.

(7) "Phase F," of possible composition $C_5S_3H_2$, seems to be an alternative recrystallization product of CSH(II), but its formation is irreproducible; it was formed most often at around 165 °C [8].

(8) At sufficiently high temperatures, C_2S α-hydrate or phase F can alter to hillebrandite. This phase is formed to a detectable extent in pastes cured for 1 to 2 days at 165 to 200 °C.

Autoclaved cement-silica pastes. The pioneer work of Thorvaldson and Shelton [22] showed that C_2S α-hydrate can be formed in cement-silica pastes. Later work, however, has shown that formation of this phase is associated with low mechanical strength, and that satisfactory strengths are obtained when tobermorite is formed.

Kalousek and co-workers [17, 86, 88, 90] studied autoclaved cement-quartz pastes using differential thermal analysis, X-ray diffraction, and chemical methods. They showed that addition of small proportions of fine quartz to the cement, before autoclaving for 24 hr at 175 °C, increased the proportion of C_2S α-hydrate in the product and decreased that of $Ca(OH)_2$. With about 9 percent of quartz (on the weight of cement) the yield of C_2S α-hydrate was at a maximum, and formation of $Ca(OH)_2$ was eliminated. At this composition, the strength is at a minimum [149]; Kalousek concluded that low strength was correlated with formation of C_2S α-hydrate. When more quartz was added, formation of C_2S α-hydrate was reduced and ultimately eliminated, tobermorite being formed instead. Maximum formation of tobermorite occurred at about the compositions known to give the highest strength [149]. High strength was thus attributed to formation of tobermorite.

Sanders and Smothers [120] obtained closely similar results. They autoclaved cement-quartz pastes for 24 hr at 182 °C and made X-ray studies and strength tests on the products. The hydrated phases were detected, and in some cases estimated quantitatively, using a diffractometer. Ten-percent addition of quartz effected a maximum in the formation of C_2S α-hydrate and a minimum in strength; 35 percent addition of quartz effected a maximum in the formation of tobermorite and a maximum in strength. Less tobermorite was formed if curing was at 159 °C, and none at all if it was at 125 °C, or if silica gel was substituted for the quartz.

Neese, Spangenberg, and Weiskirchner [106] studied the phases produced in pastes cured at 151 to 197 °C, with quartz:cement weight ratios of 1.5 and 3.0. They reported the formation of CSH(I), tobermorite, and nekoite. The detection of nekoite was based only on optical evidence, and must be considered doubtful.

In none of the investigations described in this section were any hydrated aluminate or ferrite phases detected; in particular, C_3AH_6 and other hydrogarnets were not found. It therefore appears probable that, as with autoclaved neat cement pastes, the minor components of the cement are incorporated into hydrated silicate phases.

The results discussed in this section show that when cement-silica pastes are autoclaved at 150 to 200 °C, the cement behaves to a first approximation as a source of lime and silica. The phases produced are the ones that would be formed in lime-silica pastes with the same Ca:Si ratio. Typical neat-cement pastes have a Ca:Si ratio of about 3; addition of 9 to 10 percent of quartz, which gives a maximum yield of C_2S α-hydrate, lowers the overall ratio to about 2, while 40 to 70 percent additions, which give a maximum yield of tobermorite, lower it to 0.8–1.0. The mechanism of the process also is probably not very different from that occurring in lime-silica pastes. Differences between cement and lime can be expected to arise because of the different physical state of the reactants, and because of the presence of Al_2O_3 in the cement, but they do not seem to affect the essential features of the reaction.

The fact that high strength in autoclaved cement-silica products is associated with formation of tobermorite shows that crystalline as well as gelatinous phases can have good cementing properties, though the behavior of C_2S α-hydrate shows that this is not true of all crystalline phases. The reason for this behavior is still not understood.

Note on Further Investigations

The author much regrets that he became aware of a group of papers from the U.S.S.R. too late to discuss them in this review. They are, however, included in the list of references [153–166]. References 153 and 154 deal mainly with the lime-silica reaction, 155 to 160 with the hydrothermal curing of C_3S or β-C_2S pastes with or without added silica, and 161 to 166 with the hydrothermal curing of cement or cement-silica pastes.

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Discussion

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The discussion below concerns only the reactions with saturated steam in the temperature range 100 to 240 °C, planned by the present author and published 1956–60 [1].[1]

If compounds that are in real equilibrium with the surrounding phases were to be prepared, solutions of ions heated to the required temperature would have to be used; such experiments would be impossible to perform practically. The experiments must therefore be realized with other types of components, not forgetting the fact that the relevant conclusions may be drawn only if all premises are taken into consideration. When components are used in the solid state as colloids or as crystals instead of ions, we introduce some new reaction types that could, however, be clearly explained if a sufficiently good knowledge of possibilities for the formation of the phases is available, and if it is used correctly.

In most cases the solid phases, silica and calcium hydroxide, are mixed with water and afterwards autoclaved as slurries or pastes. It has been suggested that mixtures of amorphous silica of different origin give different results. In our laboratory we have investigated some silica samples, dried on the steam bath or heated in an air bath 300 to 400 °C. The same results have always been obtained, independent of the kind of silica; the only precaution we took was to grind and sieve the silica before mixing it with the calcium hydroxide or oxide. A slurry in which a certain part of the solids could precipitate was avoided. The autoclaves, in which the platinum crucibles were hung on a silver gallows, were equipped with manometers for pressure control and valves for evacuation. The heating-up period was always performed according to a program in which the reaction temperature was reached with the least delay. In this way the experiments could be reproduced without difficulty. When quartz or silicates were used, the surface area per gram of the mineral was always determined, and it was also necessary in this case to limit the added amount of water.

The reaction between lime and silica will begin when the silicate ions are dissolved from the small lumps of amorphous silica or from the crystals of the well-crystallized compounds (quartz, feldspar, mica). The ions are monomeric and have the configuration $[SiO_4]^{4-}$. The ions will immediately be saturated by Ca ions as far as the supply of these ions in the surroundings will allow. These reactions between silicate ions and Ca ions are the initial ones that always take place in every system containing CH–S–H. Up to the present, three compounds with varying lime content are known to occur as initial phases in the systems between 100 and 250 °C, having the initial configuration according to the schematic representation below and finally crystallizing as phases established by X-ray measurements.

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[1] Figures in brackets indicate the literature references at the end of this paper.

$\left[H_4\right]^{4+}\cdot\left[SiO_4\right]^{4-}$	$\left[\begin{matrix}H_3\\ \frac{1}{2}Ca\end{matrix}\right]^{4+}\cdot\left[SiO_4\right]^{4-}$	$\left[\begin{matrix}H_2\\ Ca\end{matrix}\right]^{4+}\cdot\left[SiO_4\right]^{4-}$	$\left[Ca_2\right]^{4+}\cdot\left[SiO_4\right]^{4-}$
tetrahydrogen orthosilicate	trihydrogen hemicalcium silicate	dihydrogen calcium silicate	dicalcium silicate
Crystallizing as Ca compounds	Z-phase $CaO{\cdot}SiO_2{\cdot}2$ or $3H_2O$	Tobermorite $CaO{\cdot}SiO_2{\cdot}H_2O$	α-dicalcium silicate monohydrate $2CaO{\cdot}SiO_2{\cdot}H_2O$

After this crystallization, other reactions set in giving products of other kinds characteristic for the system in question.

The System Lime–Amorphous Silica–Water

The Low-Temperature Phases (<150 °C)

The formation of the three compounds at the saturation of the silicate ion, the Z-phase, the tobermorite phase, and the α-dicalcium silicate monohydrate phase, depends on the supply of lime. In most cases some silica seems to remain uncombined. Only one of the three phases can be in equilibrium with silica, apart from the mixture corresponding to an invariant point (two silicates + silica). At present it seems to be impossible to establish the silicate in equilibrium with silica by running experiments over a long period; other methods must be used.

This system gives the best survey of the reactions, and observations in other systems have to be based on the results; the formation of the phases is illustrated in the scheme shown in figure 1.

The High-Temperature Phases

Since the low-temperature phases always occur at higher temperature during a short period of time, they can be recovered as transition compounds. In these cases they reach the range of the high-temperature phases because of a rather slow rate of crystallization. The temperature of the transition phases is now considerably higher than their own real highest temperature of formation. The position of the substances in the thermochemical system of the compounds leads to a production of heat caused by the recrystallization. From the thermochemical point of view the compounds formed by these reactions must be stable phases. Figure 1 shows these high-temperature phases (gyrolite, xonotlite, and hillebrandite); the final high-temperature products will contain the phases in proportions that can be calculated from the compositions of the initial mixtures.

The System Lime–Quartz–Water

As mentioned above it is necessary to know the supply of lime per unit area of mineral surface, if the products formed are to be estimated. A survey of the reactions is presented in figure 2.

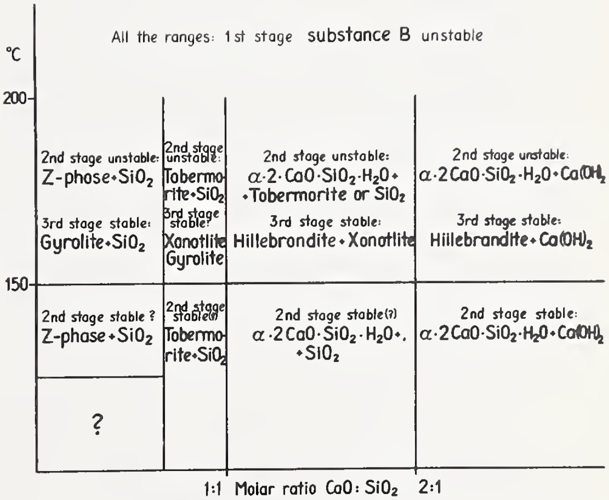

FIGURE 1. *Reactions in the system* $Ca(OH)_2$*–amorphous silica.*

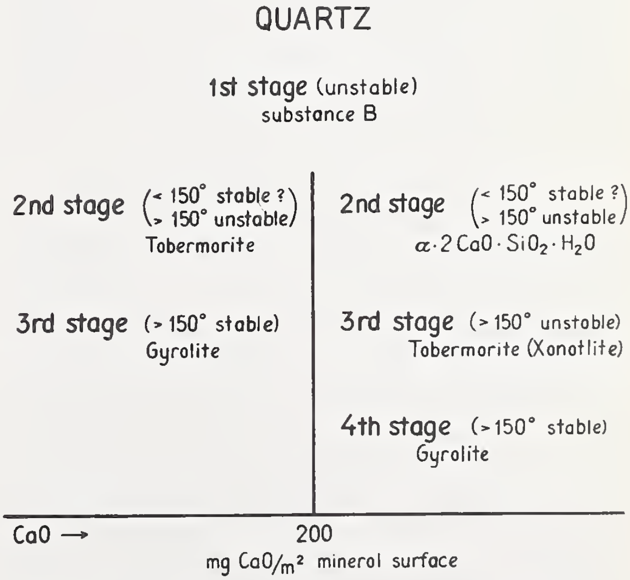

FIGURE 2. *Reactions in the system* $Ca(OH)_2$*–quartz.*

The general course of the reactions noted in the system lime-amorphous silica-water can also be followed here. The compounds first formed depend to a high degree on the supply of lime; mixtures poor in lime yield the tobermorite phase as first compound; the mixtures rich in lime, on the other hand, the α-dicalcium silicate hydrate. The boundary between these two ranges corresponds approximately to about 200 mg CaO/m^2 mineral surface. The sequence of crystallization products is the same as in the system with amorphous silica; on the assumption that solid quartz remains during the autoclave treatment the principal reaction will lead to formation of the compound poorest in lime, the gyrolite phase, at 150 to 250 °C.

In some points the system with quartz differs from that with amorphous silica. In the quartz system the hemicalcium silicate, the Z-phase, has not been recovered. There are two possible explanations of this. The Z-phase may not be a stable phase, in which case it would not be formed. Secondly, in the system with amorphous silica the production of silicate ions is abundant, in the system with quartz or silicates the supply of ions is regulated by the rate of dissolution from the surface of the crystals. Probably this rate is not sufficiently high to yield a hemicalcium silicate. Thus, the initial reaction will be extremely dependent on the state of the lattice of the reacting surface. Investigations with varying reacting surface combined with the state of the lattice have not yet been performed; they should be very elucidating for the explanation of the system.

Among the products compounds appear that would not be expected in the correct formation of solids outlined above. Small amounts of xonotlite and hillebrandite occur, possibly also other compounds. In the heterogeneous system with quartz, pores and cavities will always occur, rendering available possibilities for special compounds not subjected to the diffusion of ions which is a condition for a homogeneous reaction product. The low rate of transformation also tends to preserve these compounds.

The System Lime–Silicate–Water

For the present, only the systems with feldspar and muscovite have been investigated systemtically. The systems of this kind require special considerations.

The attack of lime on the surface of the crystals depends even in this case on the supply of lime per unit area of the mineral surface. Mixtures poor in lime yield monocalcium silicate (the tobermorite phase), and those rich in lime the α-dicalcium silicate hydrate. The boundary between these ranges corresponds to about 100 mg CaO/m^2 for feldspar, and less than 25 mg CaO/m^2 for muscovite (fig. 3). Further treatment at temperatures 150 to 250 °C leads to the formation of gyrolite, in agreement with the sequence of crystallization found for the system with quartz.

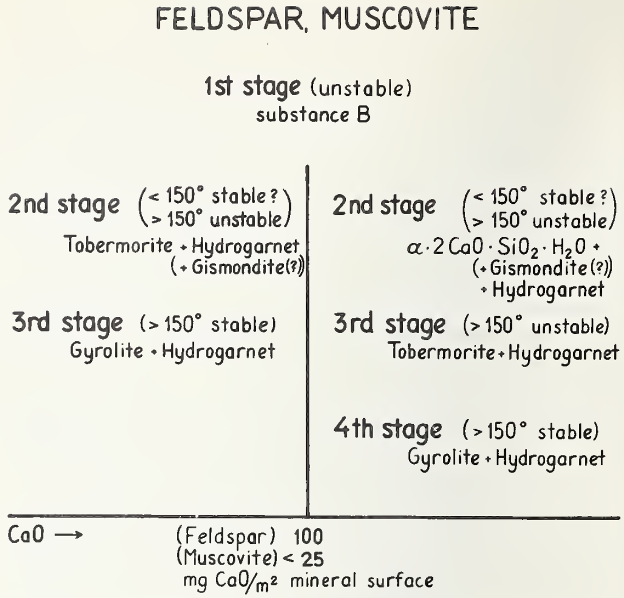

FIGURE 3. *Reactions in the systems* $Ca(OH)_2$*–feldspar and muscovite.*

The silicates contain other components than silica, in the above two cases alumina and alkalies. The alkalies do not influence the reactions to a noticeable degree. Alumina reacts with lime chiefly forming hydrogarnets. The hydrogarnets vary considerably in composition during the autoclave treatment. The compound first formed has the approximate composition $3CaO{\cdot}Al_2O_3{\cdot}1{\cdot}5SiO_2{\cdot}3H_2O$; later during the treatment the composition is changed to about $3CaO{\cdot}Al_2O_3{\cdot}0.5SiO_2{\cdot}5H_2O$. When the attack of lime on the mineral is vigorous (high temperature, easily attacked mineral lattice), the hydrogarnets are registered as bands in the X-ray photographs; with a slow attack the bands are divided into sets of distinct lines, showing a rhythmical crystallization of the compound.

At low temperature (<150 °C) a new compound appears, having a characteristic line at 10A, possibly indicating a zeolite (gismondite). This compound has not been shown in products autoclaved at higher temperatures. Some other unidentified lines occur also in the X-ray photographs. This part of the system is not investigated sufficiently, probably the occurrence of some other compounds can be established.

The Diffusion Layers

When the minerals react with calcium hydroxide, the crystal surface will immediately be covered with a cryptocrystalline layer, in the present paper designated substance B. It is identical with the substance formed when calcium hydroxide reacts with amorphous silica. The substance has been considered identical with the tobermorite phase, and its varying lime content is explained as an excess of lime adsorbed on tobermorite crystallites of low frequency with lattice units similarly oriented especially in the *c* direction. From the results of the investigations described above, however, the conclusion must be drawn that the substance B is a mixture of several substances. When lime reacts under hydrothermal conditions with silicates containing alumina or ferric oxide, these components will occur in the substances.

The thickness of the layers represents the formation rate of the solids, and the boundary concentration of lime will give a certain idea of the production of ions. The importance of the diffusion layers has been emphasized earlier in a paper concerning the system Ca almuinate–solution [2]. The same reaction types will always be found in every heterogeneous solid-liquid system, and without a detailed knowledge of the properties of the solids formed and the sequence of crystallization the character of the final reaction products cannot be shown. The reaction conditions at the crystal surface depend on the attacking agent, in this case the lime, and experiments in which the supply of lime per unit area of the crystal surface is unknown are of very little value for an understanding of the observations.

The reaction layers are of two types forming monocalcium or dicalcium silicates as first crystallizing product. The boundary concentration of lime is only approximate, but it gives a good conception of the resistance of the mineral lattice to the attacking agent and a possibility of calculating the amounts of the hydration products, at the point where the products change properties.

The three minerals investigated (quartz, feldspar, and mica) show varying resistance to the attack of lime, The most resistant mineral is quartz (200 mg CaO/m^2 mineral surface), then feldspar (100 mg CaO/m^2), and least the mica (<25 mg CaO/m^2). The thickness of the layers is listed in table 1. It is calculated on the assumption that the lime is equally distributed over the mineral surface, disregarding pores and cavities.

Table 1. *Thickness of the reaction layers ot the boundary.* CaO *concentration at the boundary: with quartz, 200 mg* CaO/m^2; *with feldspar, 100 mg* CaO/m^2; *with mica, 25 mg* CaO/m^2

Character of the layer	Quartz	Feldspar	Muscovite
	mm	*mm*	*mm*
Monocalcium silicate (tobermorite)	2.1×10^{-4}	0.6×10^{-4}	0.2×10^{-4}
α-dicalcium silicate	1.2×10^{-4}	1.4×10^{-4}	0.2×10^{-4}
2:3 calcium silicate (gyrolite)	2.5×10^{-4}	----------	----------

The first layer formed is the tobermorite or α-dicalcium silicate hydrate afterwards transformed into the gyrolite compound. The aluminous silicates also yield hydrogarnets. The thickness of the layers at the concentration boundary has a magnitude of $0.1 - 2.5 \times 10^{-4}$ mm.

The Z-Phase

The Z-phase, first prepared by the present author, is mentioned by Taylor as identical with the substance $CaH_4Si_2O_7$ prepared by Funk and Thilo [3]. The preparation method of these authors is irrelevant for the present system. The spacings given by Funk and Thilo are listed in table 2 together with new measurements of the Z-phase made by the present author. The spacings agree in some cases, in others not. The symmetry of the Z-phase is probably not orthorhombic, but monoclinic or triclinic. Considering the different methods of preparation it would be surprising if the two substances were identical.

Table 2. *X-roy data on hemicalcium silicate hydrates*

Z-phase (Assarsson) $CaO\cdot2SiO_2\cdot2$ or $3H_2O$ (autocl. 140 °C, 24 hr)			$CaH_4Si_2O_7$ (Funk and Thilo) (autocl. 180 °C, 24 hr)		
I	*d*	*hk l*	*I*	*d*	*hk l*
s	15.1	100	w	8.32	001
m	8.35	001	www	5.02	200
m	5.070	300	m	4.18	002
w	4.390		ww	3.82	010
ww	4.165	002	ww	3.35	300
w	3.786	010?	s	3.03	210
w-m	3.357		ww	2.77	003
bd w	3.80–3.36		www	2.52	400
ww	3.142		www	2.26	013
m	3.033	500	www	2.08	004
bd w	3.14–3.03		ww	1.92	020
br w	2.778	003	www	1.87	403, 313
w	2.410		s	1.82	502
w	1.911	020?			
s	1.817				
br w	1.336				
w	1.192				
			According to Funk and Thilo		
a=15.16 *b*= 3.79? *c*= 8.330			orthorhombic *a*=10.04 *b*= 3.82 *c*= 8.32		

The Tobermorite Phase

The tobermorite phase prepared by autoclaving mixtures of lime and amorphous silica has been considered to have the composition shown in some mineral species, corresponding to $C_5S_6H_5$. When mixtures of lime and amorphous silica, having the molar proportion $CaO:SiO_2=0.80:1$ and 0.85:1, are autoclaved at 180 to 200 °C, the tobermorite phase should be formed in an almost pure condition. The products, however, contain considerable amounts of the gyrolite compound. The synthetic tobermorite compound should therefore be a monocalcium silicate.

Some experiments performed in order to establish the formation of the tobermorite in the presence of alumina and kaolinite showed that the spacings of tobermorite do not change on addition of these compounds and that the formation of the tobermorite takes place in a normal manner and to the expected extent if the reaction surface area per grams of mineral is taken into consideration.

Other Compounds

The compounds mentioned in this paper are limited to three low-temperature phases (Z-phase, tobermorite, and α-dicalcium silicate hydrate) and three high-temperature phases (gyrolite, xonotlite, and hillebrandite). The high-temperature phases are the only ones occurring in equilibrium at about 150 to 250 °C. The equilibrium of the low-temperature phases is not yet established. Besides these compounds, however, some others occur that obviously belong to the system but have not yet been prepared synthetically. Their formation conditions must be extraordinary and outside common methods of preparation. They are okenite, nekoite, truscottite, foshagite, perhaps partly also afwillite and others. In the experiments on which the above results are based the lattice of the initial silicates does not contain lime. The compounds formed by autoclave treatment of mixtures with lime must therefore be independent of the configuration of the lattice of the silicate, and the calcium silicate hydrates are formed according to the normal conditions (figs 2 and 3). On the other hand, when the silicate lattice initially contains calcium ions, the positions of the ions are already occupied to some degree, a certain part of the formation energy is consumed and the conditions for the formation of hydrated products are limited. When the surplus of formation energy between the stable and unstable compounds in question is insignificant, the phases formed at the hydration behave as metastable compounds, and the real equilibrium is not reached. This relation is characteristic for the system; it seems to be the explanation of the somewhat contradictory results given in the literature. Ions extraneous to the pure systems can also cause results of this kind.

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Discussion

H. Grothe, G. Schimmel, and H. zur Strassen

The following discussion presents a report of some observations on tobermorite formed in sand-lime bricks. The electron-microscope investigations described [1] [1] are of interest for the hydrothermal reaction between quartz and lime [2].

Method of Investigation and Results

When sand-lime bricks were formed, polished quartz crystals were embedded in them. After the reaction the bricks were crushed and the crystals carefully taken out. Then a quickly hardening resin was poured on the crystal surface, which could be taken off from the quartz crystal after hardening. In this process the fine reaction layer of calcium silicate hydrate which had formed on the quartz surface adhered at least partially to the resin. To that side of the resin facing the quartz a carbon film was applied by sublimation in vacuum. When dissolving the resin the carbon film remained with the adhering crystals which could be put on a specimen screen of the electron microscope for investigation.

The photographs belonging to this investigation were made during a test series in which the reaction temperature was kept constant at 195 °C.

After a reaction lasting for 1 hr, diffraction diagrams showed some strong reflections of a tobermorite-like phase. After a reaction period of 3 hr fibrous crystals formed (fig. 1) from which single-crystal diffraction patterns could be obtained. The diffraction diagram shown in figure 2, which was obtained from 2 crystals slightly twisted against each other, shows—apart from the strong reflections (*h* and *k* even)—likewise weak ones (*h* and *k* odd) as they can be observed in a similar, but not identical way when tobermorite is produced hydrothermally [3]. The crystal rests on the (001) surface. The long axis of the lath-shaped crystal is the *b* axis corresponding to the tobermorite structure [4].

FIGURE 1. *Micrograph of the reaction product after 3 hr.*
Magnification 10,000.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Figure 2. *Single-crystal diffraction pattern of the reaction product after 3 hr.*

Crystal lying on (001), *b*-axis vertical.

Figure 3. *Single-crystal diffraction pattern of the reaction product after 4 hr.*

Crystal lying on (001), *b*-axis vertical.

Figure 4. *Single-crystal diffraction pattern of the reaction product after 5 hr.*

Crystal lying on (100), *b*-axis vertical.

After 4 hr (fig. 3) a characteristic disorder phenomenon sets in, in the reaction product, which after 3 hr could be observed at best as traces. In the crystal which has the same orientation as in figure 2 the odd zones have become distorted to form continuous lines running parallel to the *a* axis; likewise the strong reflections of the even zones show elongations. The crystals show the same disorder arrangement after a reaction time of 5 hr. Figure 4 shows the diffraction pattern of a crystal lying on (100). Here the odd zones running parallel to the *c* axis consist of continuous lines.

Since the resolving power of the electron microscope reaches down to the order of the basal spacing, it was attempted to make a direct micrograph of the same crystal, the diffraction pattern of which is shown in figure 4, by the strongest magnification possible. In figure 5 is a closeup into the crystal running parallel to the *a* axis, and the alternating light and dark streaks show clearly the various horizontal layers. The periodicity of the basal spacing in the *c* direction obtained by direct observation is in good agreement with the 11.3 A measured by electron diffraction.

Figure 5. *Electron micrograph of the same crystal as shown in figure 4.*

Crystal lying on (100), *b*-axis horizontal. Magnification 880,000.

Discussion of Results

At first we considered the reaction product formed after 4 and 5 hr to be tobermorite of the "anomalous" Loch Eynort type [3], for two reasons: the single-crystal diffraction patterns show the disorder phenomena characteristic for this type, and almost all specimens have the same inalterable basal spacing of 11.3 A. In two cases only a shrinkage of the layer distance down to 9.5 A occurred, as is to be expected in case of a "normal" tobermorite due to dehydration under electron bombardment [3, 5].

Dr. Gard [6], however, drew our attention to the fact that the strong reflections of the diffraction diagram (fig. 4) do not follow the extinction rules of tobermorite, but those of foshagite. Dr. Gard assumed that the phase should be foshagite.

For other reasons even the formation of foshagite is not plausible: The layer distance of foshagite is not 11.3 A as observed here, but 14 A, and the area of foshagite ranges only beyond 300 °C [2, 7], whilst the tests described here had been running at 195 °C.

A new discussion with Dr. Taylor had the result that the reaction product after 3 hr should be normal tobermorite, which after a longer reaction period changed to a new phase unknown to date. This new phase should be closely related to tobermorite; probably the two phases differ only in the arrangement of the metasilicate chains.

The strength carrier in the sand-lime brick is the tobermorite. Changing to the new well-crystallized phase causes a decrease in the strength.

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Discussion

D. M. Roy and R. I. Harker

Introduction

In his review paper H. F. W. Taylor [1][1] has emphasized the importance of equilibrium studies at relatively high water-vapor pressures as background information for understanding cement hydration processes, and has described many of the results which have been completed since the last symposium.

It is now possible to present a tentative series of diagrams describing the phase assemblages which develop at successively higher temperatures for all lime:silica ratios in this system. The results of equilibrium studies at The Pennsylvania State University (chiefly on that part of the system with lime:silica molar ratios of 1.0 or more) and at the Johns-Manville Research Center (on compositions in which this ratio is less than 1.0) can be combined with each other and with data in the literature to provide an overall picture for the $CaO-SiO_2-H_2O$ system. This can best be done by presenting a series of triangular diagrams which show the various assemblages as steps in a dehydration series in a manner analogous to that of Roy and Osborn [2] for the $Al_2O_3-SiO_2-H_2O$ system and to that of Bowen and Tuttle [3] for the $MgO-SiO_2-H_2O$ system. It would be imprudent to claim that all the assemblages shown represent the ultimate equilibria, especially at the lower temperatures. They do, however, represent stages which are well beyond what are obviously metastable equilibria and are of pratical significance. There is some evidence that by increasing the duration of runs, some of the earlier dehydration steps may be made to take place at slightly lower temperatures, but the order in which they take place is not changed substantially from that given below. Above 400 °C most of the reactions involving the more lime-rich phases can be made to proceed in either direction.

Many of the assemblages are not appreciably affected by moderate changes of pressure because the P–T curves for the dehydration reactions are more or less parallel to each other and, at the higher pressures, to the pressure axis on a P–T diagram. However, where there is evidence that the low-pressure (i.e., saturated steam) assemblages are different from the high-pressure assemblages at a given temperature, then the low-pressure compatibility triangles are marked in dotted lines. The effect of pressure on the assemblages involving a calcium hydroxide-rich liquid is not known but below 100 bars calcium hydroxide dissociates instead of melting (Wyllie and Tuttle [4]).

It must be emphasized that the triangular diagrams do not attempt to show every step in the dehydration series but only those for which there is experimental evidence. *Where evidence for the actual order of successive steps is lacking, they are all introduced in one combined step in the series.*

Up to the melting point of calcium hydroxide, we are concerned only with the stability of solid phases in equilibrium with extremely dilute fluids (liquids or vapors). The solubility of lime in the vapor phase at high temperatures is very low and, although the solubility of silica is probably higher, the diagrams would have to be greatly enlarged at the H_2O apex to show the true composition of the

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[1] Figures in brackets indicate the literature references at the end of this paper.

vapor. On the triangular diagrams, therefore, the solid phases all have lines running towards the H_2O apex (see Majumdar and R. Roy [5]), indicating that essentially pure H_2O is a coexisting phase.

Where there is some uncertainty in the interpretation of the experimental results or the natural rocks, dashed lines have been used. In those diagrams which show a calcium hydroxide-rich liquid, the dashed lines indicate the approximate phase boundaries as determined by preliminary experiments.

Dehydration Steps

Up to temperatures somewhat below 100 °C, CSH(I) and CSH(II) usually develop from reactive starting materials. Therefore, the first triangle shows CSH(I)–SiO_2 and CSH(II)–CH joins. These CSH phases are poorly crystallized and so far have defied precise definition in terms of structure and composition. Doubts may be cast on their true stability—hence, the dashed lines in triangle IA. More hydrated phases are, of course, known. These include okenite, nekoite, (Taylor [1]) and plombierite (as defined by McConnell [6]) found in natural rocks, and Funk and Thilo's [7] $CaH_4Si_2O_7$, probably Assarsson's [8] Z phase and CSH(II) with compositions extending towards C_2SH_4 approximately (Heller and Taylor [9]), produced in laboratories.

Triangle IB summarizes the assemblages, including natural minerals, which are probably closer to equilibrium at these very low temperatures than are the poorly-crystallized synthetic phases (see Long and McConnell [10]).

In a narrow temperature range, 100 to 160 °C approximately, CSH(I) gives way to better crystallized tobermorites ($C_4S_5H_4$ to $C_5S_5H_5$), gyrolite ($C_2S_3H_2$) develops from C/S molar ratios less than 0.8, and afwillite ($C_3S_2H_3$) and hillebrandite (C_2SH) can be synthesized. At saturated steam pressures in this range $C_3SH_{1.5}$ has also been synthesized, but it may not be stable until about 185 °C at higher pressures and, therefore, is shown in triangle II with the dotted tie lines. The formation of each phase involves an individual reaction, but lack of evidence prevents individual triangles from being drawn to represent each one. At the upper limit of this temperature range (160 °C), therefore, the assemblages in triangle II are indicated.

Between 160 and 200 °C in saturated steam (see dotted lines in triangle III), xonotlite + H_2O appears to become more stable than tobermorite (Nagai [11], Foret [12], Flint, McMurdie, and Wells [13], Heller and Taylor [14], Peppler [15]). Peppler's runs of several months' duration indicate that xonotlite and hillebrandite are stable rather than afwillite.·

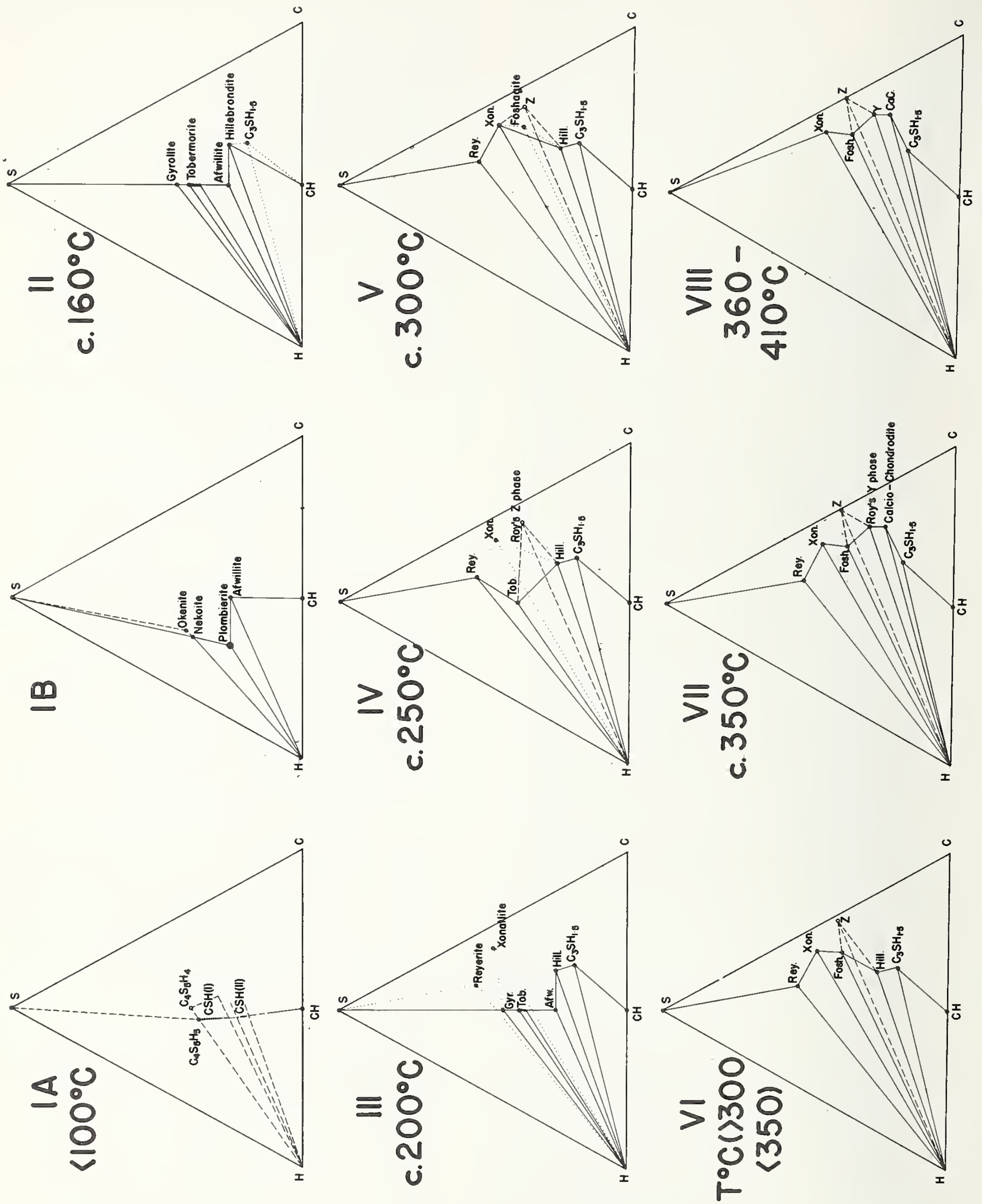
Also, in this range, gyrolite becomes unstable in the presence of excess silica, and, as a result, reyerite ($C_3S_5H_{1.5}$) tends to form (Harker [16]). With a mineralizer (2 percent of NaF) quite well-crystallized reyerite can be produced, but with no mineralizer long runs (one month) produce gyrolite-reyerite mixtures which are probably metastable and which from their nonintegral basal spacings appear to consist of randomly mixed layers on a very small scale (Brown and MacEwan [17]).

At elevated pressures (see continuous lines in triangle III), gyrolite+silica have persisted together to about 210 °C in runs of similar duration; therefore, the gyrolite-silica join remains at high pressures in triangle III. At high pressures, the stability of tobermorite is raised considerably (Buckner, Roy, and Roy, [18]) so that a gyrolite-xonotlite assemblage is stable at low pressures but not at high pressures.

Between 200 and 250 °C several reactions take place until finally at about 250 °C, the assemblages indicated in triangle IV are in equilibrium. The assemblage gyrolite+silica, already not stable at 200 °C at saturated steam pressures, now reacts to form reyerite+H_2O at high pressures (above 15,000 psi). Then gyrolite alone becomes unstable, breaking down to reyerite+xonotlite+H_2O around 220 °C at saturated steam pressures and to reyerite +scawtite (presumably reyerite+tobermorite if CO_2 could be kept out) a little above 230 °C at high pressures, 15,000–40,000 psi (Harker [16]). Afwillite breaks down to Roy's phase Z ($C_3S_2H_{0-0.33}$)+H_2O at about 220 °C above 5,000 psi (Roy [19]), but work at high temperatures and pressures of 30,000 psi or greater suggests that this phase Z may be metastable—hence, the dashed lines emanating from Z in triangle IV and subsequent triangles. The P–T curve for the breakdown of afwillite and that for the breakdown of gyrolite would be very close to each other on a P–T diagram and at present cannot be shown separately.

Triangle V represents conditions at about 300 °C. Above 290 °C high pressure fails to preserve the stability of tobermorite and tobermorite gives way to xonotlite (+reyerite) at all pressures at least up to 30,000 psi. Little work has been done on the lower limits of stability of foshagite (C_4S_3H)+H_2O, but that of Flint, McMurdie, and Wells [13] in saturated steam indicates that with rising temperature the formation of foshagite follows that of xonotlite, and that at low pressures it comes in definitely below 300 °C. If the P–T curve for its formation has a normal positive slope, as one might expect from a consideration of the volume relations, then it should form at lower pressures (dotted lines) before it would at higher pressures with rising temperature. High-pressure runs are needed to verify this conclusion.

Triangle VI represents the appearance of foshagite at high pressure at some temperature between 300 and 350 °C. One of the major equilibrium problems among well-crystallized phases in this system is that concerning the relative stabilities of foshagite and Roy's Z-phase. If Z is truly stable then its formation at temperatures lower than those covered by the hillebrandite-xonotlite and the hillebrandite-foshagite assemblages is difficult to explain.


IA
<100°C
S
C
H
CH
$C_4S_5H_5$
$C_4S_5H_4$
CSH(I)
CSH(II)
IB
S
C
H
CH
Okenite
Nekoite
Plombierite
Afwillite
II
c.160°C
S
C
H
CH
Gyrolite
Tobermorite
Afwillite
Hillebrandite
$C_3SH_{1\cdot5}$
III
c.200°C
S
C
H
CH
Reyerite
Xonotlite
Gyr.
Tob.
Afw.
Hill.
$C_3SH_{1\cdot5}$
IV
c.250°C
S
C
H
CH
Rey.
Xon.
Roy's Z phase
Tob.
Hill.
$C_3SH_{1\cdot5}$
V
c.300°C
S
C
H
CH
Rey.
Xon.
Foshagite
Z
Hill.
$C_3SH_{1\cdot5}$
VI
T°C(>300
<350)
S
C
H
CH
Rey.
Xon.
Fosh.
Z
Hill.
$C_3SH_{1\cdot5}$
VII
c.350°C
S
C
H
CH
Rey.
Xon.
Fosh.
Z
Roy's Y phase
Calcio-Chondrodite
$C_3SH_{1\cdot5}$
VIII
360–
410°C
S
C
H
CH
Xon.
Fosh.
Z
Y
CaC.
$C_3SH_{1\cdot5}$

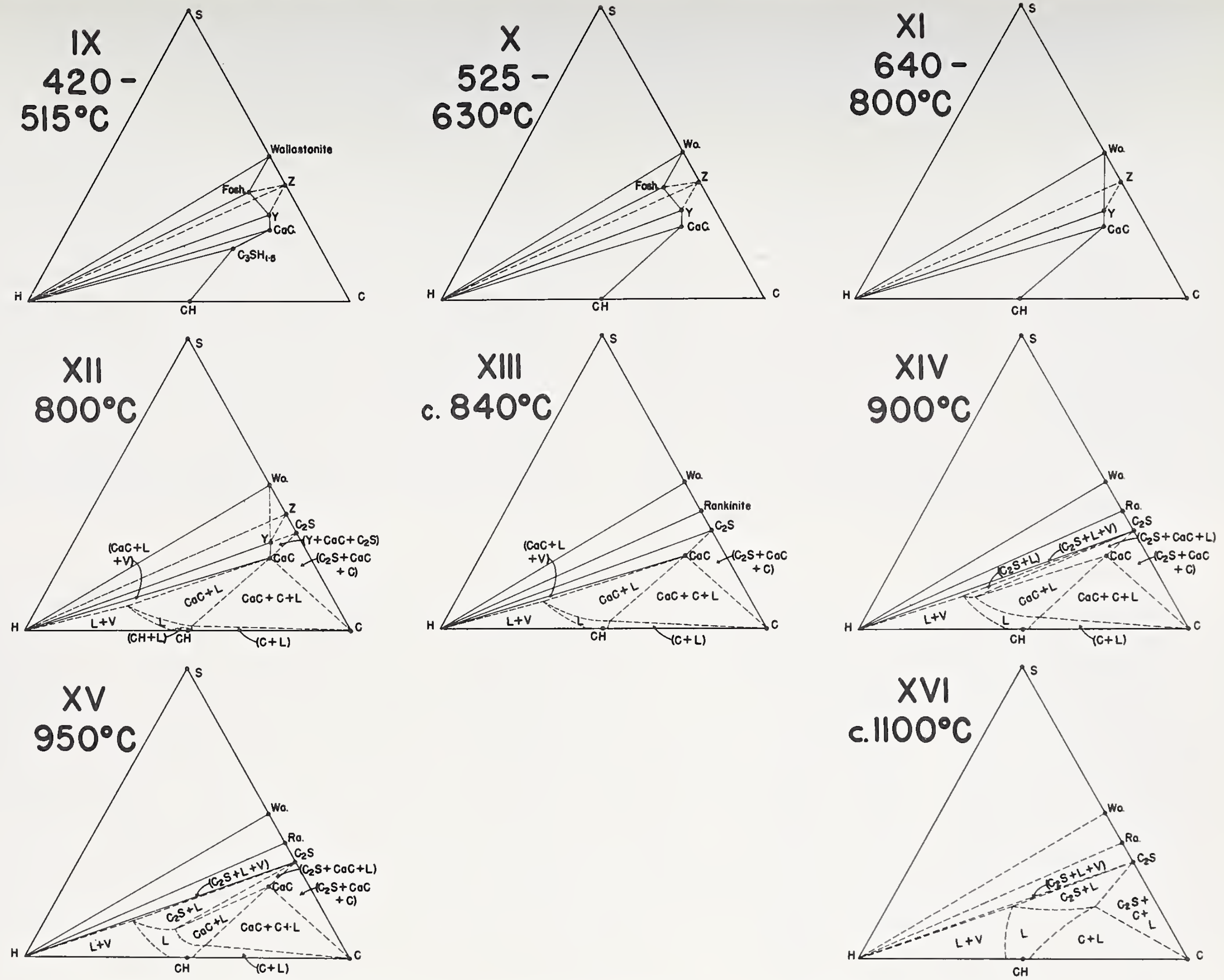


FIGURE 1. *The system* CaO–SiO$_2$–H$_2$O, *showing some of the compatibility triangles for the temperatures and temperature ranges indicated at saturated steam pressures (dotted lines) and at high pressures, about 15,000 psi (continuous lines).*

Triangle IB shows the most hydrated (lowest temperature) crystalline phases known. Dashed lines indicate some uncertainty in the equilibria as explained in the text. It has been impossible to show every step in the dehydration series and in several instances more than one reaction has taken place between two adjacent triangles. All phases are written in full the first time they appear and thereafter are abbreviated approximately. L—Liquid, V—Vapor (essentially H$_2$O), C—CaO, S—SiO$_2$, H—H$_2$O, and CaC stands for Calcio-Chondrodite or C$_5$S$_2$H.

The next step occurs when $C_3SH_{1.5}$ breaks down at 520 °C (at 15,000 psi), and the calcio-chondrodite-calcium hydroxide join is established, see Roy [19]. Triangle X represents the equilibrium assemblages between 525 and 630 °C.

At about 635 °C (and 15,000 psi) foshagite breaks down to wollastonite$+$Z$+H_2O$, but at higher pressures the product is Y$+$wollastonite$+H_2O$ (Roy, unpublished data), suggesting metastability of the Z-H_2O join which is shown as a dashed line in triangle XI as in all others containing Z. The temperature is based on data obtained using three different starting materials: the natural mineral from Crestmore, synthetic foshagite having a 4:3 CaO:SiO_2 ratio, and a gel having the same ratio.

Reactions in the Presence of Liquid and Further Dehydration Steps

Curves for decomposition of the following phases at successively higher temperatures were given by Roy [19]: Y-phase$\rightleftharpoons\alpha'$-$C_2S+H_2O$; Z-phase$\rightleftharpoons$rankinite; and X-phase (calcio-chondrodite, C_5S_2H, or CaC)$\rightleftharpoons\alpha'C_2S+CaO+H_2O$, and these data form part of the bases of the next four triangles. However, after Wyllie and Tuttle [4] described the phenomenon of melting of $Ca(OH)_2$ under elevated H_2O pressures it became apparent that the field of $Ca(OH)_2$ liquid must enter the ternary system, at least above 815 °C (the eutectic for the system $Ca(OH)_2$-H_2O at 15,000 psi), and additional information was necessary to more completely describe the equilibria. Preliminary data have therefore been obtained by the authors to investigate the probable extent of the liquid field in the ternary system at 800, 900 and 950 °C and the equilibria among the crystalline phases at these temperatures at 15,000 psi.

The next four triangles represent an attempt to present the data in a reasonable manner, although the data are by no means complete, as indicated by the dashed lines. Triangle XII shows the proposed stability relations at 800 °C and 15,000 psi, where both Z-phase and Y-phase persist in the presence of H_2O vapor, and Y-phase$+$calcio-chondrodite (CaC)$+H_2O$ are stable together. A small field of $Ca(OH)_2$$+$liquid exists, and the liquid field extends into the ternary system, but not as far as the CaC-H_2O join. A fairly large field where CaC is the primary phase in equilibrium with liquid is found at this temperature.

Roy's [19] Y-phase (C_6S_3H) comes in below 350 °C at the expense of hillebrandite. Unlike foshagite (which may occur in nature intimately intergrown with hillebrandite, e.g., see Taylor [20]), the Y-phase cannot occur in equilibrium with hillebrandite $+H_2O$ except along a univariant P–T curve. Its formation therefore probably represents a more advanced stage in the dehydration series than the development of foshagite. Phase X of Roy [19] or calcio-chondrodite (C_5S_2H or "CaC") becomes stable in this temperature region and can be in equilibrium with Y or $C_3SH_{1.5}$ depending on the exact C/S ratio. Since it has never been positively identified as coexisting with hillebrandite and the individual steps involving the incoming of Y and of CaC have not yet been differentiated they are shown as coming in together in triangle VII.

At 335 °C reyerite breaks down to xonotlite$+$silica$+H_2O$ (Harker [16]). As might be expected from a consideration of ΔV for the reaction, the P–T curve is nearly parallel to the pressure axis on a P–T diagram. Triangle VIII therefore represents the equilibrium assemblages after the breakdown of reyerite but before the breakdown of xonotlite.

It is convenient from now on to consider the various successive steps isobarically with rising temperature, as the saturated steam curve has no meaning above the critical point of water. The following triangles therefore apply at approximately 15,000 psi.

At 415 °C (and 15,000 psi) xonotlite decomposes to wollastonite$+H_2O$ and dehydration in the silica-rich half of the system is complete. Triangle IX shows the equilibrium assemblages between 420 °C and 515 °C with foshagite now coexisting with wollastonite.

It is noteworthy that the occurrence of wollastonite with hillebrandite has been reported (at Velardena, Mexico, Wright [21]), whereas experimental work indicates that in the CaO-SiO_2-H_2O system wollastonite$+$hillebrandite$+H_2O$ should not be in equilibrium, and no wollastonite-hillebrandite-H_2O compatibility triangle is seen in this series. The experimental and natural observations, however, may not really be in conflict for the following reasons: (1) It has been recently shown that natural hillebrandite and foshagite are frequently intergrown and difficult to identify separately, and that at least part of the Velardena "hillebrandite" is really foshagite (Heller and Taylor [9]). (2) At Velardena the wollastonite occurs in veins cutting the "hillebrandite" and thus may not be in equilibrium with the hydrated mineral.

Between the temperatures of triangle XII (800°) and XIII (840 °C) three changes take place in the following order: (1) At 815 °C Y-phase decomposes to $\alpha'C_2S+H_2O$ and $\alpha'C_2S+CaC+$Vapor are probably stable together for a narrow temperature interval. (2) At 820 °C Z-phase converts to rankinite. As discussed before, Z-phase may not be truly stable, in which case wollastonite$+$Y-phase could be stable together above the decomposition of foshagite as shown in triangle XI, and rankinite would form at 815 °C above the decomposition of Y-phase. (3) Finally, at 835 °C $Ca(OH)_2$ is entirely melted, and the equilibria at 840 °C are probably as shown in triangle XIII.

Triangle XIV shows the proposed equilibria at 900 °C, where C_2S exists as a primary phase in equilibrium with liquid, the field becoming larger with increasing temperature largely at the expense of the CaC$+$L field. At 950 °C the C_2S primary phase field is even larger (triangle XV) and the CaC$+$L field is smaller, suggesting that CaC melts incongruently. It should be reemphasized that the dashed lines in the past four triangles indicate that the relations described are of a highly tentative nature except for the high-silica portions.

The temperature of final melting of calciochondrodite has not been determined; however, it should be complete by 1,100 °C, and the final triangle XVI is a purely hypothetical representation of suggested equilibrium relations after the last hydrous phase is absent. In the event that CaC melts congruently, this diagram would be slightly modified with the liquid area more closely approaching C_2S.

The writers express their appreciation to Dr. O. F. Tuttle for his aid in determining the liquidus relations involving $Ca(OH)_2$, and to Dr. R. Roy for help with the manuscript. Part of the work was supported by the National Science Foundation Grant G–4648 at the The Pennsylvania State University. The authors are furthermore indebted to the staff of the Johns-Manville Research Center for their encouragement and assistance and especially to Messrs. J. P. Pellicane, Jr., and J. P. McGourty.

(Contribution No. 60–52, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.)

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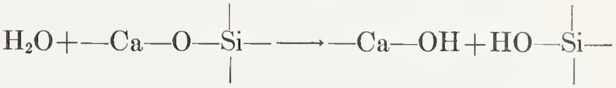
Discussion

G. C. A. Schuit and R. Wyatt

The essential point in the hydration of the calcium silicates seems to be the hydrolytic fission of the Ca—O—Si bond, hence



$$H_2O + {-Ca-O-}\overset{|}{\underset{|}{Si}}{-} \longrightarrow {-Ca-OH} + HO{-}\overset{|}{\underset{|}{Si}}{-} \qquad (1)$$

or alternatively

$$H_2O + Ca^{2+}(SiO_4)^{4-} \longrightarrow Ca(OH)^+ + (HOSiO_3)^{3-}. \qquad (2)$$

If this would continue to the ultimate end we would obtain the formal reaction

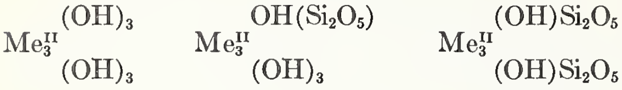
$$Ca_2(SiO_4) + 4H_2O \longrightarrow 2Ca(OH)_2 + Si(OH)_4$$

$$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O. \qquad (3)$$

There is a great similarity in structure between the orthosilicates and hydroxides, thus suggesting that the two structures are largely or completely intermiscible. This is explicitly stated by Wells [1] for the $Mg_2SiO_4\text{-}Mg(OH)_2$ case where a continuous series of minerals $(Mg_2SiO_4)_m \cdot (Mg(OH)_2)_n$ (the chondrodite series) exists.

It may therefore be predicted that the hydration product is somewhere in between the orthosilicate and a mixture of SiO_2 and $Ca(OH)_2$.

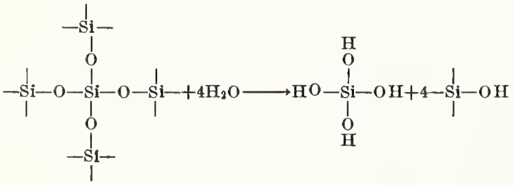
Starting from the other side, e.g., from a reaction of $Ca(OH)_2$, H_2O, and SiO_2 we obtain, as shown by Brunauer et al., a product that resembles tobermorite and that possesses a structure very similar to the layer structure of montmorillonite. This reminds us of some older work by Feitknecht and Berger [2] and Strese and Hofmann [3] for the Mg-compounds and by Van Eyk van Voorthuijsen and Franzen [4] for the Ni-compounds. The evidence shows that there can be formed *kaolinite-* (or antigorite-) type and *montmorillonite*-type compounds even at relatively low temperatures. The two types differ fundamentally in the fact that in the kaolinites we find the tetrahedral silica layer only on one side of the octahedral metal hydroxide layer while it is present on both sides in the montmorillonite-type clays



$$\mathrm{Me}_3^{\mathrm{II}}\begin{matrix}(OH)_3\\(OH)_3\end{matrix}\qquad \mathrm{Me}_3^{\mathrm{II}}\begin{matrix}OH(Si_2O_5)\\(OH)_3\end{matrix}\qquad \mathrm{Me}_3^{\mathrm{II}}\begin{matrix}(OH)Si_2O_5\\(OH)Si_2O_5\end{matrix}$$

hydroxide antigorite montmorillonite

One might visualize the formation of these layer structures as occurring in two steps



$$-\mathrm{Si}-O-\overset{\overset{\displaystyle -\mathrm{Si}-}{|}\\ O}{\mathrm{Si}}-O-\mathrm{Si}- + 4H_2O \longrightarrow HO-\mathrm{Si}(OH)_2-OH + 4-\mathrm{Si}-OH$$

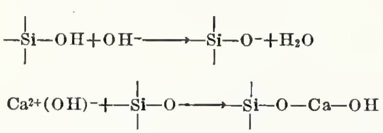
$$HO-Me-OH + Si(OH)_4 \longrightarrow HO-Me-O-Si(OH)_3 + H_2O \qquad (4)$$

The structure thus formed is a precursor of the ideal hydrosilicates (kaolinite, montmorillonite). It can, under favorable circumstances be converted into them by the two-dimensional interpolymerization of $Si(OH)_3$ groups

$$-\mathrm{Si}-OH + HO-\mathrm{Si}- \longrightarrow -\mathrm{Si}-O-\mathrm{Si}- + H_2O \qquad (5)$$

Four remarks have to be added in this connection.

a. Reaction (4) is to be considered a formal representation; in reality it will be more plausible to state it as



$$Ca(OH)_2 \longrightarrow Ca^{2+}(OH)^- + OH^-$$

$$-\mathrm{Si}-OH + OH^- \longrightarrow -\mathrm{Si}-O^- + H_2O$$

$$Ca^{2+}(OH)^- + -\mathrm{Si}-O \longrightarrow -\mathrm{Si}-O-Ca-OH$$

b. Close packing of O^{2-} of OH^- puts a limit to the number of O^{2-} or OH^- ions in the tetrahedral Si-layers. Hence the stoichiometry relations will be premontmorillonite structure, $Me_3(O\overset{*}{H})_4(SiO^*(OH)_3)_2$; montmorillonite structure, $Me_3(O\overset{*}{H})_2(Si_2O_2^*O_3)_2$; in which the asterisk marks the O ions in the octahedral layer, the others being the oxygens at the outerside of the tetrahedral layer.

c. Reaction (4) will probably occur in a random manner, i.e., the $Si(OH)_3$ groups will occur on both sides of the octahedral layer deriving from the hydroxide layer, thus simulating a montmorillonite layer.

d. The protons of the "acid" OH groups connected to the Si will be changed by the Ca^{2+} ions because the protons react with the "basic" OH groups on the metal cation. The Ca^{2+} and H_2O then becomes located between the sandwich layers of the hydrosilicate structure as stated in various papers in this Symposium (Brunauer and Greenberg; Kurczyk and Schwiete). This should occur in such manner that the Ca^{2+} ion should remain in six-coordination with O^{2-}. In a faulty layer structure this would involve incorporation of H_2O, the water molecules fitting then in the vacancies of the outer O^{2-} and OH^- layers.

Our final conclusion is therefore that the hydration of β-Ca_2SiO_4 and the reaction of $Ca(OH)_2$ and silica gel would lead to the same products. These products possess a layer structure that is derived from $Ca(OH)_2$ and $Si(OH)_3$ groups or two-dimensional SiO layers (Si_2O_5) on both sides of the octahedral layer. The tetrahedral Si-O layers are random structures. If enough $Ca(OH)_2$ is present, parts of the structure will be pure $Ca(OH)_2$; on other parts we have SiO layers, isolated $Si(OH)_3$ groups, or structures in between. The outer OH groups, pertaining to the Si-layer, have partially replaced their protons with Ca^{2+} which involves an incorporation of H_2O in the structure.

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Closure

H. F. W. Taylor

I believe that Dr. Roy and Dr. Harker have made a valuable contribution in showing that much of our present knowledge of equilibria in the C–S–H system can be represented on compatibility triangles. There are no significant points of data or of interpretation in their contribution with which I disagree. The triangles at 800 °C. and above are especially valuable, as they summarize the first results of a new line of study, which is clearly going to provide a link between the existing studies on the hydrated and anhydrous systems.

Dr. Assarsson has put forward a most interesting view of the initial stages of the hydrothermal reactions between lime and siliceous materials. His suggestion that ions such as $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ are initially formed, to relative extents that depend on the supply of calcium and silicate ions, appears reasonable enough; one might expect $H_3SiO_4^-$ ions to condense extensively giving the probably lamellar anions in Z-phase, $H_2SiO_4^{2-}$ somewhat less extensively to give the chains characteristic of the tobermorite group, and SiO_4^{4-} (or $HSiO_4^{3-}$?) not at all, to give C_2S α-hydrate. There is, however, a certain conflict of opinion, and perhaps also of evidence, as to what are the first detectable solid products. Most investigators have assigned this role to a poorly crystallized, lime-rich tobermorite mineral of the CSH(II) variety, which subsequently reacts with more silica if this is available. Dr. Assarsson's suggestion that this stage can be bypassed if enough silicate ions are available ought to stimulate much new research on a difficult experimental problem.

Some minor points of Dr. Assarsson's contribution demand comment. Gyrolite, xonotlite, and hillebrandite are not the only ternary phases stable in contact with saturated steam at 150 to 250 °C; reyerite and tricalcium silicate hydrate should be added. Contrary to his statement, afwillite, foshagite, and reyerite (or truscottite) have all been synthesized. Dr. Assarsson disagrees with my view that his "Z-phase" and the "$CaH_4Si_2O_7$" of Funk and Thilo are identical. Of course, one cannot be certain, but the X-ray data which he quotes impress me more as regards similarities than differences. This is the more true if one takes into account our observation that the specimen prepared by Funk and Thilo gives a spacing of about 15A, as well as those originally reported by them. Neither the unit-cell data given by Dr. Assarsson, nor those proposed by Funk and Thilo, can be considered significant, as in both cases they were derived merely by attempting to index the powder data. With such complicated and poorly crystallized structures, the chance of obtaining in this way a unit cell that is even simply related to the true one must be very small. Single-crystal data, or failing that, help from analogy with a substance of known unit cell, are essential. The similarities between the patterns for Z-phase and that of gyrolite are such as to suggest that the two compounds have closely related layer structures. If this is so, Z-phase is hexagonal or pseudohexagonal, with approximate parameters $a=9.73$, $c=15.1$A.

I think that I agree with some of the concepts expressed by Drs. Schuit and Wyatt. The tobermorite structure is indeed derived very broadly from that of $Ca(OH)_2$, the most important difference being the substitution of silicate ions for hydroxyl on both sides of the elementary layer. When a tobermorite mineral is precipitated from aqueous solution, there is presumably a competition between silicate and hydroxyl ions for places in the surfaces of these layers. Under not too basic conditions above 100 °C, the silicate ions eventually win (probably through a complicated mechanism involving several intermediate stages), and 11.3-A tobermorite is formed. Under more basic conditions, the competition is more nearly equal, and both hydroxyl and silicate ions may be expected to find places in the layer. When this happens under conditions favoring crystallization, as in suspensions treated hydrothermally, CSH(II) is formed; I believe this may have a relatively well-ordered, halloysite-like structure in which one side of the layer contains only silicate ions and the other hydroxyl. Under conditions not favoring crystallization, as in normally cured cement pastes, the product resembles CSH(II) in composition, but is considerably less ordered. It seems possible that, in this case, both silicate and hydroxyl ions are attached in a largely random manner to both sides of the layer. This would explain the observed very low degree of crystallinity.

The contribution of Drs. Grothe, Schimmel, and zur Strassen is of exceptional interest. It is becoming increasingly clear that there is more than one form of 11-A tobermorite, and that in some cases at least, these forms are difficult or impossible to distinguish by X-ray powder methods. Because of the differences in morphology, it is possible that they make very different contributions to the strength and other mechanical properties of autoclaved cement products. Further study of them is therefore of practical as well as theoretical importance.

My colleague, Dr. J. A. Gard, has pointed out that the lath-like tobermorite obtained by Drs. Grothe, Schimmel, and zur Strassen after 4 or 5 hours' autoclaving (their figs. 3, 4, and 5) is apparently not quite the same as the Loch Eynort mineral. In the latter, the (100) face of the reciprocal pseudocell (obtained by ignoring the streaky layer lines with k odd) is centered, whereas in the synthetic material (fig. 4) it is primitive. Assuming figures 3 and 4 relate to the same phase, the latter would appear to be a tobermorite in which the pseudocell is C-centered with $c=11.3$A, and not, as in the Loch Eynort and all other known 11.3-A tobermorites, body-centered with $c=22.6$A. Such a pseudocell would correspond to a different kind of packing between each 11.3-A layer and its neighbors, and there is no obvious structural reason to suppose that this is impossible. Since the pseudocell is different, this variety of 11.3-A tobermorite would probably be distinguishable by X-ray powder methods. Further study of this material would be of the greatest interest.

Hydration of Calcium Aluminates and Ferrites

F. E. Jones

Synopsis

Some of the literature of cement hydration bearing on the development of hydrated calcium aluminates and ferrites is reviewed, with some reference to the more complex sulfo- and chloroaluminates and ferrites which may be formed in the presence of calcium sulfate added as retarder, or calcium chloride added to hasten development of strength in a concrete.

Discussion is first based broadly, not on individual hydrated compounds, but on three basic crystal lattices which play a dominant role in cement hydration, and on various solid solutions based on these structures. The place of individual compounds or possible compounds in these structures is discussed in the light of available information, and conclusions are drawn as to compounds or solid solutions which can be formed.

Only the two ternary systems $CaO-Al_2O_3-H_2O$ and $CaO-Fe_2O_3-H_2O$ are discussed in detail. The more recent literature on the former system is considered fairly exhaustively, more particularly in the light of a recent study by Jones and Roberts. The latter system has received much less study and is experimentally much more difficult using normal "phase-rule" techniques, owing to the very slight solubility of the relevant iron compounds. Formation of hydrated ferrites by the action of solutions on anhydrous compounds "in situ" is much more important than in the corresponding $CaO-Al_2O_3-H_2O$ system. Recognition of this, and indirect approach based on analogy yields, however, a useful picture of the realities and possibilities of hydrated iron compound and solid solution formation in the cement-water system.

A simplified picture of hydrated calcium aluminates or ferrites and solid solutions, including reactions with sulfate or chloride, is presented. On present evidence, aluminates appear to be restricted within the range 22 to 100 °C to $C_4A\cdot 19H_2O$ and $C_2A\cdot 8H_2O$ both metastable, however, with respect to $C_3A\cdot 6H_2O$. Below 22 °C, $C_2A\cdot 8H_2O$ is replaced by $CA\cdot 10H_2O$. Above about 100 °C only stable $C_3A\cdot 6H_2O$ and possibly a high-temperature $C_2A\cdot 3H_2O$ hydrate is formed up to about 215 °C, and above 215 °C, $C_4A_3\cdot 3H_2O$. Corresponding hydrated ferrites are limited to metastable C_4F·aq. and $C_3F\cdot 6H_2O$, the latter requiring some Si or Al or both in the structure to stabilize it. Solid solutions and compounds or solid solutions with sulfate or chloride are also discussed.

Résumé

L'exposé passe en revue une partie de la littérature de l'hydration du ciment en cequi concerne le développement de ferrites et d'aluminates de calcium hydratés. Référence est fait aux sulfo- et chloro-aluminates et ferrites plus complexes qui peuvent se former en présence de sulfate de calcium ajouté en qualité de retardateur, ou de chlorure de calcium ajouté pour hâter le développement de la résistance d'un béton.

La discussion est d'abord largement basée non pas sur les composés individuels hydratés, mais sur trois réseaux fondamentaux qui jouent un rôle prépondérant dans l'hydratation du ciment, et sur différentes solutions solides basées sur ces structures. La position des composés individuels ou des composés possibles dans ces structures est examinée à partir des informations disponibles, et des conclusions sont tirées quant aux composés ou aux solutions solides qui peuvent être formés.

On discute en détail seulement sur les deux systèmes ternaires $CaO-Al_2O_3-H_2O$ et $CaO-Fe_2O_3-H_2O$. La littérature la plus récente qui traite du premier de ces systèmes est étudiée à fond, tout particulièrement à l'aide d'une étude récente de Jones et Roberts. On a étudié tant moins le second système. A cause de la solubilité très faible des composés du fer pertinents, l'expérimentation de ce système-ci en utilisant les techniques normales du règle des phases se trouve beaucoup plus difficile. La formation de ferrites hydratés par l'action de solutions sur les composés anhydres "in situ" est beaucoup plus importante que dans le système correspondant $CaO-Al_2O_3-H_2O$. La reconnaissance de ce fait et une approche indirecte basée sur l'analogie présentent cependant un tableau utile des réalités et des possibilités de la formation de composés hydratés ferriques et d'une solution solide dans le système ciment-eau.

Un tableau simplifié des ferrites ou aluminates de calcium hydratés et des solutions solides est présenté, comprenant les réactions avec sulfate ou chlorure. D'après l'évidence actuelle, les aluminates, entre 22 et 100 °C, semblent limités à $C_4A\cdot 19H_2O$ et $C_2A\cdot 8H_2O$, tous deux métastables cependant quant à $C_4A\cdot 6H_2O$. Au-dessous de 22 °C, $C_2A\cdot 8H_2O$ est remplacé par $CA\cdot 10H_2O$. Audessus de 100 °C environ et jusqu'à une température d'environ 215 °C, seulement $C_3A\cdot 6H_2O$ stable (et peut-être un hydrate $C_2A\cdot 3H_2O$ de haute température) est formé, et au-dessus de 215 °C, $C_4A_3\cdot 3H_2O$. Les ferrites hydratés correspondants sont limités au métastable C_4F·aq. et au $C_3F\cdot 6H_2O$. La stabilisation de la structure de ce dernier exige du Si ou de l'Al ou des deux. Les solutions solides et les composés ou les solutions solides avec sulfate ou chlorure sont également discutés.

Zusammenfassung

Ein Teil der Literatur der Zementhydratation, der sich mit der Entwicklung des hydratisierten Kalziumaluminates und -Ferrites befäßt, wird besprochen, und die mehr komplizierten Sulfo- und Chloroaluminate und Ferrite, welche in Gegenwart des Kalziumsulfates, wenn dieses als Verzögerer benutzt wird, gebildet werden, oder wenn diese Produkte entstehen, wenn Kalziumchlorid einem Zement beigemischt wird, um seine Festigkeit zu erhöhen, werden kurz erwähnt.

Die Diskussion ist auf einer breiten Grundlage gehalten, daher werden zuerst nicht einzelne hydratisierte Verbindungen, sondern die drei Grundkristallgitter besprochen, die die vorherrschende Rolle in der Zementhydratation spielen, und die verschiedenen festen Lösungen, die von diesen Strukturen zusammengesetzt werden, werden erörtert. Die Rolle der einzelnen Verbindungen oder der Verbindungen, die möglicherweise vorhanden sein könnten, wird unter Bezugnahme auf alle Kenntnisse, die man heutzutage davon hat, besprochen, und Schlüsse werden gezogen, welche Verbindungen oder feste Lösungen überhaupt geformt werden könnten.

Nur die beiden ternären Systeme $CaO-Al_2O_3-H_2O$ und $CaO-Fe_2O_3-H_2O$ werden ausführlicher besprochen. Die neuere Literatur, die sich mit dem ersten System befäßt, wird in allen Einzelheiten erörtert, und große Aufmerksamkeit wird den neuesten Untersuchungen von Jones und Roberts geschenkt. Dem anderen System ist in der Literatur weniger Beachtung geschenkt worden, die Experimente hier, wenn man normale Phasenregeltechniken benutzen will, sind viel schwieriger, weil die Eisenverbindungen, mit denen man arbeiten muß, nur wenig löslich sind. Die Bildung der hydratisierten Ferrite als Folge der Wirkung der Lösungen auf wasserfreie Verbindungen *in situ* ist hier von größerer Wichtigkeit als in dem entsprechenden $CaO-Al_2O_3-H_2O$ System. Wenn man sich dessen bewußt ist und die Fragen mit Analogie-schlüssen zu lösen versucht, kann man sich doch ein gutes Bild davon machen, was in Wirklichkeit vorgeht, und wenn es möglich ist, daß hydratisierte Eisenverbindungen und feste Lösungen in einem Zement-Wasser-System geformt werden.

Eine vereinfachte Idee betreffs hydratisiertem Kalziumaluminat oder -Ferrit und fester Lösungen, welche die Reaktionen mit Sulfate oder Chloride umfäßt, wird angegeben. Auf Grundlage der jüngsten Forschungen kann man sagen, daß nur zwei Aluminate zwischen 22 und 100 °C vorkommen können, nämlich $C_4A\cdot 19H_2O$ und $C_2A\cdot 8H_2O$, die jedoch beide nur metastabil sind und in $C_3A\cdot 6H_2O$ übergehen wollen. Unterhalb 22 °C wird $C_2A\cdot 8H_2O$ durch $CA\cdot 10H_2O$ ersetzt. Oberhalb ungefähr 100 °C ist nur $C_3A\cdot 6H_2O$ stabil, und es ist möglich, daß ein Hochtemperaturhydrat $C_2A\cdot 3H_2O$ bis zu ungefähr 215 °C gebildet wird; oberhalb 215 °C bildet sich dann $C_4A_3\cdot 3H_2O$. Die entsprechenden hydratisierten Ferrite sind durch das metastabile C_4F·aq. und das $C_3F\cdot 6H_2O$ vertreten, und die letztgenannte Verbindung benötigt ein wenig Si oder Al oder beide, um ihre Struktur zu stabilisieren. Feste Lösungen, Verbindungen oder feste Lösungen mit Sulfate oder Chloride werden auch besprochen.

Paper III-3. Hydration of Calcium Aluminates and Ferrites*

F. E. Jones

Introduction

The purpose of the present paper is to review the knowledge of cement hydration with reference to the hydrated calcium aluminates and calcium ferrites which may now be taken as reasonably established, or on which research is still needed, and of certain of the more complex sulfo- and chloro-aluminates and ferrites which also play an important part.

Perhaps as useful a starting point as any is contained in two papers published in the Proceedings of the Second Symposium on the Chemistry of Cements held at Stockholm in 1938, one by Bessey [1][1] on the calcium aluminate and silicate hydrates, only the first part of which now concerns us, and the other by the present author [2] on the calcium aluminate complex salts. A selected list of references up to that time is given at the end of these two papers.

The most important methods which have been used in the determination of and study of these compounds include phase-rule studies of various systems, and attempts to elucidate the crystal structure of various compounds and "solid solutions." The term "solid solution" is retained in this paper as a convenient one. It covers the possibilities of mutual replacement of various atoms or groups of atoms or ions such as Al or Fe, Si, Cl, or SO_4 within relevant crystal lattices under defined conditions of temperature and environment which modify the relative stability of different possible lattice structures.

Structural Considerations

It seems essential to a discussion of hydrated calcium aluminates and ferrites to base this on their context in relation to the wider concept of structural possibilities in the cement-water system. Apart from the structure of calcium silicate hydrates, there appear to be at least three basic crystal lattice structures in hydrated cement compounds or solid solutions. These structures are:

(1) A "hexagonal" lattice typified by such compounds as $C_3A{\cdot}Ca(OH)_2{\cdot}aq.$, $C_3A{\cdot}CaCl_2{\cdot}aq.$, $C_3A{\cdot}CaSO_4{\cdot}aq.$, etc., and including also hexagonal or pseudo-hexagonal structures of compounds, $C_2A{\cdot}8H_2O$, $CA{\cdot}10H_2O$ and $C_2AS{\cdot}8(?)H_2O$.

(2) A "hexagonal" lattice typified by such compounds as $C_3A{\cdot}3Ca(OH)_2{\cdot}aq.$, $C_3A{\cdot}3CaCl_2{\cdot}aq.$, $C_3A{\cdot}3CaSO_4{\cdot}aq.$, etc.

(3) A cubic lattice typified by $C_3A{\cdot}6H_2O$.

It is well known that structure (1) is generally found (when sufficiently well-formed crystals are produced) as very thin hexagonal-shaped plates, which give a silken sheen in suspension in the mother-liquor, (2) as needles, often long and thin, of hexagonal cross section, and (3) as cubic crystals or various modifications based on a cubic lattice.

One point of interest in connection with structure is the difference in habit, as typically plates or needles, in structures (1) and (2) respectively. It may be noted too that Budnikov and Gorshkov [3] have recently demonstrated the splitting of needles of $C_3A{\cdot}3CaSO_4{\cdot}aq.$ (and $C_3F{\cdot}3CaSO_4{\cdot}aq.$) of structure (2) by passing through freezing cycles (−17 °C to +20 °C). It was found that the needles split along planes of cleavage parallel to the long (*c*) axis, giving smaller needles. The writer has long since observed a tendency for longitudinal splitting to occur on heating the high-sulfate calcium sulfoaluminate needles to 110 °C. There is this difference however. On heating, there is a loss of water ($32H_2O \rightarrow 8H_2O$, at 110 °C) with a consequent rise in refractive indices, whereas on freezing, water is retained, and there is no change in the properties of the solid phase.

Another paper of some interest, dealing with the crystalline habits of calcium aluminate hydrates is that of Sersale [4], summarizing to a large degree two earlier papers [5, 6]. This author has recently carried out experiments on the change of the metastable hexagonal calcium aluminate hydrates (structure (1)) to $C_3A{\cdot}6H_2O$ under the influence of various factors, including temperature, CaO/Al_2O_3 ratio in mother-liquor, *p*H, etc. Tests were carried out at 20°, 50°, and 80 °C. Confirming Koyanagi's results, it was found that hexagonal plates converted first into icositetrahedra, then into rhombododecahedra, and finally into cubes. As is well known, it was found that the rate of change increases with temperature. From the initial mixes of metastable lime and alumina solutions mixed with lime solution, it appears in the light of recent work by Jones and Roberts [7], that Sersale's initially precipitated phases were either $C_4A{\cdot}19H_2O$ or this compound together with its solid solution with α_1–$C_2A{\cdot}8H_2O$ (see later). It would seem, therefore, that the development of structure (3) from

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Building Research Station, Department of Scientific and Industrial Research, Watford, England. (Owing to the untimely death of the author in 1960, this paper was presented at the Symposium by M. H. Roberts.)

[1] Figures in brackets indicate the literature references at the end of this paper.

structure (1), leading to the variety of habits indicated, may perhaps provide useful supporting evidence for the precise structure of $C_4A\cdot 19H_2O$ ($C\ A\cdot Ca(OH)_2\cdot 18H_2O$).

Within the above structures, it is possible to replace the aluminum cation by iron, in greater or less degree, giving an increase in the size of the lattice owing to the spatial demands of the larger iron cation. In the cubic lattice it is also possible to replace $2H_2O$ by SiO_2 (i.e., $4H^+$ by Si^{4+}), resulting in a shrinkage of the lattice as the replacement proceeds completely to a compound C_3AS_3. In both hexagonal lattices (1) and (2) it is also possible to substitute various equivalent anionic groupings [2].

Thus, depending on considerations of stability and of elements involved, it may or may not be possible to produce compositions based on these three lattices which are sufficiently near end members of the possible solid-solution series to be termed compounds.

It is important however to realize that although solid solutions are formed, it does not follow that there is necessarily complete replacement of one ion by another throughout a theoretically conceivable range from one "compound" to another; e.g., it does not appear possible stably to replace Al by Fe completely in $C_3A\cdot 6H_2O$, and a pure $C_3F\cdot 6H_2O$ seems to be formed only exceptionally, as an unstable phase. Fundamentally, this replacement appears to be governed only by the size of the Fe ion. Thus it appears that room can be made for a 100 percent replacement of Al by Fe, by at the same time replacing 4H by Si to a limited extent, since less room is required by Si than 4H, and so space is made available for more Fe.

There are several possibilities for solid-solution formation. Thus in structures (1) and (2), the replacement of Al^{3+} by Fe^{3+} and of 2 OH^- by $2Cl^-$ or SO_4^{2-} (with any consequential change in H_2O) implies the possibility of a variety of solid-solution structures involving any or all of these ions, so that solid solutions of varying degrees of complexity are possible. In structure (3), where it appears that such ions as Cl^- or SO_4^{2-} do not enter, solid solution is correspondingly limited. However, the entry of silica into structure (3) as a replacement for some of the H_2O introduces a further complication, while silica may also enter into structures (1) and (2).

Solid solution of the kind shown between $C_3A\cdot Ca(OH)_2\cdot 18\ H_2O$ and $C_2A\cdot 8H_2O$ [7] is another variant.

Finally, the possibilities for different hydrates of the same compound may be noted. An example of this occurs in the hydrates of the tetracalcium aluminate, only one of which exists in the aqueous system $CaO\text{-}Al_2O_3\text{-}H_2O$. It may be noted that Turriziani and Schippa [8] (1954–55) consider that there are three hydrates of $C_3A\cdot CaSO_4\cdot$aq. since, depending on the drying conditions, they obtained compounds which, after X-ray powder-pattern examination, they characterized by the basal spacings as:

α_2 (moist solid); basal spacings d=10.39, 5.15 A.

α_1 (dried at 94 percent R.H.); basal spacings d=9.50, 4.79 A (13–14 H_2O).

α (dried at 55 percent R.H.); basal spacings d=8.99, 4.48 A (11–12 H_2O).

Schippa [9] (1958) has also concluded that there are two hydrated monosulfoferrites:

Moist solid; basal spacings d=10.45, 5.15 A

Dried at 55 percent R.H. and also over $CaCl_2$ & KOH; basal spacings d=9, 4.45 A.

It appears to be too early as yet to assess the significance of these alleged different hydrates of monosulfoaluminate and ferrite.

Reference should be made to table 1 for some X-ray data on compounds relevant to the lattice structures now discussed.

TABLE 1. *X-ray data on some relevant compounds*

$CA\cdot 10H_2O$ [a]		$C_2AS\cdot 8?H_2O$ [b]		$C_3A\cdot 3CaSO_4\cdot 32H_2O$ [c]		$C_3F\cdot 3CaSO_4\cdot 32H_2O$ [d]	
d(A)	*I*	*d(A)*	*I*	*d(A)*	*I*	*d(A)*	*I*
14.3	10	12.7	VS	9.8	10	9.8	10
7.16	10	6.30	S	5.7	8	8.9	2
5.39	4	4.20	VS	4.9	6	5.6	7
4.75	4	3.22	VW	4.67	7	5.0	3
4.52	3	2.89	M	4.34	2	4.81	4
4.16	3	2.62	M	3.87	8	4.06	1
3.93	1	2.51	M	3.60	3	3.95	8
3.72	5	2.41	W	3.45	6	3.65	4
3.56	7	2.38	MW	3.26	4	3.49	4
3.26	6	2.09	MW	3.02	3	3.24	3
3.10	5	1.90	M	2.79	9	3.07	2
2.88	6	1.83	M	2.67	3	2.80	7
2.69	5	1.66	MW	2.57	8	2.60	7
2.55	7	1.55	W	2.43	3	2.50	1
2.47	5	1.43	W	2.36	1	2.47	1
2.36	6			2.20	8	2.42	3
2.26	6			2.14	6	2.23	5
2.18	6			2.06	3	2.18	3
2.11	4			1.94	3	2.13	1
2.06	4			1.89	2	2.07	1
1.94	5			1.84	4	1.94	2
1.87	1			1.80	1	1.89	2
1.83	3			1.75	4	1.84	1
1.79	4			1.70	4	1.82	1
1.75	1			1.66	6	1.81	1
1.71	3			1.62	2	1.77	2
1.64	5			1.57	4	1.71	2
1.60	6			1.54	2	1.68	2
1.56	1			1.50	4		
1.52	2			1.45	3		
1.47	3			1.34	3		
1.40	2			1.30	3		
1.38	4						
1.27	1						
1.24	2						
1.18	2						
1.07	2						

[a] $CA\cdot 10H_2O$. Midgley [18]. On preparation described by Jones and Roberts [7].

[b] $C_2AS\cdot 8(?)H_2O$. Fratini and Turriziani [21]. Calculated from values for 2θ given by the authors. Fratini and Turriziani give hexagonal cell with a=8.85±0.05 A, c=12.66 A ±0.07 A.

[c] $C_3A\cdot 3CaSO_4\cdot 32H_2O$. Midgley [18] quoted by Lea [26]. Hexagonal cell, a=11.10 A, c=21.58 A.

[d] $C_3F\cdot 3CaSO_4\cdot 31\text{–}33H_2O$. Aruja and Rosaman [15]. On preparation by Jones [27]. Aruja and Rosaman give hexagonal cell, with a=11.23 A, c=22.14 A.

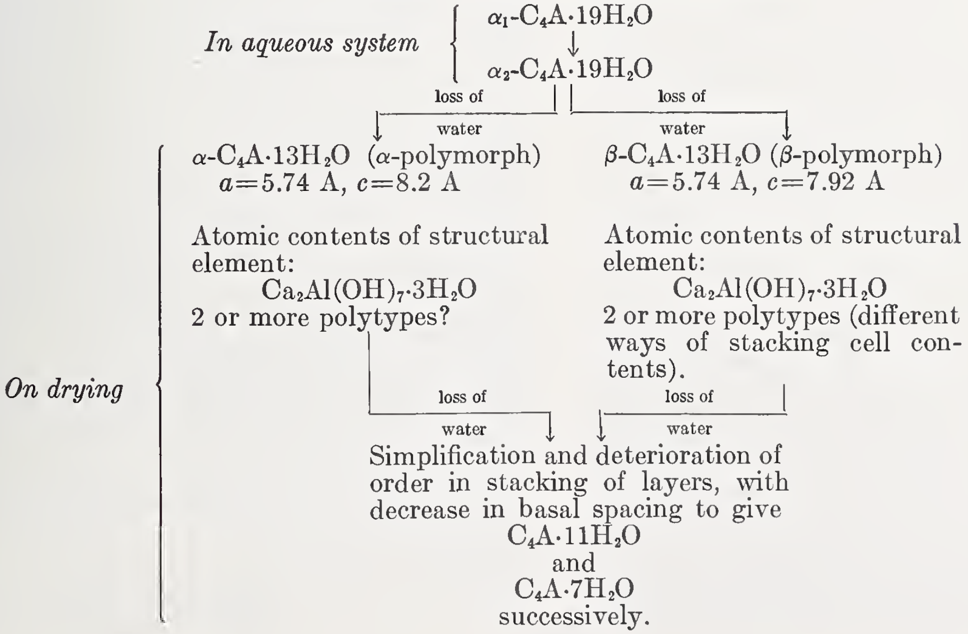
An attempt has been made to prepare, in a number of tables, X-ray powder-pattern data on as many compounds or solid solutions as possible relevant to these structures. It has however been concluded that the best available data are in many cases not sufficiently complete, or not always on pure phases or preparations of precisely known chemical composition, to justify at present their inclusion. Such tables must await further precise experimental work. It appears desirable to emphasize the importance of examining pure phases, free from carbonation, of precisely known chemical composition, including water content. It has been noted also that at least four different methods of recording intensities of lines in the patterns are in use in the literature, while the accuracy appears to vary. This variation is combined with slight differences in spacings and in numbers of lines recorded, etc., depending on the kind of camera used and slightly varying techniques. It is hoped that more precise tables may be published later.

(a) The Hexagonal Layer Lattice Typified by $C_3A \cdot Ca(OH)_2 \cdot aq.$

The most recent attempt to solve the problem of the structure of the crystal lattice of "hexagonal" tetracalcium aluminate hydrate appears to be that of Buttler, Dent Glasser, and Taylor [10] (1959). It seems clear from recent papers by Roberts [11] and Jones and Roberts [7] that in the work of Buttler, Dent Glasser, and Taylor, which dealt with both $4CaO \cdot Al_2O_3 \cdot 13H_2O$ and the natural mineral hydrocalumite, containing 1.8 percent CO_2, only one form, beta (c=7.9A) of $4CaO \cdot Al_2O_3 \cdot 13H_2O$ was studied. Furthermore, this is a form obtained only after drying the $\alpha_1 \rightarrow \alpha_2$ forms of $C_4A \cdot 19H_2O$; i.e., the fully hydrated variety which exists in the aqueous equilibria of the system $CaO-Al_2O_3-H_2O$. Nevertheless the paper makes a valuable contribution to our understanding of the lattice structure of this group as a whole. The relationship between the fully hydrated forms and the structures obtained on drying to various stages of water content is conveniently summarized in table 2.

This is not the place for a detailed consideration of the structure, nor is the writer sufficiently experienced in experimental crystal-structure techniques to undertake it. However, the conclusions reached by the authors are very important. Previously it has been generally accepted that the structure is based on alternate layers of $Ca(OH)_2$ and $Al(OH)_3$ (Brandenberger [12] (1933)), a view supported by the work of Tilley (with Megaw and Hey) [13] (1934) on hydrocalumite. The structure proposed by the latter authors for synthetic $4CaO \cdot Al_2O_3 \cdot 13H_2O$, based on their study of hydrocalumite, was of $Ca(OH)_2$ layers (one Ca^{2+} ion in three replaced by H_2O) alternating with layers of Al^{3+} and the remaining H_2O and OH^-. For various reasons, Buttler, Dent Glasser, and Taylor consider this arrangement unsatisfactory and although not able to determine the exact structure of the compound, they suggest that six of the OH^- ions in the "structural element" $Ca_2Al(OH)_7 \cdot 3H_2O$ occur in an octahedral layer, and the seventh, outside, closely associated with H_2O molecules (presumably in a separate layer). Furthermore, it is indicated that the structural element is only one octahedral layer thick (though this does not seem to accord with the suggestion above, that the seventh OH^- is outside the octahedral layer and closely associated with H_2O) and that the three octahedral sites in the structural element are occupied by 2 Ca^{2+} and 1 Al^{3+} in "ordered" positions. The octahedral groups formed (Al^{3+} or Ca^{2+} at centers of the octahedra and OH^- at the 6 corners) then share OH^- at the corners along two edges to form a layer containing both Ca^{2+} and Al^{3+}. The alternate layers, according to the views of the authors, therefore appear to contain the remaining OH^- (outside the octahedral layer) and associated H_2O

TABLE 2. *Tetracalcium aluminate hydrates*



In aqueous system

α_1-$C_4A \cdot 19H_2O$

$\downarrow$

α_2-$C_4A \cdot 19H_2O$

loss of water

On drying

α-$C_4A \cdot 13H_2O$ (α-polymorph)
a=5.74 A, c=8.2 A

Atomic contents of structural element:
$Ca_2Al(OH)_7 \cdot 3H_2O$
2 or more polytypes?

β-$C_4A \cdot 13H_2O$ (β-polymorph)
a=5.74 A, c=7.92 A

Atomic contents of structural element:
$Ca_2Al(OH)_7 \cdot 3H_2O$
2 or more polytypes (different ways of stacking cell contents).

loss of water

Simplification and deterioration of order in stacking of layers, with decrease in basal spacing to give
$C_4A \cdot 11H_2O$
and
$C_4A \cdot 7H_2O$
successively.

molecules. The actual structure in this layer is not discussed.

A complicating conclusion reached by Buttler, Dent Glasser, and Taylor is that the structural elements in the layers "appear to be stacked in a complex way, so that the 'true structure' only repeats after a large number of layers" giving "polytypes" (varieties with different systems of stacking). References are given to this type of structure in other compounds. For the present purpose it appears that such variations in stacking can be ignored, except for their effect in modifying a hexagonal lattice to a monoclinic one.

The relationship of $4CaO \cdot Al_2O_3 \cdot 13H_2O$ and hydrocalumite is however important since the differences between the two structures appear to be significant, in particular in relation to carbonation of $C_4A \cdot 13H_2O$ and the structure of such compounds as $C_3A \cdot CaCl_2 \cdot$aq., $C_3A \cdot CaSO_4 \cdot$aq., $C_3A \cdot CaCO_3 \cdot$aq., etc. It merits therefore a brief description.

The authors state, "The unit cell of hydrocalumite (a=9.9 A, b=11.4 A, c=16.84 A, β=111°) is closely related to that of $4CaO \cdot Al_2O_3 \cdot 13H_2O$. If the systematically weak groups of reflections are ignored, a pseudocell is obtained that contains two identical structural elements related by a pseudo glide plane. These structural elements are hexagonal with a=5.7 A, c=7.86 A and are thus almost identical in size with those in $4CaO \cdot Al_2O_3 \cdot 13H_2O$. They are stacked differently in the two cases: in hydrocalumite the stacking is such as to make the crystal monoclinic, and some of the structural elements must contain carbonate ions. The true unit cells and the powder patterns therefore differ."

Although it would appear that differences in stacking alone may lead as suggested to a monoclinic structure in hydrocalumite, it is not clear to the writer why emphasis should necessarily be placed here. From Buttler, Dent Glasser, and Taylor's work, it would appear that it is the seventh OH^- of $4CaO \cdot Al_2O_3 \cdot 13H_2O$ ($Ca_2Al(OH)_7 \cdot 3H_2O$) outside the octahedral layer, that is involved in replacement by other ions. According to the authors, also, in hydrocalumite one in eight structural elements contains CO_3^{2-} replacing $2OH^- + 3H_2O$. It seems possible that the fundamental difference between hydrocalumite and $4CaO \cdot Al_2O_3 \cdot 13H_2O$ may lie in the structural elements, those containing CO_3^{2-} conforming to a monoclinic lattice as opposed to a hexagonal lattice for the OH^- of $4CaO \cdot Al_2O_3 \cdot 13H_2O$. (Although the authors refer to the structural elements in hydrocalumite as hexagonal, they do not discriminate between those not containing and those containing carbonate ions.) It appears therefore to be a possibility that in hydrocalumite there is a mixture of hexagonal and monoclinic structural elements, making the structure as a whole monoclinic, and that this may be of greater importance than stacking differences.

Brief reference is made to synthetic compounds of the type $C_3A \cdot CaX_2 \cdot$aq., and $C_3A \cdot CaY \cdot$aq. as being formed by complete replacement of the OH^- group outside the octahedral layer, while, depending on the size of the anion X or Y and the number of water molecules displaced by it, the thickness of the structural element can either increase or decrease.

Presumably the structures so produced may strictly be monoclinic rather than hexagonal.

It may be noted that Buttler, Dent Glasser, and Taylor do not discuss the possibility of other carboaluminate compositions besides that of natural hydrocalumite. It is not clear whether they regard it as a unique compound or as a stage in a solid-solution series $C_3A \cdot Ca(OH)_2 \cdot$aq.-$C_3A \cdot CaCO_3 \cdot$aq. although on the whole the latter seems to be inferred. There appears however to be no clear evidence of such a solid solution at present. Carlson [14] has recently commented in his work on the system CaO-Al_2O_3-H_2O at 1 °C, that in X-ray patterns obtained by him, the carboaluminate $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ and $4CaO \cdot Al_2O_3 \cdot 13H_2O$ appeared to exist side by side, with no evidence of solid solution. A similar observation has been made in investigations at the Building Research Station [15]. Although the monocarboaluminate is not directly involved in the system CaO-Al_2O_3-H_2O it is important as a possible contaminant. Since Bessey [1] first prepared "low" and "high" forms of carboaluminate, little work has been published, though reference is made by Carlson [14] and a paper has been published by Turriziani and Schippa [16].

Returning to the general consideration of the hexagonal layer lattice structure, several instances are known where Al is replaceable by Fe. They include the compounds "$C_3F \cdot Ca(OH)_2 \cdot 11$–$13H_2O$", "$C_3F \cdot CaCl_2 \cdot xH_2O$", "$C_3F \cdot CaSO_4 \cdot xH_2O$", or solid solutions, which will be discussed later. The existence of carboferrites must also be visualized, though no preparation appears to have been recorded. One such preparation has however been made at the Building Research Station and X-ray data obtained. (Roberts [15].)

In addition to compounds of the above general lattice type, we have also to consider the structures of $C_4A \cdot 19H_2O$ (from which $C_4A \cdot 13H_2O$ is presumably derived by loss of H_2O), of $C_2A \cdot 8H_2O$, of $CA \cdot 10H_2O$, and of $C_2AS \cdot 8(?)H_2O$.

Accepting the proposal of Buttler, Dent Glasser, and Taylor on the structure of $C_4A \cdot 13H_2O$, the additional $6H_2O$ of the $C_4A \cdot 19H_2O$ hydrate may tentatively be assigned to the intermediate layers containing OH^- and H_2O only, possibly constituting in effect a separate H_2O layer.

The $C_2A \cdot 8H_2O$ structure may then be derived from that of $C_4A \cdot 19H_2O$ by substitution of $Al(OH)_3$ for $3H_2O$ in these layers, thus:

$$C_4A \cdot 19H_2O + A - 3H_2O \rightarrow C_4A_2 \cdot 16H_2O \quad (C_2A \cdot 8H_2O)$$

or

$$Ca_2Al(OH)_7 \cdot 6H_2O + Al(OH)_3 - 3H_2O \rightarrow Ca_2Al_2(OH)_{10} \cdot 3H_2O.$$

Possible layer relationships may be indicated as

$$[Ca_2Al(OH)_6][(OH)\cdot 6H_2O]+Al(OH)_3-3H_2O \rightarrow [Ca_2Al(OH)_6][Al(OH)_4\cdot 3H_2O]$$

$$\tfrac{1}{2}C_4AH_{19} \qquad C_2AH_8 \qquad \text{or}$$

$$[Ca_2Al(OH)_6][(OH)\cdot 3H_2O][3H_2O]+Al(OH)_3 -3H_2O \rightarrow [Ca_2Al(OH)_6][Al(OH)_4][3H_2O]$$

$$\text{or} \qquad [Ca_2Al(OH)_6][(OH)\cdot 3H_2O][Al(OH)_3]$$

The very similar dimensions of the unit cells of α_2-$C_4A\cdot 19H_2O$ and α_2-$C_2A\cdot 8H_2O$ (Jones and Roberts [7]), which can be satisfactorily indexed (reference [7] and Aruja [15]) on unit cells of dimensions $a=5.77$ A, $c=21.37$ A and $a=5.80$ A, $c=21.59$ A respectively, support the indications from the phase-rule equilibrium studies by Jones and Roberts that a solid solution may be formed between these two compounds. The hexagonal plate solid solution of composition $C_{2-2.4}A\cdot 8\text{–}10.2H_2O$ appears to be formed in a crystal lattice which is virtually that of α_1-$C_2A\cdot 8H_2O$. Thus the X-ray patterns are indistinguishable. Tentatively we may write:

$$6C_2A\cdot 8H_2O=12Ca(OH)_2\cdot 12Al(OH)_3\cdot 18H_2O =C_{12}A_6\cdot 48H_2O$$

$$3C_4A\cdot 19H_2O=12Ca(OH)_2\cdot 6Al(OH)_3\cdot 36H_2O =C_{12}A_3\cdot 57H_2O$$

$$5C_{2\cdot 4}A\cdot 10.2H_2O=12Ca(OH)_2\cdot 10Al(OH)_3\cdot 24H_2O =C_{12}A_5\cdot 51H_2O$$

It may be that this solid solution is formed by replacement of up to one-sixth of $Al(OH)_3$ in the $C_2A\cdot 8H_2O$ by H_2O ($Al(OH)_3\equiv 3H_2O$) without significant change in structure other than removal of some Al^{3+} and consequent replacement of equivalent $3OH^-$ by $3H_2O$ in the structure, and that further replacement results in a slight modification of structure to that of the $C_4A\cdot 19H_2O$ lattice. Since the unit-cell dimensions are practically identical, it would appear that the slight requisite rearrangement is wholly in the layers containing only $Al^{3+}+OH^-+H_2O$.

From the cell dimensions and densities of α_2-$C_2A\cdot 8H_2O$ and α_2-$C_4A\cdot 19H_2O$, it may be calculated that for a cell for α_2-$C_2A\cdot 8H_2O$ of $a=5.80$ A, $c=21.59$ A, with density 1.95, there are present 2 molecules of $C_2A\cdot 8H_2O$, corresponding to $4Ca(OH)_2\cdot 4Al(OH)_3\cdot 6H_2O$, and for a cell for α_2-$C_4A\cdot 19H_2O$ of $a=5.77$ A, $c=21.37$ A with density 1.81, there is present 1 molecule of $C_4A\cdot 19H_2O$, corresponding to $4Ca(OH)_2\cdot 2Al(OH)_3\cdot 12H_2O$. This does not accord with the suggestion implicit above that the unit cells may contain 6 and 3 molecules respectively to accord with $12Ca(OH)_2\cdot 12Al(OH)_3\cdot 18H_2O$ and $12Ca(OH)_2\cdot 6Al(OH)_3\cdot 36H_2O$ and with the solid solution indicated experimentally. The unit cells may however be based on multiples or submultiples of the dimensions given. Dimensions corresponding to found maximum solid solution are respectively α_2-$C_2A\cdot 8H_2O$, $a=5.80$ A, $c=64.8$ A, α_2-$C_4A\cdot 19H_2O$, $a=5.77$ A, $c=64.1$ A.

The pattern of $CA\cdot 10H_2O$ (table 1) is markedly different from that of $C_2A\cdot 8H_2O$. Carlson [17] has obtained it as weakly birefringent hexagonal prisms, with a mean refractive index of 1.471. This author gives the X-ray pattern together with that of an analogous monostrontium aluminate. A pattern has also been published by Midgley [18]. Brocard [19] had already indicated in 1948 that a product of hydration of CA obtained by him had an X-ray pattern which he assigned to a hexagonal lattice with $a=9.45$ A, $c=14.6$ A. From later work the pattern appears to be that of $CA\cdot 10H_2O$. It seems likely that there is an appreciable difference between the structures of $C_2A\cdot 8H_2O$ and $CA\cdot 10H_2O$, but the mode of transition and the relationship between the two structures is still not clear.

Finally, in the case of a compound C_2AS·aq., zur Strassen [20] writes the formula as C_2ASH_8. It appears from the literature that it crystallizes as hexagonal plates. Fratini and Turriziani [21] had previously given an X-ray pattern (table 1) and stated that they had indexed it satisfactorily on a hexagonal cell, with $a=8.85\pm 0.05$ A, $c=12.66\pm 0.07$ A. These values may be compared with those given previously by Wells, Clarke, and McMurdie [22] for $C_4A\cdot 13H_2O$ and $C_2A\cdot 8H_2O$; i.e., $a=8.8$ A, $c=8.2$ A (apparently for α-$C_4A\cdot 13H_2O$) and $a=8.8$ A, $c=10.6$ A, respectively. There appears thus to be a close similarity between all these structures. The parameters given by these authors are not necessarily the true parameters of the cell, though they will be simply related to them.

(b) The Hexagonal Layer Lattice Typified by $C_3A\cdot 3Ca(OH)_2$·aq., $C_3A\cdot 3CaCl_2$·aq., $C_3A\cdot 3CaSO_4$·aq., etc.

Of the three "type" compounds given, one, $C_3A\cdot 3Ca(OH)_2$·aq., appears to be formed only under conditions of exceptionally high lime concentrations, which do not occur in the cement-water system. Thus Flint and Wells [23] (1944) prepared it by mixing a metastable monocalcium aluminate solution with a strong solution of lime in a sugar solution. Again, the corresponding $C_3A\cdot 3CaCl_2$·aq. compound has been prepared by Serb-Serbina, Savvina, and Zhurina [24] (1956), by hydration of C_3A in a 23 percent $CaCl_2$ solution at −10 °C. (The authors state that the preparation of this compound below 0 °C was first reported by V. E. Leirikh.) At +20°C the "low" chloroaluminate was obtained ($3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$), but the "high" form was also stated to be obtained at this temperature with a high solution/C_3A ratio. The formation of the "high" chloroaluminate appears to be partly dependent on temperature and partly on $CaCl_2$ concentration in solution. It would not be formed under normal practical conditions in hydrated cement, but the possibility at sufficiently low temperatures must be borne in mind.

The only structure of this type which appears to have been examined is that for $C_3A{\cdot}3CaSO_4{\cdot}aq.$ as the mineral ettringite, by Bannister [25] (1936), referred to most recently by Lea [26]. The latter states: "The hexagonal unit cell of ettringite contains two molecules of $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$ and has $a_0=b_0=11.10$ A, $c_0=21.58$ A. The space group is C$\bar{3}$1c. Four close-packed layers of O or OH ions make up the structure, with embedded Ca, S, and Al. The latter form $Al(OH)_6$ groups in octahedral coordination and the sulfur is present as SO_4 tetrahedra. Four of the Ca ions have sevenfold coordination and eight sixfold. Forty-eight water molecules are located in channels parallel to the *c* axis and two are more closely built into the structure. The structural formula thus becomes $Ca_{12}Al_4(OH)_{24}(SO_4)_6{\cdot}50H_2O$. On dehydration at about 100–110 °C the 48 interstitial water molecules are lost and the lattice shrinks so that $a_0=8.4$ A and $c_0=10.21$ ($=\frac{1}{2}$ 20.42) A."

It is noteworthy that the length of the *c* axis is very close to that of $C_4A{\cdot}19H_2O$, $a=5.77$ A, $c=21.37$ A and of $C_2A{\cdot}8H_2O$, $a=5.80$ A, $c=21.59$ A [7].

Few instances are known of replacement of Al by iron in structures of this type. They include $C_3F{\cdot}3CaSO_4{\cdot}aq.$ and solid solutions (stated to be only partial) between $C_3A{\cdot}3CaSO_4{\cdot}aq.$ and $C_3F{\cdot}3CaSO_4{\cdot}aq.$ Both Jones [27] and Budnikov and Gorshkov [3] have claimed the preparation of a pure $C_3F{\cdot}3CaSO_4{\cdot}aq.$ Cirilli [28] had concluded that it was not possible to obtain it by addition of ferric sulfate solution to saturated lime-calcium sulfate solution, but concluded that a partial mixed solid-solution series could be formed in this way. There is not necessarily any conflict of evidence here. An X-ray powder pattern obtained by E. Aruja and D. Rosaman at the Building Research Station on the preparation by Jones [27] is given in table 1. It will be seen that it is closely similar to that of $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$. Aruja and Rosaman indexed the data on a hexagonal unit cell with $a=11.23$ A, $c=22.14$ A, only very slightly larger than that for $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ ($a=11.10$ A, $c=21.58$ A).

(c) The Cubic Lattice Typified by $C_3A{\cdot}6H_2O$

Lea [26] has quoted Brandenberger [29] and states that $C_3A{\cdot}6H_2O$ is "cubic with $a=12.56$ A, body centered, space group Ia3d; eight formula units are contained in the unit cell". As discussed later, an isomorphous series of solid solutions can be formed in which A is replaced by F and $2H_2O$ by SiO_2 giving the garnet-hydrogarnet series found by Flint, McMurdie, and Wells [30]. An important point here is how far Fe can replace Al in the structure without causing instability. This point is discussed.

With reference to this section of the paper as a whole, it appears to the author that the development of discussion of structural considerations in a unified sense, as incompletely attempted above, should lead to significant advances in the understanding of what calcium aluminates and ferrites, as well as related complex chloro- or sulfocompounds or solid solutions, are practically possible. The X-ray data obtained by various authors appear to be as yet incomplete and of unequal value as between those available for different compounds, or known compositions approximating to probable compound compositions. The importance of precise control over "H_2O" content has already been stressed among other difficulties of obtaining a pure single phase for examination. The importance of knowing the precise chemical composition of the solid phase examined is also emphasized by the close similarity in X-ray powder patterns shown by different compounds or their solid solutions; e.g., compounds $C_4A{\cdot}19H_2O$ and $C_2A{\cdot}8H_2O$ or $C_3F{\cdot}Ca(OH)_2{\cdot}aq.$ and $C_3F{\cdot}CaCl_2{\cdot}aq.$ There is much yet to be done, but there are clearly many interesting possibilities, not fully worked out here, of simple relations between the various lattice structures under review.

In the remaining parts of this paper, the systems $CaO\text{-}Al_2O_3\text{-}H_2O$ and $CaO\text{-}Fe_2O_3\text{-}H_2O$ are discussed in detail, the former in particular from the phase-rule point of view, in relation to the calcium aluminates or ferrites or solid solutions which can be formed.

The System Lime–Alumina–Water

(a) Introduction and Review of Phase-Rule Equilibrium Studies

In the study of this system, Bessey's [1] original warning about the difficulty of avoiding carbonation of phases in carrying out experiments is still apt, and it is strongly emphasized by the present author that the utmost care should be taken to exclude carbon dioxide at every stage. Carbonation is probably responsible for much erroneous interpretation in the past.

In this connection, it may be noted that in recent years several authors have used polyethylene vessels as an alternative to glass vessels in order to avoid attack of the glass. Carlson [14] has recently drawn attention to a paper by Myers, Rogers, Stannett, and Szwarc [31] which gives data on the permeability of polyethylene to gases, including carbon dioxide. It is not clear at present how much risk of carbonation is involved, but it is evident that in order to reduce or eliminate it, consideration needs to be given to this factor in relation to the temperature of use, the grade, density, and wall thickness of the polyethylene, or other protective measures.

Apart from carbonation, the vital importance of the control of water content of solid phases has been made clear by recent work of Jones and Roberts [7].

The list of artificially prepared hydrated calcium aluminates given by Bessey in his 1938 paper was increased to include $C_6A{\cdot}33H_2O$ in Steinour's very full review of 1951 [32]. D'Ans and Eick [33] also gave a tabulated chronological survey of individual solid phases in their 1953 paper, which covers substantially the same list but gives in detail different water contents reported by various authors. Perhaps the time has come when we can dismiss such varying water contents as partly the result of slightly varying drying conditions and varying amounts of carbonation, and assign, on grounds of precise control of experimental conditions and appeal to structural concepts, precise values of "H_2O" in the normal "oxide" formulation, whether this "H_2O" is present as actual H_2O groupings or OH^- groupings or both.

Preliminary Brief Chronological Survey

(1) Bessey [1] (In Collaboration With Lea) at 25 °C (1938)

Bessey gave a statement of general relationships in the system at 25 °C (fig. 1) as concluded by him and Lea on the basis of previous investigations carried out by them and others. They considered that there had been established a stable solubility curve *OA* for $Al_2O_3{\cdot}aq.$, an invariant point *A* for $Al_2O_3{\cdot}aq.\text{-}C_3A{\cdot}6H_2O$ (also indicating congruent solubility of $C_3A{\cdot}6H_2O$), a stable solubility curve *AB* for $C_3A{\cdot}6H_2O$, an invariant point *B* which was either for $C_3A{\cdot}6H_2O\text{-}C_4A{\cdot}13H_2O$ or $C_3A{\cdot}12H_2O\text{-}C_4A{\cdot}13H_2O$, a solubility curve *BC* which was either a continuation of the solubility curve for $C_3A{\cdot}6H_2O$, or the stable solubility curve for $C_4A{\cdot}13H_2O$, and *C*, the solubility of calcium hydroxide in water. *OD* was then described as a metastable solubility curve for $Al_2O_3{\cdot}aq.$, either passing through *A*, or an entirely separate curve, "possibly of a different hydrate of alumina." *D* is stated to represent the approximate solubility of $C_2A{\cdot}8H_2O$, apparently congruent, in water, and also a metastable invariant point $C_2A{\cdot}8H_2O\text{-}Al_2O_3{\cdot}aq.$ Finally, it was considered that the metastable solubility curves for $C_4A{\cdot}13H_2O$, $C_3A{\cdot}12H_2O$, $C_2A{\cdot}8H_2O$ and $C_3A{\cdot}18H_2O$ lay within the area *DEB*.

(2) Wells, Clarke, and McMurdie [22] at 21 °C and 90 °C (1943)

At 21 °C these authors made a substantial step forward. In precipitation from mixtures of metastable calcium aluminate solutions and lime solutions, they obtained a "practical" curve *ABD* (fig. 2) for a hexagonal-plate solid phase in which the CaO/Al_2O_3 ratio varied from 2 to 4. They considered that either (a) there are overlapping solubility curves for $C_4A{\cdot}13H_2O$ and $C_2A{\cdot}8H_2O$ or (b) the curve is a solid solution curve throughout the entire range. They preferred the former interpretation and concluded that the ends of the experimental curve relate primarily to one or other of the two hydrates respectively, with a middle portion where the two aluminates markedly intercrystallize. They expressed the belief that "the hydrated dicalcium and tetracalcium aluminates, being of a very similar structure parallel to the *a* axis, can intercrystallize and give masses which are made up of the one compound so intimately mixed with layers of the other that average indices of refraction are obtained." In spite of this region of postulated intercrystallization, Wells, Clarke, and McMurdie suggested that a metastable invariant point $C_4A{\cdot}13H_2O\text{-}C_2A{\cdot}8H_2O$ existed at about 0.5 to 0.6 g CaO per liter and 0.10–0.15 g Al_2O_3 per liter. It was also concluded that the hitherto supposed compound $C_3A{\cdot}12H_2O$ is a mixture of $C_2A{\cdot}8H_2O$ and $C_4A{\cdot}13H_2O$ intercrystallizing in equimolar proportions.

It may be observed that at this stage the conclusions on the precise significance of the curve *ABD* are still left in the realm of conjecture.

At 90 °C, hexagonal phases were so unstable that no attempt was made to study their solubility relationships. Only curves for stable phases were therefore determined, gibbsite, $C_3A{\cdot}6H_2O$, and $Ca(OH)_2$. No other stable hydrated calcium aluminates were found.

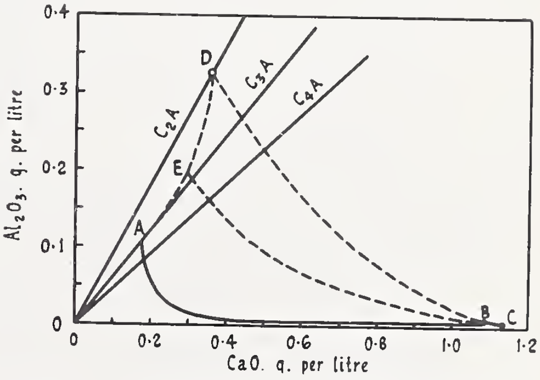


FIGURE 1. *Solubility relations in the system* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 25 °C (Bessey [1], 1938).*

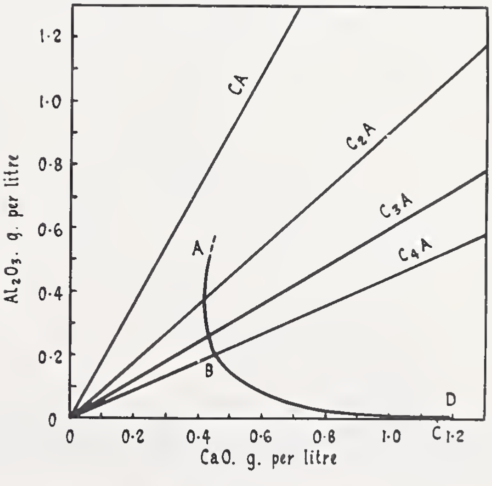


FIGURE 2. *System* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 21 °C.*

Hexagonal plate "practical curve" from precipitation. (Wells, Clarke, and McMurdie [22], 1943.)

(3) D'Ans and Eick [33] at 20 °C (1953)

The solubility curves suggested by D'Ans and Eick are indicated in figure 3, which is based on their figure 4. From two series of mixtures of metastable calcium aluminate and lime solutions, D'Ans and Eick obtained precipitates which, following Wells, Clarke, and McMurdie, establish a "practical" equilibrium curve for metastable hexagonal plate phases. Certain of the mixtures are stated to precipitate immediately hexagonal mixed crystals. Filtration after two hours gave filtrates which yielded the solution compositions used to define a large part of the "practical" curve to the left of a deduced invariant point $C_2A{\cdot}8H_2O$-$C_4A{\cdot}13H_2O$. These mixed crystals are stated to consist mainly of crystals rich in α-$C_4A{\cdot}13H_2O$ with a little rich in $C_2A{\cdot}8H_2O$ and a little or some $C_3A{\cdot}12H_2O$. There was slow conversion to $C_2A{\cdot}8H_2O$. Two mixes (*D* and *E*) were also stated to give $C_3A{\cdot}18H_2O$, $C_3A{\cdot}12H_2O$, or $Al(OH)_3$. D'Ans and Eick refer specifically to the hexagonal-plate phases precipitated as having no uniform composition, and of being a mixture of plates, but state that pure compounds are rare and that there is a strong tendency toward the formation of anomalous "mixed-crystals." There seems little reason to doubt that the "practical" curve obtained is essentially similar to that of Wells, Clarke, and McMurdie, though it is not coincident with it.

Apart from this "practical" curve, D'Ans and Eick have concluded, on the basis of data which appear to be open to criticism as discussed later, that two distinct curves for $C_2A{\cdot}8H_2O$ and α-$C_4A{\cdot}13H_2O$ exist, each throughout a long range of solution concentrations, intersecting in an invariant point *Y* at 0.610g CaO per liter, 0.095 g Al_2O_3 per liter, that a solubility curve for a β-$C_4A{\cdot}13$-$14H_2O$ exists, extending into regions of low lime and low alumina concentrations, and that there are solubility curves for $C_3A{\cdot}12H_2O$ and $C_3A{\cdot}18H_2O$ situated between what are termed the "limit curves" for α-$C_4A{\cdot}13H_2O$ and $C_2A{\cdot}8H_2O$. Apart from the "practical" curve, none of the conclusions listed above seem to be built on very sure foundations.

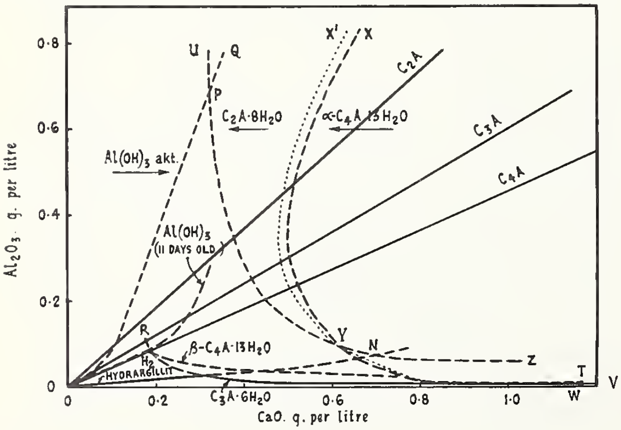


FIGURE 3. *System* CaO-Al_2O_3-H_2O *at 20 °C (D'Ans and Eick* [*33*], *1953).*
(Used by permission, Zement-Kalk-Gips.)

(4) Peppler and Wells [34] at 50 °C to 250 °C (1954)

Examination was made at 50 °, 120 °, 150 °, 200 °, and 250 °C at pressures from 1 to 39 atmospheres. The only new hydrated calcium aluminate phase formed was a compound $4CaO{\cdot}3Al_2O_3{\cdot}3H_2O$ (first prepared by Harris, Schneider, and Thorvaldson [35] (1943)), stable above 215 °C. Below this temperature the cubic $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ remains the stable hydrated calcium aluminate phase. The compound $C_4A_3{\cdot}3H_2O$ [34] "was prepared by heating a lime-alumina clinker for seven days at 278 °C. The resulting product was found to be homogeneous when examined microscopically. It consisted of rectangular plates having low birefringence with indices very close to 1.627". Properties had been given previously by Johnson and Thorvaldson [36] (1943) who stated that it crystallized in colorless elongated rectangular plates with parallel extinction, positive elongation, and low birefringence, of average R.I.=1.627, $d_{20\,°C}=2.71$, probably orthorhombic.

(5) Majumdar and Roy [37] at 100° to 1,000 °C (1955)

These authors state that the X-ray powder pattern they obtained of the compound $4CaO{\cdot}3Al_2O_3{\cdot}3H_2O$ varied from that reported by Johnson and Thorvaldson [36].

(6) Schippa and Turriziani [38] at 15°, 18°, 20 °C (1957)

Schippa and Turriziani carried out precipitation experiments from supersaturated solutions. Their data fall on a curve roughly coincident with that obtained by Wells, Clarke, and McMurdie at 21 °C, but again with no clear indication of an invariant point. X-ray examination of moist solids of CaO/Al_2O_3 ratio near to 4 yielded spacings similar to those for $C_2A{\cdot}8H_2O$, but which could not relate to this compound. This matter was not however cleared up.

(7) Buttler and Taylor [39] at 5 °C (1958)

The main feature of the behavior at 5 °C as compared with that at higher temperatures investigated by previous authors is the formation of the $CA{\cdot}10H_2O$ phase (see fig. 4, after Buttler and Taylor's fig. 2). This compound was originally prepared by Assarsson [40]. The establishment of an equilibrium curve for this compound appears however to be difficult because of the unstable or highly metastable nature of the equilibria, the formation of unstable hydrated alumina, and the apparent difficulty of obtaining equilibria from undersaturation. From undersaturation it appears that at 5 °C an equilibrium curve (*HC* in Buttler and Taylor's fig. 2) falls well below that for the hexagonal plate phase. There is, however, an apparent conflict of evidence from supersaturation and undersaturation, and it seems open to question whether in fact the curve *HC* concluded by Buttler and Taylor as that for $CA{\cdot}10H_2O$ can be taken as established in the position assigned to it.

(8) Carlson [14] at 1 °C (1958)

The general scheme of this work was again to approach equilibrium from supersaturation (by mixing calcium aluminate solutions and saturated limewater) and from undersaturation (by treating various prepared solid phases with water or lime solutions). The solid phases found in the system were stable $Ca(OH)_2$ and $C_3A \cdot 6H_2O$ and metastable $CA \cdot 10H_2O$, $C_2A \cdot 8H_2O$ and $C_4A \cdot 13H_2O$ (fig. 5).

(9) Percival and Taylor [41] at 21 °C (1959)

In a recently published note, these authors consider that they have established a curve for $CA \cdot 10H_2O$ in the system at 21 °C, obtained by shaking $CA \cdot 10H_2O$ with water or lime solutions. They could not however establish such a curve by precipitation from supersaturation, nor was any curve obtained by shaking $CA \cdot 10H_2O$ with water or lime solutions at 50 °C. Further, in their precipitation tests from supersaturation at 21 °C, they always obtained $C_2A \cdot 8H_2O$ (fig. 6).

(10) Buttler and Taylor [42] at 5 °C (1959)

This paper is restricted to the behavior of CA, CA_2, and mixtures of these when treated with water or lime solution in dilute suspension.

(11) Jones and Roberts [7] at 25 °C (1955–60)

The results of a re-examination of the system CaO-Al_2O_3-H_2O at 25 °C (to be published) show that the hydrates α- and β-$C_4A \cdot 13H_2O$ previously thought to exist in the aqueous system, are formed only on drying a $C_4A \cdot 19H_2O$ hydrate which is the only tetracalcium aluminate hydrate in the system. This hydrate can, however, exist in two forms, one of which is relatively unstable with respect to the other. The latter can be satisfactorily indexed on a hexagonal unit cell. In addition, a solid solution of composition range $C_{2-2.4}A \cdot 8$–$10.2H_2O$, is formed, and also two $C_2A \cdot 8H_2O$ hydrates of closely similar structures, one of which is unstable with respect to the other. The more stable of the two, when passed through a dehydration and rehydration cycle, converts to a form of $C_2A \cdot 8H_2O$ which appears to conform strictly to a hexagonal lattice. The results give a substantial clarification of previous work on the system. Figure 7 shows the solubility relationships and curves for various solid phases as given by these authors.

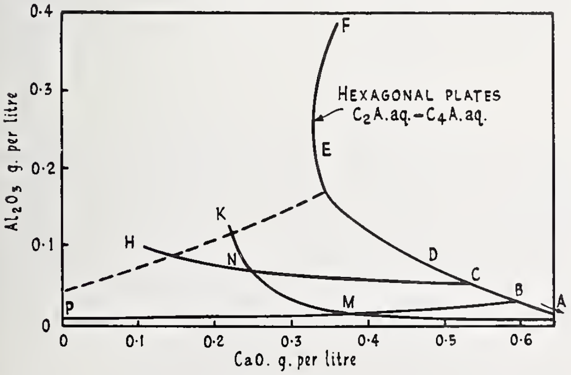


FIGURE 4. *System* CaO-Al_2O_3-H_2O *at 5 °C (Buttler and Taylor [39], 1958).*

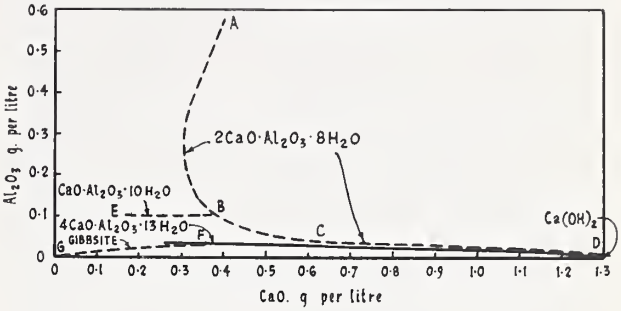


FIGURE 5. *System* CaO-Al_2O_3-H_2O *at 1 °C (Carlson [14], 1958).*

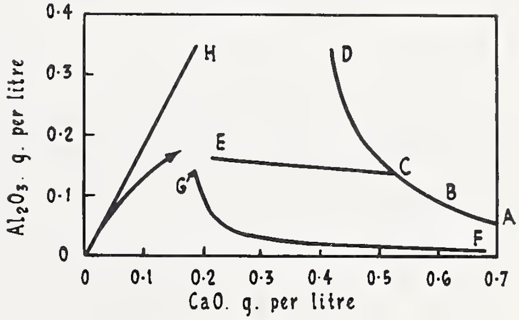


FIGURE 6. *System* CaO-Al_2O_3-H_2O *at 21 °C (Percival and Taylor [41], 1959).*

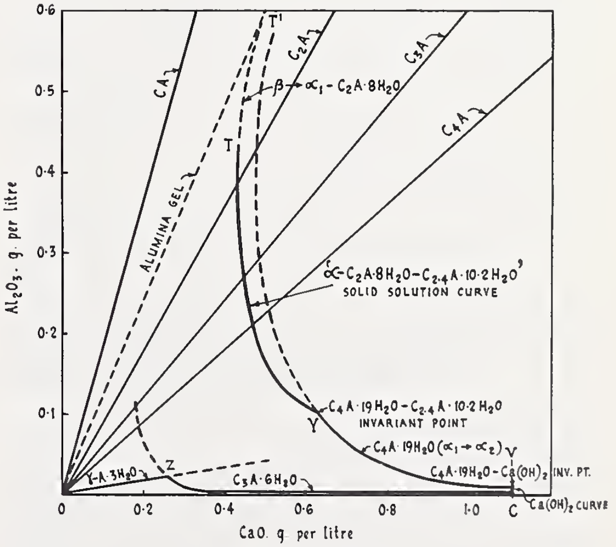


FIGURE 7. *System* CaO-Al_2O_3-H_2O *at 25 °C (Jones and Roberts [7], 1960).*

Review of Other Studies in the Light of Jones and Roberts' Work at 25 °C

It appears that the results and conclusions of Jones and Roberts may be used to reinterpret results previously obtained by other workers, and it is proposed to test this in the following discussion.

Jones and Roberts have concluded that at 25 °C:

(1) As previously recognized the only stable solid phases are crystalline $C_3A{\cdot}6H_2O$, $Ca(OH)_2$, and gibbsite (γ-$Al_2O_3{\cdot}3H_2O$).

(2) Hydrated (or hydrous) alumina, $Al_2O_3{\cdot}aq.$, can exist in the system in various unstable→stable states, ranging from a highly gelatinous hydrous alumina, through γ-$Al_2O_3{\cdot}H_2O$ (boehmite) and α-$Al_2O_3{\cdot}3H_2O$ (bayerite) to γ-$Al_2O_3{\cdot}3H_2O$ (gibbsite).

(3) Metastable hexagonal-plate phases can exist based on $C_4A{\cdot}aq.$ and $C_2A{\cdot}aq.$ structures as follows:

(a) *α_1- and α_2-$C_4A{\cdot}19H_2O$.* These are modifications of a new hydrate $C_4A{\cdot}19H_2O$.

The α_1-form is considered to possess an unstable or "disordered" layer structure. Where formed in the aqueous equilibria, it is unstable with respect to the α_2- structure and converts to it.

The α_2- form is basically the only C_4A hydrate which has a more than transient existence. The X-ray pattern is simpler than for the α_1- form and can be satisfactorily indexed on a hexagonal unit cell of dimensions $a=5.77$ A, $c=21.37$ A.

(b) *Solid solution $C_{2-2.4}A{\cdot}8$-$10.2H_2O$.* A metastable phase of varying CaO/Al_2O_3 ratio between 2 and 2.4, and varying H_2O/Al_2O_3 ratio between 8 and 10.2. It appears to be formed between α_1- or α_2-$C_4A{\cdot}19H_2O$ and α_1-$C_2A{\cdot}8H_2O$ (below).

(c) *α_1-$C_2A{\cdot}8H_2O$.* The previously known metastable $C_2A{\cdot}8H_2O$.

The X-ray pattern of this compound cannot be satisfactorily indexed on a hexagonal unit cell, apparently because of a "disordered" layer structure. In this respect it is similar to α_1-$C_4A{\cdot}19H_2O$. It does not transform to a more stable structure in solution (so far as observations have at present gone), but it can be so converted (to α_2-$C_2A{\cdot}8H_2O$ (below)) by passing through a dehydration and rehydration cycle.

(d) *β-$C_2A{\cdot}8H_2O$.* A new metastable hydrate, less stable than α_1-$C_2A{\cdot}8H_2O$ (above), into which it gradually converts in the aqueous system; i.e., in contact with solution. It cannot be satisfactorily indexed on a hexagonal unit cell, also apparently because of a "disordered" layer structure, which now, however, involves a slight decrease in the basal spacings (longest basal spacing 10.7 to 10.5 A).

(4) $C_4A{\cdot}19H_2O$ (α_1 or α_2) is the only tetracalcium aluminate hydrate which exists in the aqueous system (i.e., in contact with solution) and the α- and β-$C_4A{\cdot}13H_2O$ hydrates previously thought to be present in the aqueous equilibria are formed only as a result of dehydration of the $C_4A{\cdot}19H_2O$ hydrates according to the equation:

$$C_4A{\cdot}19H_2O-6H_2O\rightarrow C_4A{\cdot}13H_2O.$$

It follows that no "solubility" curves for α- or β-$C_4A{\cdot}13H_2O$ can exist in the aqueous equilibria, and that what have hitherto been interpreted as curves for these compounds are really curves for α_1- and α_2-$C_4A{\cdot}19H_2O$, or are not truly "solubility" curves.

(5) No hexagonal-plate form of tricalcium aluminate hydrate $C_3A{\cdot}12H_2O$ exists in the aqueous system. A solid hydrated hexagonal phase of C/A ratio=3 must at equilibrium consist of a mixture of $C_4A{\cdot}19H_2O$ and solid solution of composition $C_{2.4}A{\cdot}10.2H_2O$.

(6) Monocalcium aluminate hydrate does not form in the aqueous system at 25 °C except as a transient stage which passes into α_1-$C_2A{\cdot}8H_2O$.

(7) There is a transition temperature at approximately 22 °C at which $CA{\cdot}10H_2O$ and $C_2A{\cdot}8H_2O$ are relatively unstable with respect to one another in the aqueous phase, $CA{\cdot}10H_2O$ being relatively stable below, and $C_2A{\cdot}8H_2O$ relatively stable above that temperature.

$$2CA{\cdot}10H_2O\xrightleftharpoons{22\ ^\circ C}C_2A{\cdot}8H_2O+A{\cdot}aq.$$

In addition, there has been found

(8) *α_2-$C_2A{\cdot}8H_2O$.* A new metastable hexagonal plate hydrate, not so far found in the aqueous system in contact with solution, but into which α_1-$C_2A{\cdot}8H_2O$ converts on dehydration to the $5H_2O$ hydrate, followed by rehydration. This compound has the most stable structure of the different forms of $C_2A{\cdot}8H_2O$, one which can be satisfactorily indexed on a hexagonal unit cell of dimensions $a=5.80$, A, $c=21.59$ A. These dimensions are practically the same as those for α_2-$C_4A{\cdot}19H_2O$.

Since the most significant range of temperature for portland and high-alumina cement hydration is contained within the limits of 0 °C and 100 °C, we may exclude from immediate consideration the studies by Peppler and Wells and Majumdar and Roy in the higher range of temperature. Accepting as a basis the work of Jones and Roberts at 25 °C, it is proposed to consider first various studies, in order of decreasing temperature down to 1 °C (table 3), and then such work as has been done between 25 °C and 100 °C, leaving for final consideration work above 100 °C.

Range 25 °C to 1 °C

The investigations of Bessey (and Lea) at 25 °C, prior to 1938, have already been briefly referred to. Little information was given as to experimental detail. Only an alumina-gel phase, other than various hydrated calcium aluminates, was mentioned, while compounds $C_4A{\cdot}13H_2O$ and $C_3A{\cdot}12H_2O$ were then accepted as existing in the system. The last two compounds we now know do not exist in the aqueous system.

Jones [43] at 25 °C briefly considered the system CaO-Al_2O_3-H_2O as part of the quaternary system CaO-Al_2O_3-$CaSO_4$-H_2O and has described a little relevant experimental work. Special emphasis was laid on the equilibrium relations of hydrated alumina, separating out initially as a gel and changing both in crystal form and crystal size on aging, thus:

$$Al_2O_3\cdot aq.\ (\text{gel } \gamma\text{-}Al_2O_3\cdot H_2O)\rightarrow \alpha\text{-}Al_2O_3\cdot 3H_2O \rightarrow \gamma\text{-}Al_2O_3\cdot 3H_2O.$$

It was considered that the solubility "curve" must be regarded as unstable, sweeping out an area as its position changes with age, until a final stable position for γ-$Al_2O_3\cdot 3H_2O$ is reached.

The position of a solubility curve for a crystalline $A\cdot 3H_2O$ near to γ-$Al_2O_3\cdot 3H_2O$ was determined by Jones at 25 °C by shaking a preparation of $Al_2O_3\cdot 3H_2O$ with lime solutions of increasing concentrations for 7 or 28 days. This curve, combined with Bessey's curve for $C_3A\cdot 6H_2O$ at 25 °C, was accepted as defining with sufficient accuracy the stable equilibria for gibbsite, $C_3A\cdot 6H_2O$, and $Ca(OH)_2$ at 25 °C. No other work was done at this period in the ternary system, although it was clear that Jones' curve *SW* in the quaternary system CaO-Al_2O_3-$CaSO_4$-H_2O at 25 °C (his fig. 6) (considered at the time as a solid solution curve—conveniently then written as "$C_3A\cdot 12H_2O+C_3A\cdot CaSO_4\cdot 12H_2O+C_3A\cdot Ca(OH)_2\cdot 12H_2O+Ca(OH)_2$") corresponded to a similar curve in the ternary system. This in turn was to be identified with the solubility curve or curves within Bessey's area *DEB*.

Shortly before Jones' publication, Wells, Clarke, and McMurdie had published their study of the system CaO-Al_2O_3-H_2O at 21 °C. This fortunately presents a satisfactory amount of experimental data, which from supersaturation yielded their "practical" curve *ABD*. This, however, they found difficult to interpret satisfactorily. It seems evident now, in the light of Jones and Roberts' work, that this curve is really made up of a well-defined curve for the new $C_4A\cdot 19H_2O$ hydrate and a solid solution curve of composition range in the solid of $C_{2-2.4}A\cdot 8$–$10.2H_2O$. Data from undersaturation confirmed the practical curve *ABD*.

Wells, Clarke, and McMurdie had considered the problem of determining the exact water content of the various hexagonal-plate phases. However, they state that these hydrates "were, for the most part, washed with alcohol (and ether), and then were dried at room temperature in a desiccator containing $CaCl_2$". It has been shown by Roberts [11] that these procedures result in loss of water from the $C_4A\cdot 19H_2O$ hydrate to give $13H_2O$ and $11H_2O$ hydrates, respectively, and that although washing with alcohol does not affect the water content of $C_2A\cdot 8H_2O$, drying over anhydrous $CaCl_2$ results in a loss to $C_2A\cdot 5H_2O$. From this result it is clear that Wells, Clarke, and McMurdie could not detect the $C_4A\cdot 19H_2O$ hydrates in these dried products. In some instances, however, the samples were not dried over $CaCl_2$.

X-ray diffraction patterns on freshly-prepared samples (assumed washed with alcohol and ether, but not dried over $CaCl_2$) with CaO/Al_2O_3 ratios varying between 2.04 and 3.88, and H_2O/Al_2O_3 ratios varying between 7.92 and 12.60 were obtained by these authors. It was found that the extreme compositions gave the lines of

TABLE 3. *Studies of the system* CaO-Al_2O_3-H_2O *in range 25 °C—1 °C*

	Authors	Temperature °C	General procedure
1	Bessey (with Lea)	25 °C	
2	Wells, Clarke, and McMurdie	21 °C±1°	Precipitation from mixtures of supersaturated monocalcium aluminate solutions and lime solutions. The mixtures were contained in tightly stoppered flasks in a room at 21±1 °C. Approach to equilibrium from undersaturation by placing solid phases $C_2A\cdot aq.$ and $C_4A\cdot aq.$ in calcium hydroxide solutions of various concentrations. Phases examined by chemical analysis, optical examination, and to some extent X-ray diffraction. Solid phases dried, prior to examination, over $CaCl_2$.
3	D'Ans and Eick	20 °C±?	Precipitation from mixtures of supersaturated monocalcium aluminate solutions and lime solutions. Not apparently shaken, and precise condition of storage not given. Approach to equilibrium from undersaturation by shaking a preparation of $C_2A\cdot 8H_2O$ (of actual composition 2.25 CaO : 1 Al_2O_3 : 7.7 H_2O) with limewater of various concentrations. Phases examined by chemical analysis, but solids almost wholly by optical examination. No X-ray examination.
4	Buttler and Taylor	5 °C±0.5°	Precipitation from mixtures of supersaturated monocalcium aluminate solution and solid CaO shaken continuously for at least a week and then at least daily. Polyethylene bottles. Approach to equilibrium from undersaturation by adding solid phases $CA\cdot 10H_2O$, $C_3A\cdot 6H_2O$ and hydrated alumina to water or lime solutions in polyethylene bottles and shaking at least part of time. Phases examined by chemical analysis and X-ray diffraction.
5	Carlson	1 °C±1 °C	Precipitation from mixtures of supersaturated monocalcium aluminate solution and lime solutions and from undersaturation by treating various prepared solid phases with water and lime solutions. The mixes were stored in polyethylene bottles, with occasional shaking, in a refrigerator at 1 °C. Solid phases usually dried over $CaCl_2$. Identification by microscopic examination was stated to be often impossible and reliance was placed on X-ray examination.
6	Jones and Roberts	25 °C±1 °C	Precipitation from mixtures of supersaturated monocalcium aluminate solution and solid $Ca(OH)_2$, solid CaO, or lime solutions. Polyethylene vessels with very few exceptions. Continuous shaking. Solid phases examined in either moist solid condition or after controlled drying at definite relative humidities. Microscopic and X-ray examinations.

$C_2A \cdot 8H_2O$ and $C_4A \cdot 13H_3O$ hydrates, while intermediate compositions gave the lines of both, in appropriate proportions. In particular, a sample with $CaO/Al_2O_3=3.15$ gave a pattern in which the two 001 lines were of almost equal intensity. On these grounds the authors concluded that the so-called hexagonal tricalcium aluminate hydrate is in reality "a mixture of hexagonal hydrated dicalcium and tetracalcium aluminates in equal molecular proportions." From Jones and Roberts' work, it would appear that such a composition is, in the highly hydrated state, as present in the aqueous equilibria, a mixture of $C_4A \cdot 19H_2O$ and "solid solution" of composition $C_{2.4}A \cdot 10.2H_2O$ in appropriate proportions, and is, after drying, a mixture of $C_4A \cdot aq.$ and $C_2A \cdot aq.$ in conditions determined by the intensity of the drying procedure.

One interesting matter raised by Wells, Clarke, and McMurdie was their conclusion that in the dry state $C_2A \cdot 8H_2O$ decomposes to give $C_4A \cdot 13H_2O$ and $Al(OH)_3$. This conclusion was not confirmed by Jones and Roberts. It is of course not directly significant as regards compounds present in the aqueous equilibria, though Bessey has stated that the conversion also occurs when $C_2A \cdot 8H_2O$ is kept in contact with the saturated equilibrium solution in water. The latter statement is explicable on the basis of the relations in the aqueous equilibria as found by Jones and Roberts. Thus $C_2A \cdot 8H_2O$ in contact with its saturated solution is at the point *T* of Jones and Roberts' figure 1. Since this compound represents a highly metastable equilibrium, it will tend to change along Jones and Roberts' curve *TYV*, $Al(OH)_3$ separating out and gradually changing to a more crystalline and stable state, tending finally to gibbsite, while the composition of the equilibrium hexagonal-plate phase changes through the solid-solution range and finally converts to $C_4A \cdot 19H_2O$.

It is difficult to explain the conclusion reached by Wells, Clarke, and McMurdie. However, drying conditions were intense enough to give $C_2A \cdot 5H_2O$, the X-ray powder pattern of which may have been confused with that of $C_4A \cdot 13H_2O$.

Returning to the aqueous equilibria, it may be noted that Wells, Clarke, and McMurdie in 1943 had approached close to the definite conclusions reached by Jones and Roberts, in the former's tentative interpretation of their practical curve *ABD*. Thus the part of the curve which they concluded "applies primarily to the dicalcium aluminate hydrate" together with the "region where the two aluminates markedly inter-crystallize because of the close similarity of their crystal structures" clearly correspond to the solid solution curve *TY* of Jones and Roberts, and the part of the curve "pertaining mainly to the solubility of the hexagonal tetracalcium aluminate hydrate" to the definite solubility curve for $C_4A \cdot 19H_2O$ now established.

Consideration was also given by Wells, Clarke, and McMurdie to the precipitation of hydrated alumina in the system. Since the region in which this can occur is also one in which the compound $CA \cdot 10H_2O$ may be found, and the temperature (21 °C) is approximately or slightly below that of the stability limit of this compound with respect to $C_2A \cdot 8H_2O$, it is desirable to discuss the findings of these authors. They make no reference to $CA \cdot 10H_2O$. Later it may be noted that Percival and Taylor [41] could not establish a curve for $CA \cdot 10H_2O$ by precipitation at this temperature. Wells, Clarke, and McMurdie found that either mixtures of hydrated alumina and hexagonal plate phases were formed, with solution concentrations along the *AB* portion of their curve *ABD*, or that hydrated alumina alone was precipitated over an area which is within the general area where alumina gel in various stages of crystallization may be formed. These areas clearly correspond with the unstable invariant point curve for aging alumina gel and solid solution concluded by Jones and Roberts and the area swept through for an aging alumina gel curve. It may be noted however that the alumina gel precipitated in Wells, Clarke, and McMurdie's experiments as an apparent single solid phase contained some lime ($CaO/Al_2O_3=0.07$ to 0.36).

E. T. Carlson [17] (1957) later expressed surprise that Wells, Clarke, and McMurdie had not found any $CA \cdot 10H_2O$ compound at 21 °C. This apparent absence is however not so surprising in view of the closeness of the temperature to the transition point. However, Jones and Roberts obtained this phase at 20 °C together with hydrated alumina.

Wells, Clarke, and McMurdie's data, as indicated above, show that the hydrated alumina phase tends to become increasingly rich in lime with increase in lime concentration of the solution from which precipitation occurs. The question arises therefore as to the precise way in which this lime is linked with the hydrated alumina. The authors state that the hydrated alumina when first formed had a refractive index of about 1.50 (variable) increasing with age, more rapidly near the surface. This observation does not suggest any formation of $CA \cdot 10H_2O$, which has a refractive index of about 1.47. The surface index is stated to have increased eventually to from 1.56 to 1.58, the interior index being definitely less. Although increase in index might be due to aging of hydrated alumina to gibbsite (R.I. 1.56 to 1.59), the observation was also made that the increase in index near the surface was linked with increase in lime content. The possibility of formation of $C_3A \cdot 6H_2O$ was considered, although it was pointed out that it had not gone far enough to raise the external index to 1.605, the value for $C_3A \cdot 6H_2O$. Wells, Clarke, and McMurdie draw attention to similar results of Assarsson [40]. They found that X-ray diffraction patterns of aged hydrated alumina showed the presence of gibbsite, increasing with age, that the H_2O/Al_2O_3 ratio was often greater than 3 and increased with the CaO/Al_2O_3 ratio. No lines of the pattern of $C_3A \cdot 6H_2O$ were detected (possibly because the amount was too small). Thus if the lime present exists as a surface skin of $C_3A \cdot 6H_2O$, this fact could not be established. The weight of evidence points to a change to gibbsite near the surface as explaining the rise in surface index. It remains a possibility that some $CA \cdot 10H_2O$ was present.

A curve which was accepted (reasonably so) as the solubility curve for gibbsite at 21 °C was drawn through maximum solubility values for a gibbsite preparation allowed to stand in contact with lime solutions of different concentrations for periods of up to more than 2 yr.

Following Wells, Clarke, and McMurdie's work, no further comprehensive investigation of the system was published until that of D'Ans and Eick in 1953. As previously indicated, it seems to the writer that some of their conclusions are open to criticism. They state categorically that they determined at 20 °C the solubility curves of stable $C_3A \cdot 6H_2O$, hydrargillite (i.e., gibbsite), and $Ca(OH)_2$; and metastable "active hydroxides of aluminum," $C_2A \cdot 8H_2O$, α-$C_4A \cdot 13H_2O$ and β-$C_4A \cdot 13$–$14H_2O$.

As in the case of Wells, Clarke, and McMurdie the existence of $C_4A \cdot 19H_2O$ rather than $C_4A \cdot 13H_2O$ as the hydrated tetracalcium hydrate in the aqueous phase was not then realized, and their conclusions therefore need revision in the light of Jones and Roberts' work.

The "practical" curve obtained for hexagonal-plate phases by plotting data from supersaturation is given by D'Ans and Eick in their figure 4 (fig. 3 of this paper). The curve lies somewhat to the right of the similar curve obtained by Wells, Clarke, and McMurdie under very similar conditions of mixing metastable monocalcium aluminate solutions and lime solutions. The reason for the higher solution concentrations of D'Ans and Eick's curve is not clear. In the writer's experience, approach to equilibrium in the mixing of two such solutions and consequent precipitation is *on shaking* quite rapid, and there is no significant difference in the position of the curve for data obtained after two hours or up to 60 to 80 days. However there is little doubt that both curves have the same practical significance.

Of more immediate interest is the statement by D'Ans and Eick, based apparently only on optical evidence, that: (as the CaO/Al_2O_3 ratio of the initial mixed solution decreased) their mix *C* included, amongst other hexagonal-plate phases, small amounts of $C_3A \cdot 12H_2O$; mix *D* included first a little $C_3A \cdot 12H_2O$, then $C_3A \cdot 18H_2O$; and mix *E* included (together with $Al(OH)_3$) $C_3A \cdot 18H_2O$ of indices $\alpha=1.475$, $\gamma=1.495$, as well as $C_2A \cdot 8H_2O$ and $C_3A \cdot 12H_2O$. Again, their mix C_4 developed $C_3A \cdot 18H_2O$.

It is believed that D'Ans and Eick were mistaken in their assumption that compounds $C_3A \cdot 12H_2O$ or $C_3A \cdot 18H_2O$ exist at all in the aqueous system. They do however say that $C_3A \cdot 12H_2O$ may be $C_2A \cdot 8H_2O$ crystals with a higher lime content, or mixed crystals of $C_2A \cdot 8H_2O$ and $C_4A \cdot 13H_2O$. Both Wells, Clarke, and McMurdie, and Jones and Roberts have concluded that $C_3A \cdot 12H_2O$ does not exist in the system.

The position of the alleged $C_3A \cdot 18H_2O$ is of some interest. Bessey included this compound in his 1938 list as consisting, according to Mylius [44] of long needles with refractive indices $\alpha=1.479$, $\beta=1.489$, $\alpha=1.495$, but comments that it had only been observed in precipitation experiments in which ions other than those of the calcium aluminates were present. It seems unlikely that such a compound exists in the CaO–Al_2O_3–H_2O, system. It seems possible that this alleged compound may have been confused with $CA \cdot 10H_2O$ precipitation of which is possible at 20 °C in the precipitation regions concerned. The monocalcium aluminate hydrate can occur as prismatic needles and has a refractive index of about 1.47, rising on drying ($CA \cdot 10H_2O \rightarrow CA \cdot 7H_2O$) to $\omega=1.477$, $\epsilon=1.480$ [17].

With regard to Schippa and Turriziani's experiments at 20 °C, 18 °C, and 15 °C, it will be observed that they have also carried out moist solid examinations, but did not pursue the investigations to the conclusions reached by Jones and Roberts. No new hydrates were identified, and their experiments did not include mixes where the compound $CA \cdot 10H_2O$ is a likely or possible solid phase.

It has been shown by Jones and Roberts that the hydrated calcium aluminate phase precipitated with hydrated alumina from monocalcium aluminate solutions of $CaO/Al_2O_3=1$ is $C_2A \cdot 8H_2O$ above 22 °C and $CA \cdot 10H_2O$ below this temperature, though $CA \cdot 10H_2O$ may be formed occasionally in minor amounts above 22 °C and $C_2A \cdot 8H_2O$ may also be formed initially at 20 °C, but transforming into $CA \cdot 10H_2O$ with longer times of shaking. It was concluded that a transition temperature exists at 22 °C below which the $C_2A \cdot 8H_2O$ structure is unstable with respect to $CA \cdot 10H_2O$ within certain solution concentration limits. It follows that at the temperature of 21 °C or below, $CA \cdot 10H_2O$ is to be expected from supersaturation. Percival and Taylor carried out some work from supersaturation at 21 °C but state that it was not found possible to define the curve (for $CA \cdot 10H_2O$). They state that they did succeed in defining a curve by shaking $CA \cdot 10H_2O$ with water or lime solutions. It will be further discussed following consideration of the results of Buttler and Taylor at 5 °C.

Considering the data obtained by Buttler and Taylor from supersaturation at 5 °C, it is clear that their curve *A B C D E F* is similar to the general form of the curves *VY*, *YT* obtained in the investigation of Jones and Roberts at 25 °C, but is displaced to the left; i.e., to solution concentrations with less lime and alumina. The authors were not able to distinguish separate solubility curves. However, their own data seem to provide clear evidence of an invariant point similar to that of *Y* in the present work. Using data

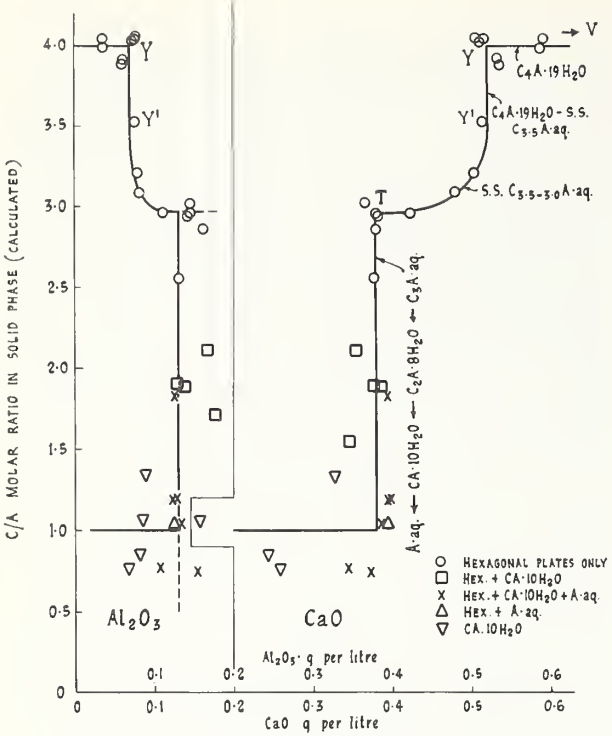


FIGURE 8. *System* CaO-Al_2O_3-H_2O *at 5 °C.*

Variation of C/A ratio in solid phase with solution composition. From supersaturation. Data of F. G. Buttler and H. F. W. Taylor [39].

obtained by Buttler and Taylor with mixes of total initial CaO/Al_2O_3 ratio greater than 1.6 (table 4), the CaO/Al_2O_3 ratio in the final solid phases is plotted against the lime and alumina concentrations in solution in figure 8. This figure is comparable to figure 2 of Jones and Roberts. Data obtained from some series of mixes (21, 22, and 23) have not been plotted at shorter times than 99 days. A number show a transition with time from the hexagonal-plate phase into $CA\cdot10H_2O$ or $CA\cdot10H_2O$ plus $A\cdot H_3$.

Although Buttler and Taylor have not adopted the procedure of direct analysis of the solid phases, and their data suggest that the calculated CaO/Al_2O_3 ratios may therefore be subject to error, the results are neverthless of considerable interest. The first thing to be noted is that there is a clear break in the equilibria data at a point *Y* corresponding to a solution concentration of 0.52 g CaO per liter, 0.07 g Al_2O_3 per liter. This break evidently relates to an invariant point for mixtures of $C_4A\cdot19H_2O$ and a second hexagonal plate phase. The corresponding phase at 25 °C has been concluded by Jones and Roberts to be a solid solution of composition $C_{2.4}A\cdot10\cdot2H_2O$. At 5 °C, the X-ray data of Buttler and Taylor, obtained only from solids dried at 34 percent rh at room temperature, indicate the presence of mixtures of $C_4A\cdot13H_2O$ and $C_2A\cdot8H_2O$ in these dried solids as the solution

TABLE 4. *System* CaO–Al_2O_3–H_2O *at 5°C*

(Selected data of F. G. Buttler and H. F. W. Taylor)
Equilibria from supersaturation

Mix No.[a]	Age	Total composition of initial mix, g/liter			Composition of filtrate, g/liter		C/A in solid (calculated)	Solid phases found in X-ray examination of solids dried over saturated $CaCl_2$ solution at room temperature
		CaO	Al_2O_3	C/A	CaO	Al_2O_3		
	Days							
6E	256	0.652	0.960	1.23	0.243	0.082	0.85	CAH_{10}
9C	574	.475	.593	1.46	.258	.068	.75	CAH_{10}
C5 (undersaturation)	94				.157	.085	1.05	CAH_{10}
13B	137	.569	.638	1.62	.372	.155	0.74	$C_2AH_8+CAH_{10}+AH_3$
13C	574	.569	.638	1.62	.346	.108	.76	$AH_3+C_4AH_{13}+CAH_{10}$
16D	100	.976	1.016	1.75	.394	.127	1.19	$C_2AH_8+CAH_{10}+AH_3$
16E	212	.974	1.016	1.74	.397	.124	1.18	Do.
18D	99	.744	.768	1.76	.385	.134	1.03	$AH_3+CAH_{10}+C_2AH_8$
18E	212	.767	.768	1.79	.392	.125	1.03	$AH_3+C_2AH_8$
21B	136	.676	.566	2.17	.346	.176	1.54	$CAH_{10}+C_2AH_8$
21C	577	.676	.666	2.17	.327	.089	1.33	CAH_{10}
22D	100	1.342	1.016	2.40	.354	.166	2.11	$C_2AH_8+CAH_{10}+$tr. C_4AH_{13}
22E	213	1.312	1.016	2.35	.387	.128	1.89	$CAH_{10}+C_2AH_8$
23D	99	1.025	.768	2.43	.374	.137	1.88	$C_2AH_8+CAH_{10}+$tr. C_4AH_{13}
23E	214	1.042	.768	2.47	.394	.125	1.83	$C_2AH_8+CA+AH_3$
28A	124	.570	.268	3.87	.377	.131	2.56	C_2AH_8
28B	578	.570	.268	3.87	.366	.145	3.02	$C_2AH_8+C_4AH_{13}$
24	20	1.657	.974	3.09	.379	.162	2.86	$C_2AH_8+C\cdot AH_{13}$
25A	7	1.795	1.016	3.21	.384	.142	2.94	Do.
25B	223	1.795	1.016	3.21	.379	.147	2.96	Do.
26	36	1.825	0.974	3.41	.422	.111	2.96	Do.
27	22	2.010	.974	3.75	.478	.081	3.09	Do.
29	36	2.087	.974	3.90	.502	.077	3.21	Do.
30	23	2.259	.974	4.22	.512	.074	3.53	Do.
31A	4	2.054	.768	4.86	.515	.076	4.04	$C_4AH_{13}+C_2AH_8$
31B	13	2.054	.768	4.86	.506	.068	4.02	Do.
31C	214	2.052	.768	4.83	.503	.077	4.05	Do.
32A	109	0.853	.208	7.46	.535	.059	3.88	C_4AH_{13}
32B	353	.853	.208	7.46	.532	.059	3.92	Do.
33A	109	.909	.183	9.03	.589	.034	4.04	Do.
33B	567	.909	.183	9.03	.585	.035	3.98	Do.

[a] For mixes giving final solid phases containing CAH_{10}, only mixes of 99 days or older are included owing to the apparent slowness in attainment of equilibrium. In mixes not developing CAH_{10} equilibrium appears to be attained within a very short time and accordingly short period mixes are here included.

concentrations change from that at Y to that at T (i.e., to 0.38g CaO per liter, 0.13 g Al_2O_3 per liter). From the work of Jones and Roberts it is concluded that the actual C_4A·aq. phase present in the corresponding moist solid before drying, and therefore in the aqueous system, is probably $C_4A·19H_2O$ (as at 25 °C) and that the $C_2A·8H_2O$ phase at 5 °C is a solid solution. We have also to consider the fact that the $C_2A·8H_2O$ is unstable with respect to $CA·10H_2O$ below 22 °C in regions where $C_2A·8H_2O$ would otherwise form, though it appears however to be a possibility that a solid solution based on the $C_2A·8H_2O$ and $C_4A·19H_2O$ structures may still remain a metastable phase within a range of compositions before suffering breakdown in the direction

$$C_4A·19H_2O \rightarrow C_2A·8H_2O \rightarrow CA·10H_2O \rightarrow A·3H_2O.$$

In figure 8, the extent of the vertical drop YY' at constant solution composition in the portion $YY'T$ suggests that a solid solution of composition $C_{3.5}A$·aq. is first formed on decomposition of the compound $C_4A·19H_2O$ and that these two phases at first coexist at the invariant point Y. The composition $C_{3.5}A$·aq. corresponds to 3 moles of C_4A·aq. and 1 mole of C_2A·aq., and one would therefore expect the X-ray pattern to be dominantly that of $C_4A·19H_2O$. However, Buttler and Taylor's X-ray examinations were made on solids dried over saturated $CaCl_2$ solution (34 percent rh) at room temperature, and the result of this treatment has to be considered. Under these conditions, a solid solution would be expected to dehydrate to α- and β-$C_4A·13H_2O$ and $C_2A·8H_2O$ (Buttler and Taylor did not distinguish between different forms of $C_4A·13H_2O$ or $C_2A·8H_2O$). Following conversion of $C_4A·19H_2O$ to the solid solution of maximum CaO/Al_2O_3 ratio of 3.5, the CaO/Al_2O_3 ratio is indicated in figure 8 to fall gradually to 3, the solution compositions changing gradually to another sharp break at T corresponding to 0.38 g CaO per liter, 0.13 g Al_2O_3 per liter. It appears reasonable to infer (on this data) that a solid solution is therefore formed of composition range $C_{3.5-3.0}$ A·aq., in equilibrium with solutions along the curve $Y'T$ (see also fig. 13). At T, the data (fig. 8) indicate a progressive breakdown in the structure from the solid solution through $C_2A·8H_2O$ to $CA·10H_2O$ and eventually to $A·3H_2O$ at a more or less constant solution composition. The sequence of X-ray patterns obtained by Buttler and Taylor is limited to $C_4A·13H_2O$ (derived partly from $C_4A·19H_2O$ and partly the solid solution, according to Jones and Roberts), $C_2A·8H_2O$, $CA·10H_2O$ and A·aq. Along YT the line intensities in the X-ray patterns of the dried solids indicated that $C_2A·8H_2O$ increased in amount with respect to $C_4A·13H_2O$, while from T, accompanying the rapid fall in CaO/Al_2O_3 ratios in the solid phase at the approximately constant solution composition, they indicated conversion to $C_2A·8H_2O$, $CA·10H_2O$ and $A·3H_2O$ respectively in order. It should be noted that since the $C_2A·8H_2O$ observed in the X-ray patterns of Buttler and Taylor obtained on dried solids could be derived from solid solution by dehydration and decomposition on drying, it is possible that there is direct breakdown of solid-solution phase to $CA·10H_2O$ and hydrated alumina with no actual intermediate formation of $C_2A·8H_2O$, which is unstable at this temperature.

The above appears to be consistent with the conclusion that in the aqueous system at 5 °C, the following sequence of curves and invariant points occur along the curve $A\ B\ C\ D\ E\ F$ obtained by Buttler and Taylor.

Using the lettering of Jones and Roberts:

$CV = Ca(OH)_2$
$YV = C_4A·19H_2O$
$YY' = C_4A·19H_2O$ and ss $C_{3.5}$ A·aq.
$Y'T =$ ss $C_{3.5-3}$ A·aq.
$T =$ Invariant point ss C_3A·aq.$-CA·10H_2O$
$TT' =$ Metastable or unstable prolongation of ss curve $Y'T$.

Although, because of uncertainty in Buttler and Taylor's calculated data, the actual composition of the solid solution is somewhat in doubt, it

Table 5. *System* $CaO–Al_2O_3–H_2O$ *at 5 °C*

(Selected data of F. G. Buttler and H. F. W. Taylor). Equilibria from undersaturation

Mix No.[a]	Age	Wt. CA·aq.	Volume solution	CaO, g/liter	Composition of filtrate, g/liter		C/A in solid (calculated)	Solid phases found in X-ray examination of solids dried over saturated $CaCl_2$ solution at room temperature.
					CaO	Al_2O_3		
	days	*g*	*ml*					
C2	131	0.654	393	0	0.145	0.091	0.62	$CAH_{10}+AH_3$
C3	160	.818	394	0	.143	.080	.68	Do.
C5	94	.385	441.6	0.124	.157	.085	1.05	CAH_{10}
C7	31	.595	431.7	.224	.247	.064	1.00	$CAH_{10}+AH_3$
C9	50	.486	422.2	.252	.286	.072	.97	Do.
C11	35	.462	425.7	.440	.438	.062	1.12	CAH_{10}
C12	117	.347	420.2	.440	.430	.062	1.29	$CAH_{10}+AH_3$
C14	44	.327	398.7	.874	.604	.030	2.96	$C_4AH_{13}+C_3AH_6+AH_3$
C15	106	.404	409.2	.874	.565	.043	2.93	Do.
C16	28	.157	412.0	1.174	.994	.002	3.23	C_4AH_{13}
C17	131	.168	404.6	1.174	.960	.003	3.48	Do.

[a] Only mixes with longer periods of contact are included in the above table from Buttler and Taylor's data, since it is assumed that in the presence of CA H_{10} and A H_3 in the solid phase these relatively long period mixes are more likely to have reached an appropriate metastable (or unstable) equilibrium..

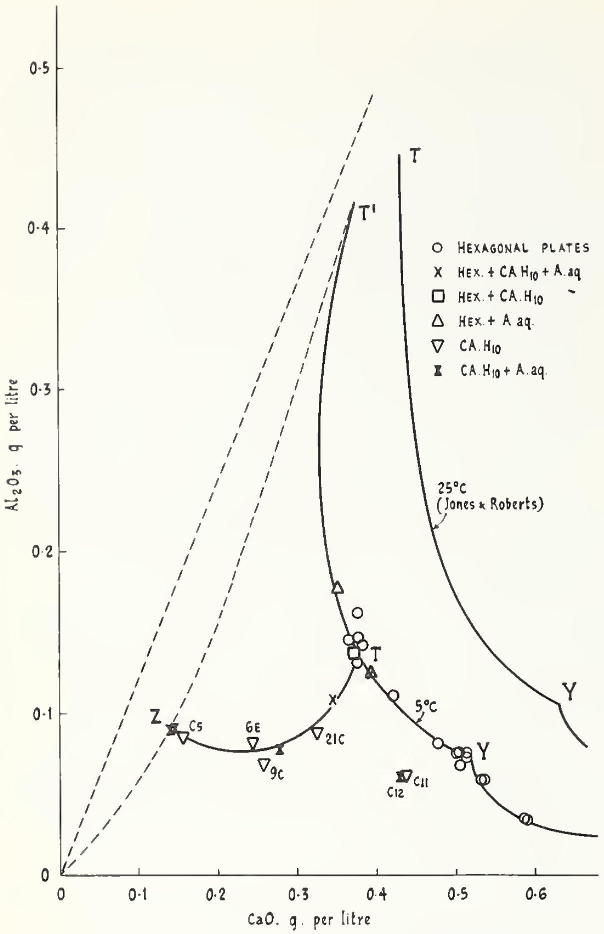


Figure 9. *System* CaO-Al_2O_3-H_2O *at 5 °C.*

Suggested metastable and unstable equilibria. Data (from supersaturation and undersaturation) of Buttler and Taylor [39].

would appear on this interpretation that a solubility curve for CA·10H_2O should start from *T* and proceed to intersect an unstable hydrated alumina curve. Such a curve *TZ*, based on Buttler and Taylor's data, from both supersaturation and undersaturation, is drawn in figure 9, which gives suggested possible metastable and unstable equilibrium curves.

Selected data obtained by Buttler and Taylor from undersaturation are given in table 5. They were obtained by shaking CA·10H_2O with water or lime solutions, and are plotted on figure 10. This figure includes the curve *HC* drawn by Buttler and Taylor as the CA·10H_2O curve in the system. The position assigned by Buttler and Taylor was based mainly on the data obtained from undersaturation (table 5). The difference between the position assigned by Buttler and Taylor for the CA·10H_2O curve and that which seems to be suggested by their data in the present discussion is difficult to reconcile. Note also that in figure 8, the position for a CA·10H_2O curve assigned by Buttler and Taylor would imply a vertical drop from a point on the curve *YV* and an invariant point C_4A·19H_2O-CA·10H_2O. This hardly fits the data.

It may be relevant to note that the mixes were not continuously shaken throughout the duration of the test. The authors considered that continuous shaking for some indeterminate time above a week, followed by a daily shake (presumably brief hand shaking in the storage room) was sufficient. This assumption may not be correct, especially for the approach from undersaturation. It may also be noted that many of Buttler and Taylor's relatively short-period mixes from supersaturation, starting below an initial CaO/Al_2O_3 ratio of 1.5 and falling in many cases to final CaO/Al_2O_3 con-

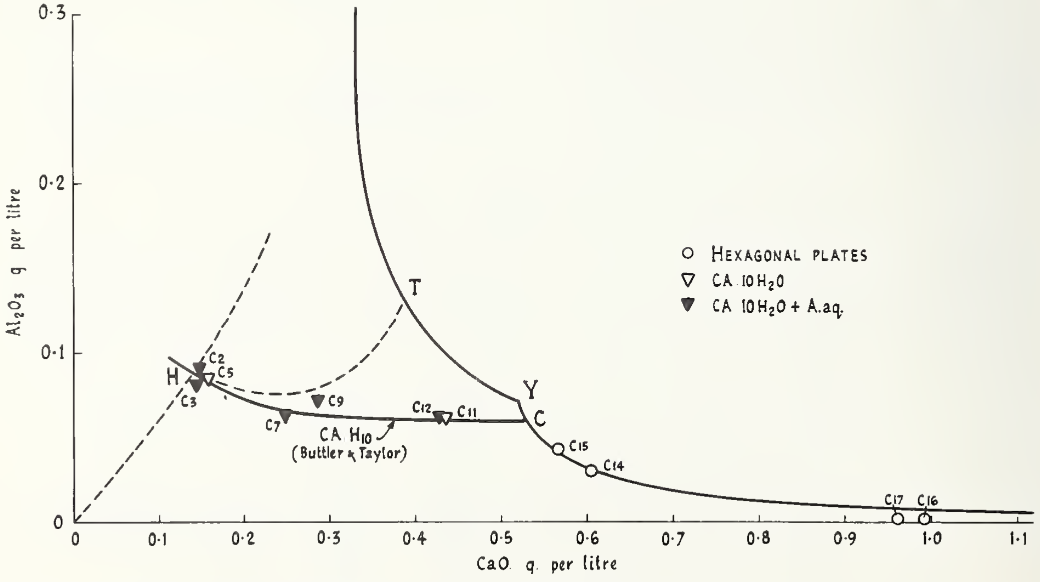


Figure 10. *System* CaO-Al_2O_3-H_2O *at 5 °C.*

Selected longer period data from undersaturation in relation to the position for a CA·H_{10} curve (F. G. Buttler and H. F. W. Taylor as concluded by them [39]).

centrations below those of curve *C D E F*, had final CaO/Al_2O_3 ratios in the solid phase well below unity. Also they were generally indicated, from X-ray data, to contain varying amounts of $CA\cdot 10H_2O$ and hydrated alumina, the latter generally increasing as the initial CaO/Al_2O_3 ratio decreased. From undersaturation also, alumina gel is present in most of the solid phases obtained by shaking $CA\cdot 10H_2O$ in water or lime solution. It seems possible therefore that either unstable invariant points $CA\cdot 10H_2O$–hydrated alumina may be obtained, the position of which will vary with the state of the hydrated alumina, or the latter phase may be dominant, as a protective layer, in determining the equilibrium solution.

Such a behavior is suggested by the solution compositions obtained in some experiments at the Building Research Station (Roberts [15]) in which monocalcium aluminate solutions were allowed to precipitate at 1 °C. For a series of 10 mixes, it was observed that the CaO concentrations were in the range 0.14 to 0.23 g CaO per liter and the Al_2O_3 concentrations in the range 0.1 to 0.24 g Al_2O_3 per liter, with a tendency for the latter to decrease with age. X-ray examination indicated that only $CA\cdot 10H_2O$ was precipitated. However, analysis of the solid phase usually showed CaO/Al_2O_3 ratios slightly less than 1 (0.89–1.01) indicating the possible presence of alumina gel.

A further paper relevant to the present discussion has very recently been published by Buttler and Taylor [42] (1959). This paper deals with the action of water and lime solutions on anhydrous calcium aluminates at 5 °C. It is chiefly noted here in so far as it considers the hydration of CA_2 and the possibility of a hydrated $CA_2\cdot$aq. compound. Reference is made to the work of Cocco [45]. The latter author found that pastes made from CA_2 were slow to set, but after about a month had a strength at least equal to that of ones made from CA. He deduced, but without any X-ray evidence, that a new hydrate $CA_2\cdot xH_2O$ was formed. Buttler and Taylor found that CA_2 with relatively strong lime solutions, reacts at a rate comparable with that of CA under similar conditions (though they point out that in their experiments the CA_2 was more finely ground). Reaction with water was however very slow and incomplete. The authors state that "The only hydrated compounds formed with water at 5 °C were CAH_{10} and hydrated alumina, no evidence was obtained for a hydrate of CA_2." It seems most probable that Cocco's original deduction is erroneous. It may be worth noting that in Buttler and Taylcr's paper figure 1 should be figure 2 and vice versa.

Returning to Percival and Taylor's determination, from undersaturation, of a curve for $CA\cdot 10H_2O$ at 21 °C [41], it will be seen (fig. 6) that the position assigned to the curve indicates that it meets the hexagonal-plate curve to the left of the position assigned by Jones and Roberts as most probable from the data of Wells, Clarke, and McMurdie for an invariant point $C_4A\cdot 19H_2O$-solid solution at 21 °C; i.e., 0.600 g CaO per liter, 0.100 g Al_2O_3 per liter. While this position seems more likely than one in which it meets the hexagonal-plate curve to the right of the invariant point, as assumed by Buttler and Taylor at 5 °C, with the implied invariant point (on Jones and Roberts' conclusion) of $C_4A\cdot 19H_2O$–$CA\cdot 10H_2O$, the actual point of intersection at 0.52 g CaO per liter and 0.14 g Al_2O_3 per liter (at 21 °C) does not accord well with the solid solution range of compositions which appear most probable at 21 °C.

The remaining investigation of the system CaO-Al_2O_3-H_2O in the range 25 °C to 1 °C is that by Carlson at 1 °C [14]. The general scheme of the work was again to approach equilibrium from supersaturation (by mixing calcium aluminate solutions and saturated limewater) and from undersaturation (by treating various prepared solid phases with water or lime solutions). The mixes were stored in polyethylene bottles, with occasional shaking, in a refrigerator at 1 °C. The solid phases were usually dried over $CaCl_2$ before examination, or by washing with alcohol and ether. It is stated that "With certain precipitates containing $2\ CaO\cdot Al_2O_3\cdot 8H_2O$ it was found essential to obtain the X-ray pattern while the material was still damp, as important phase changes occurred on drying."

It may be noted here that some confusion and misinterpretation in identification appears to have arisen in Carlson's work owing to the nonrecognition at that time of the pattern of $C_4A\cdot 19H_2O$. This pattern may have been confused with that of $C_2A\cdot 8H_2O$. Thus Carlson states that precipitates consisting of mixtures of di- and tetra-calcium aluminate hydrates, after drying over $CaCl_2$, often gave patterns showing only the lines of $4CaO\cdot Al_2O_3.13\ H_2O$. This effect was not reversible, and it was concluded that $C_2A\cdot 8H_2O$ had undergone decomposition to the tetracalcium compound and alumina. Accordingly, Carlson determined the X-ray patterns for such mixtures in the moist condition. From the work of Jones and Roberts, however, it appears that the correct explanation is that Carlson really obtained an unrecognized $C_4A\cdot 19H_2O$ in several moist mixes, and mistook this for $C_2A\cdot 8H_2O$, while some of the $C_4A\cdot 19H_2O$ decomposed to $C_4A\cdot 13H_2O$ and was identified as such. Such misidentification may have, e.g., arisen with mix 8 (11 days and 11 mo) and mix 9 at 11 days, in Carlson's table 2, and mixes 9, 10, 11, 12, and 13, in his table 3, all of which probably do not actually contain $C_2A\cdot 8H_2O$.

Carlson does not attempt to plot CaO/Al_2O_3 ratios in solid phases against solution concentrations. This is done however in figure 11, which is comparable with figure 2 of Jones and Roberts' paper at 25 °C and with figure 8 of the present paper for Buttler and Taylor's investigation at 5 °C. Based on the conclusions developed at 25 °C, the same kind of curves may be drawn. These appear reasonably to fit the data. It is assumed that the $C_4A\cdot 13H_2O$ found in the dried solid is equivalent, as at 25 °C, to $C_4A\cdot 19H_2O$ in equilibrium with the aqueous phase, and that the carboaluminate identified is the result of accidental carbonation, and has no significant bearing on results. A suggested interpretation of the data (table 6), as plotted in figure 11 and figure 12, is that they are consistent with an invariant point *Y*: $C_4A{\cdot}19H_2O$–solid solution "$C_{2.4}A{\cdot}aq.$" at a solution composition CaO=0.50 g per litre, Al_2O_3= 0.075 g per liter, a solid solution curve *Y′T* ("$C_{2.4-2.1}A{\cdot}aq.$") with metastable prolongation *TT′*, and invariant point *T*: "solid solution $C_{2.1}A{\cdot}aq.$"-$CA{\cdot}10H_2O$, and a curve *T*(*T″*)*Z* for $CA{\cdot}10H_2O$. *Z* is an invariant point $CA{\cdot}10H_2O$–$A{\cdot}aq.$, while the curve *OT′* in figure 12 is a tentative position for a "most unstable" hydrated alumina curve. The unstable invariant point *T′* for alumina gel and a solid phase along any prolongation *TT′* of the curve *YT* is probably not realizable in practice.

It will be seen therefore that much of Carlson's data at 1 °C can be applied to a series of curves similar to those established at 25 °C by Jones and Roberts, and in addition indicate a $CA{\cdot}10H_2O$ curve starting from an invariant point *T* similar to that which can be deduced from Buttler and Taylor's data at 5 °C.

Carlson has drawn his relevant equilibrium curves to correspond with data obtained from undersaturation, but because of their apparent difficulty in reaching a true equilibrium in this way, owing to the formation of protective films, the present author prefers to place greater reliance on data obtained from supersaturation. Accordingly, the curves of figure 12 are drawn to fit the latter.

The present author's interpretation places reliance on the recent detailed work of Jones and Roberts at 25 °C and what appears to be a reasonable "extrapolation" to 1 °C, bearing in mind the similarly interpreted work of Wells, Clarke, and McMurdie at 21 °C, that of Buttler and Taylor at 5 °C, and the further additional work of Percival and Taylor at 21 °C and Jones and Roberts at 25 °C.

Carlson interprets his work as indicating that tetracalcium aluminate hydrate is stable with respect to $C_3A{\cdot}6H_2O$ at 1 °C and that there are two curves *ACD* and *FCD* (fig. 5) for $C_2A{\cdot}8H_2O$ and $C_4A{\cdot}13H_2O$ respectively which are practically coincident with one another along the portion *CD*. (Note that the scale of CaO in solution along the abscissa of Carlson's figure 2 is incorrect in that it starts at 0.1 instead of zero.)

The present author feels however that the evidence for a curve for $C_4A{\cdot}aq.$ along *FC* is probably misleading. It depends on points obtained by placing water in contact with increasing amounts of a preparation of $C_4A{\cdot}13H_2O$ containing $Ca(OH)_2$. Thus the final lime concentration varied in the "equilibrium" solutions by virtue of the fact that increasing amounts of $Ca(OH)_2$ were added in with the $C_4A{\cdot}13H_2O$ at the start. The small amount of alumina dissolved can only arise by decomposition of some of the $C_4A{\cdot}aq.$ and, on the basis of the present interpretation, possibly some hydrated alumina. This could form a protective coating giving therefore the equilibrium for hydrated alumina rather than for $C_4A{\cdot}aq.$ With higher concentrations of lime initially, no formation of hydrated alumina would occur, and equilibrium solution concentrations would therefore be expected to fall, as they do, along the curve *CD*.

TABLE 6. *System* $CaO–Al_2O_3–H_2O$ *at 1°C*

(Selected data of E. T. Carlson)
Equilibria from supersaturation

Mix no.	Age	Total composition of initial mix, g/liter			Composition of filtrate, g/liter		C/A in solid (calculated)	Solid phases found in X-ray examination of solids
		CaO	Al_2O_3	C/A	CaO	Al_2O_3		
1	13 mo	0.833	1.278	1.18	0.152	0.112	1.06	CAH_{10}, probably little A·aq., trace $C_2A\ H_8$.
11	7 mo	.970	1.310	1.35	.260	.092	1.06	CAH_{10}
2	75 days	.879	1.150	1.39	.300	.104	1.01	CAH_{10}, trace $C_2A\ H_8$, trace $C_3A{\cdot}CaCO_3{\cdot}H_{11}$.
3	13 mo	.925	1.022	1.64	.388	.112	1.07	C_2AH_8, CAH_{10}, $C_3A{\cdot}CaCO_3{\cdot}H_{11}$
4	15 mo	.970	.895	1.97	.394	.120	1.35	C_2AH_8, CAH_{10}, $C_3A{\cdot}CaCO_3{\cdot}H_{11}$
12	10 mo	1.066	.916	2.12	.372	.153	1.65	C_2AH_8, CAH_{11}
5	9 mo	1.014	.767	2.40	.366	.203	2.09	C_2AH_8, tr. $C_3A{\cdot}CaCO_3{\cdot}H_{11}$
6	9 mo	1.058	.639	3.01	.384	.085	2.21	C_2AH_8, $C_3A{\cdot}CaCO_3{\cdot}H_{11}$
7	11 mo	1.108	.511	3.94	.503	.078	2.54	C_2AH_8, C_4AH_{13}
8	11 mo	1.154	.383	5.47	.499	.072	3.83	C_4AH_{13}, C_2AH_8,[b] $C_3A{\cdot}CaCO_3{\cdot}H_{11}$
9	11 mo	1.191	.256	8.45	.695	.016	3.76	C_4AH_{13}, $C_3A{\cdot}CaCO_3{\cdot}H_{11}$
10	9 mo	1.246	.128	17.7	.963	.004	4.15	C_4AH_{13}
CA157 [c]	11 days (shaker)	1.744	.997	3.18	.464	.075	[a] 2.47	*Moist solid* Much α_1-C_2AH_8(+trace α_1-C_4AH_{19}?) *Dried over* $(NH_4)_2SO_4$ Much α_1-C_2AH_8, little α-C_4AH_{13}
CA158 [c]	11 days (shaker)	2.134	.997	3.89	.478	.077	[a] 3.26	*Moist solid* Much α_1-C_4AH_{19}, little α_1-C_2AH_8 *Dried over* $(NH_4)_2SO_4$ Some α-C_4AH_{13}, some β-C_4AH_{13}, some α_1-C_2AH_8.

[a] By analysis.
[b] Probably not C_2AH_8 but C_4AH_{19}.
[c] Mixes prepared by Jones and Roberts.

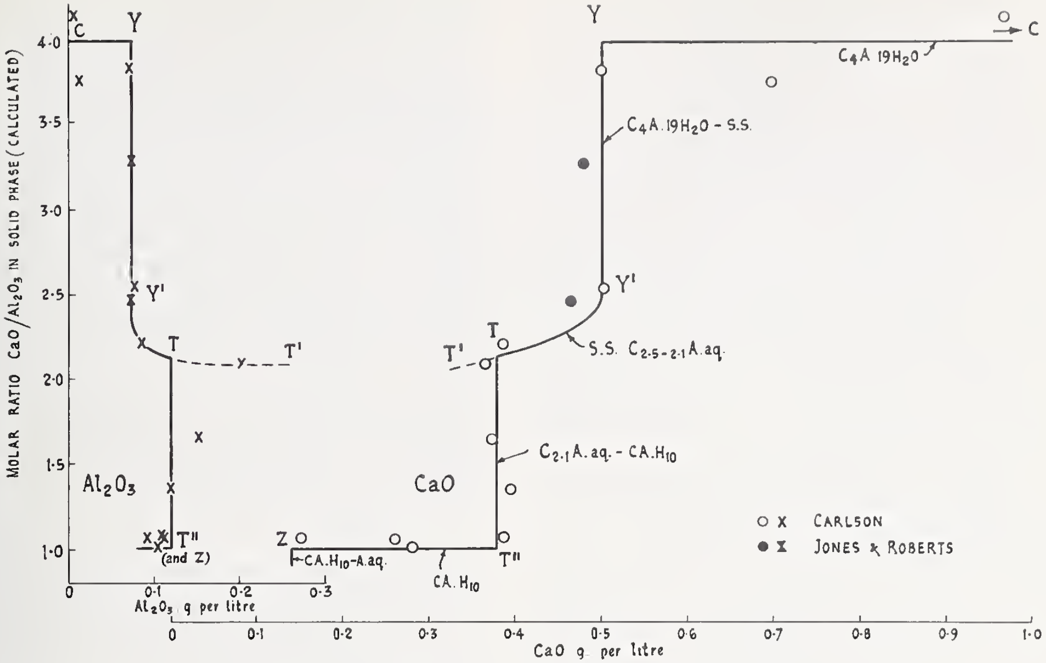


FIGURE 11. *System* $CaO-Al_2O_3-H_2O$ *at 1 °C.*

Variation of lime/alumina ratio in solid phase with equilibrium solution composition. From data of E. T. Carlson [14].

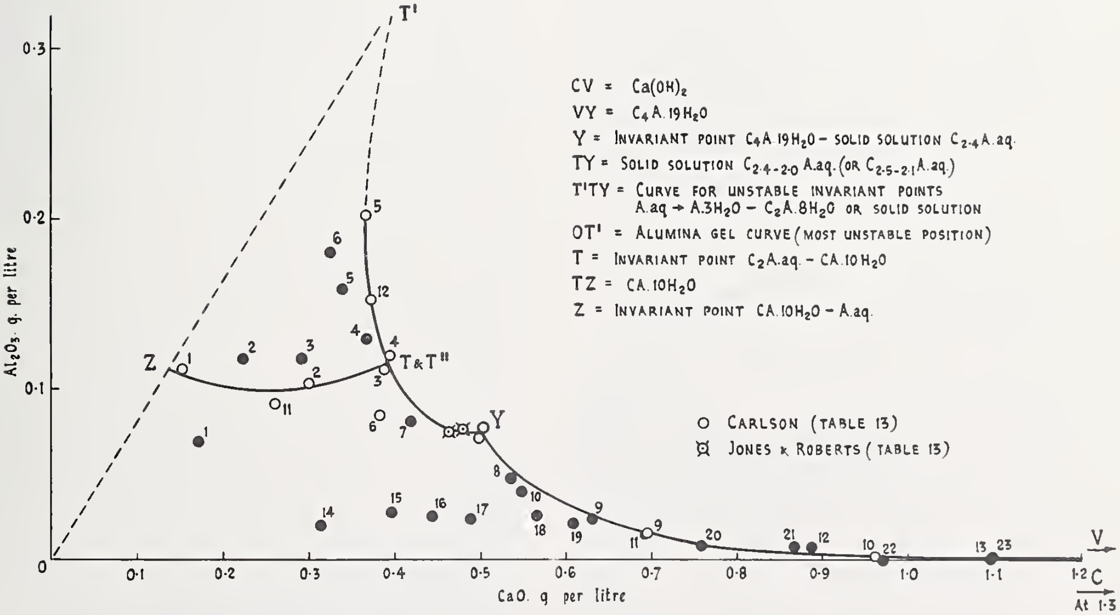


FIGURE 12. *System* $CaO-Al_2O_3-H_2O$ *at 1 °C.*

Suggested metastable and unstable equilibria. Data (from supersaturation ○ and undersaturation ●) of E. T. Carlson [14].

Before proceeding to a general tentative interpretation of the equilibria in this range of temperatures, it is necessary to consider a point of difference which is apparent from Buttler and Taylor's data at 5 °C as compared with data at 25 °C, 21 °C, and 1 °C. From figures 2 of Jones and Roberts and 8 and 11 of this paper it will be seen that the indicated solid solution composition range along respective curves *YT* is 2.4–2.0 at 25 °C, 3.5–3.0 at 5 °C, and 2.5–2.1 at 1 °C. (Data at 21 °C do not give a satisfactory indication of composition range.) The reason for the higher range in Buttler and Taylor's data is not clear. Although the molar ratios both in Buttler and Taylor's and in Carlson's investigations are calculated ratios and subject therefore to the likelihood of increased error as compared to the ratios obtained by direct analysis of the solid phase in the work at 25 °C, the curve *Y'T* based on Buttler and Taylor's data appears to be well defined, whilst Carlson's data at 1 °C, which fit the curve *YY'T* as drawn in figure 11, is supported by two mixes examined in the course of the work by Jones and Roberts. These were designed to repeat two of Buttler and Taylor's mixes (Nos. 25 and 29 of table 3), though at 1 °C, not 5 °C. The monocalcium aluminate solution used required dilution to give approximately the same initial Al_2O_3 concentration as the solution used by Buttler and Taylor. The relevant data are given with Carlson's data in table 6 and are plotted in figures 11 and 12. It will be seen that they support the curves drawn through Carlson's data from supersaturation. Further, the results of X-ray examination of moist and dry solids supports the expectation from solution analyses that the solid phases consist of $C_4A \cdot 19H_2O$ and solid solution in mix CA 158 and solid solution alone in mix CA 157.

Apart from this difference which calls for further work with careful direct analysis of solid phases, it seems possible to suggest tentatively a reasonably satisfactory picture of compound formation and equilibria in the system in the range 25 °C to 1 °C.

Relevant curves are given together in figure 13, the actual curves for hexagonal plate phases being those of the different authors, but drawn to include an invariant point *Y* as concluded by Jones and Roberts. At 20 °C and below, curves for $CA \cdot 10H_2O$ are drawn as deduced in the present discussion from a consideration of the various data.

It appears that at 20 °C or below, the equilibria include the following curves or invariant points.

OZ: Unstable alumina gel curve
Z: Unstable invariant point for A·aq.–$CA \cdot 10H_2O$
ZT: Unstable or metastable curve for $CA \cdot 10H_2O$
T: Unstable or metastable invariant point for $CA \cdot 10H_2O$–solid solution at minimum CaO/Al_2O ratio of its composition range
TY: Metastable solid solution of varying composition
Y: Metastable invariant point for solid solution at maximum CaO/Al_2O_3 ratio of its composition range–$C_4A \cdot 19H_2O$
YV: Metastable curve for $C_4A \cdot 19H_2O$
V: Metastable invariant point $C_4A \cdot 19H_2O$–$Ca(OH)_2$
VC: Metastable curve for $Ca(OH)_2$
C: Solubility of $Ca(OH)_2$

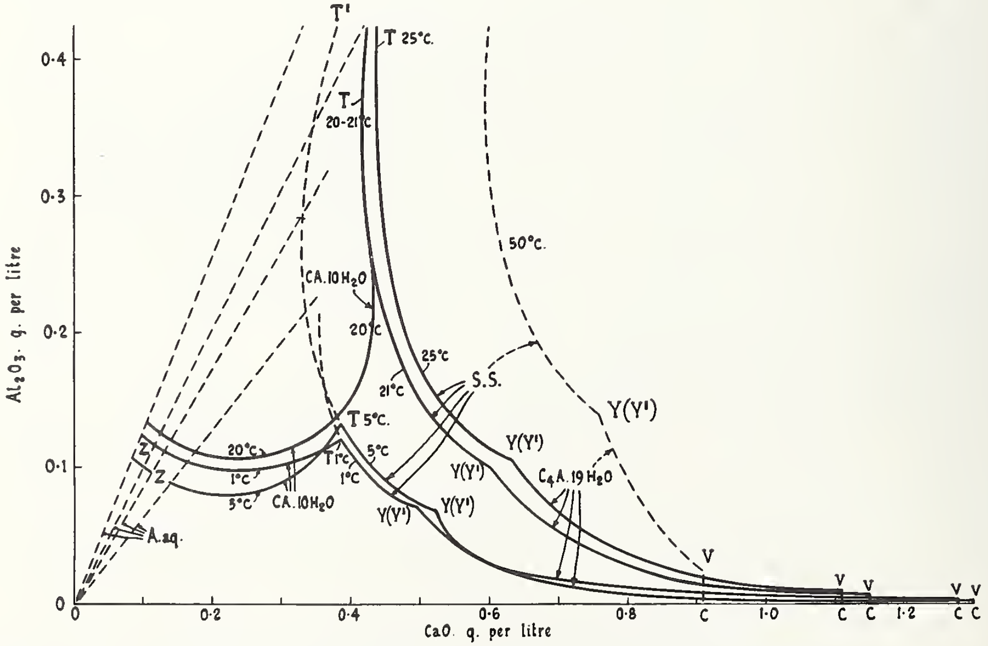


FIGURE 13. *System* CaO-Al_2O_3-H_2O *at various temperatures.*

Additionally, there are the stable curves for gibbsite (γ-$A \cdot 3H_2O$), $C_3A \cdot 6H_2O$, $Ca(OH)_2$ and stable invariant points for γ-$A \cdot 3H_2O$–$C_3A \cdot 6H_2O$ and $C_3A \cdot 6H_2O$–$Ca(OH)_2$.

Solution compositions for the invariant point *Y* at the various temperatures investigated appear to be: 25 °C, 0.630 g and 0.105 g per liter of CaO and Al_2O_3 respectively; 21 °C, 0.600 and 0.100; 5 °C, 0.520 and 0.07; 1 °C, 0.500 and 0.075.

Above about 22 °C, $CA \cdot 10H_2O$ is no longer formed in the system, the curve for $CA \cdot 10H_2O$ disappears, and the phase in metastable equilibrium with hydrated alumina may be $C_2A \cdot 8H_2O$, a solid solution, or ultimately $C_4A \cdot 19H_2O$, depending on the condition of the hydrated alumina.

Range 25 °C to 100 °C

The work of Peppler and Wells at 50 °C and of Wells, Clarke, and McMurdie at 90 °C will be considered again in the light of Jones and Roberts' work at 25 °C.

At 50 °C, Peppler and Wells [34] obtained a hexagonal-plate curve (fig. 14) the position for which was drawn through "equilibrium" solution concentrations for a number of 3-day mixes and for 3 1-hr mixes. As in previous work, an approach was made to equilibrium from supersaturation, starting with mixtures of calcium aluminate solutions and limewater. Final solids, however, included other, as well as hexagonal phases. For 3-day periods it was stated that mixes 1 to 8 of figure 14 contained alumina gel and hexagonal phases with only a very little $C_3A \cdot 6H_2O$. Mixes 9 to 11 after three days showed no hydrated alumina, and a predominating amount of $C_3A \cdot 6H_2O$ together with hexagonal phases. The reason for this behavior may lie in the composition of the final solid hexagonal phases which are to be expected prior to conversion to the cubic $C_3A \cdot 6H_2O$. The investigations at 25 °C suggest that along the more vertical portion of the curve, precipitation of $C_2A \cdot 8H_2O$ or solid solution is to be expected, the composition range of the solid solution at 25 °C being $C_{2-2.4}A \cdot 8$–$10.2H_2O$, while above an invariant point *Y* for solid solution and $C_4A \cdot 19H_2O$ (if this exists as such at 50 °C), $C_4A \cdot 19H_2O$ is to be expected. Actually, some tests at the Building Research Station have shown that at 50 °C and still more so at 90 °C, $C_4A \cdot 19H_2O$ originally formed in mixes at 25 °C is, on raising the temperature to 50 °C or 90 °C, rapidly converted into $C_3A \cdot 6H_2O$ and $Ca(OH)_2$, although some $C_4A \cdot 19H_2O$ was still present after 4 hr at 50 °C, and a trace of $C_4A \cdot 13H_2O$ remained after 1 hr or 20 hr at 90 °C. Accordingly, therefore, $C_3A \cdot 6H_2O$ could only arise by decomposition of $C_2A \cdot 8H_2O$, solid solution or $C_4A \cdot 19H_2O$. In the first two cases, this involves liberation of hydrated alumina to give an invariant point, probably yielding a protective film (in contact with the precipitating and changing hexagonal solid phases) which may retard the conversion. Where $C_4A \cdot aq.$ however is the expected final metastable solid phase, conversion to $C_3A \cdot 6H_2O$ involves only liberation of lime from the solid, and no protective film is to be expected. The reason for the absence of hydrated alumina in mixes 9 to 11 at three days appears simply to be that we are now concerned with mixes from which alumina gel is theoretically not expected to precipitate. So far as the hexagonal-plate curve is concerned, it appears that since from mixes 1 to 8 only a little $C_3A \cdot 6H_2O$ has been precipitated after three days, and the unstable invariant point curve $A \cdot aq.$–$C_2A \cdot 8H_2O$ or solid solution is expected to be coincident with the hexagonal plate curve, the 3-day points for these mixes may provide an approximation to the correct position of the latter curve. Owing however to the more rapid conversion for mixes 9 to 11, shorter periods of contact must be employed. The one-hr mixes are therefore a compromise (though note that Al_2O_3 gel, as well as hexagonal phases, is also stated to be present), and the curve drawn by Peppler and Wells is therefore probably too low to accord with the true position in the complete absence of $C_3A \cdot 6H_2O$. An approximate location for the true position is given in figure 13. First a position for the expected invariant point *Y* is made by a straight line extrapolation of the similar invariant points suggested at 1 °C, 5 °C, 21 °C, and 25 °C, and a curve similar to that at 25 °C is then drawn, based on this invariant point. It will be seen that the curve given by Peppler and Wells falls somewhat below this.

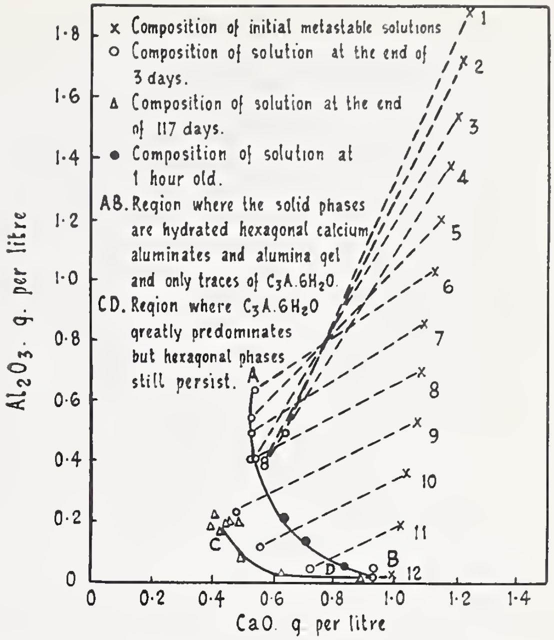


FIGURE 14. *System* CaO-Al_2O_3-H_2O *at 50 °C (Peppler and Wells [34], 1954).*

Owing to the presence of other phases in the final solids besides hexagonal plates, a plot of CaO/Al_2O_3 ratios in solids against CaO and Al_2O_3 concentrations of solutions is of little or no value

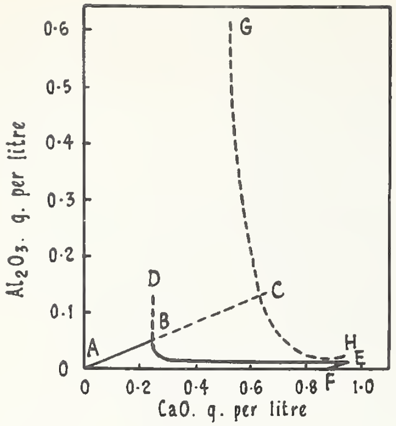


FIGURE 15. *System* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 50 °C (Peppler and Wells [34], 1954).*

in throwing light on the equilibria. Peppler and Wells incidentally discuss the possibility of the hexagonal phases being stable with respect to the cubic $C_3A{\cdot}6H_2O$ at high lime concentrations. The discussion of their relevant mixes is however not clear to the author, and he is of the opinion that the hexagonal-plate phase at the high lime end of the curve is a tetracalcium aluminate hydrate and that this is always metastable with respect to cubic $C_3A{\cdot}6H_2O$. Finally, Peppler and Wells quote values of interplanar spacings in the hexagonal plate phases obtained by them, as determined from X-ray diffraction patterns. It must be borne in mind that, as shown in the work of Jones and Roberts, spacings are dependent on the water content to which the various compounds are dried, and this depends on precise control. The limited spacings reported by these authors could very well fall within the range for the structures of hydrated di- and tetracalcium aluminates possible, following the drying technique (not stated) used by Peppler and Wells.

However, the X-ray pattern of the hexagonal phases at 50 °C given by Peppler and Wells does not appear to correspond to any of the hydrates of $C_4A{\cdot}$aq. or $C_2A{\cdot}$aq., whether fully hydrated or in various stages of dehydration, given by Roberts [11]. It may be noted that, apart from spacings at 5.15 A (strong) and 1.680 A (strong) ($C_3A{\cdot}6H_2O$?) the spacings quoted are very similar or almost identical to those of $C_3A{\cdot}CaCO_3{\cdot}$aq. The authors do not appear to have obtained the hexagonal-plate phases alone, free from alumina gel or $C_3A{\cdot}6H_2O$. Thus it seems probable that not only was some $C_3A{\cdot}6H_2O$ present in the sample or samples X-rayed (these are not indicated) but that carbonation has occurred. As previously noted, it has been pointed out by Carlson [14] that Myers, Rogers, Stannett, and Szwarc [31] have reported that polyethylene is somewhat permeable to carbon dioxide, and Peppler and Wells themselves refer to leakage of carbon dioxide through rubber stoppers.

In the light of the above discussion, there appears to be no conflict in the data of Peppler and Wells with the general interpretation of the metastable-plate phase equilibria in their paper.

Stable equilibria were also determined by Peppler and Wells at 50 °C. It is stated that "although the conversion of the hexagonal phase to the isometric phase is more rapid at 50 °C than at 21 °C, it is too slow to try to define the position of the stable isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ curve from supersaturation". The closest approach to this curve is shown in their figure 4 (fig. 14 of this paper) at the end of 117 days. Peppler and Wells base their curve for $C_3A{\cdot}6H_2O$ at 50 °C on data obtained from undersaturation (as at 21 °C and 90 °C) by shaking $C_3A{\cdot}6H_2O$ with lime solution in polyethylene bottles. Similarly a stable curve for gibbsite was determined. These authors' conclusions as to the positions for the gibbsite, $C_3A{\cdot}6H_2O$, and $Ca(OH)_2$ curves are given in figure 15.

An investigation of the system at 90 °C had previously been published by Wells, Clarke, and McMurdie [22]. They had considered that so far as metastable hexagonal-plate phases were concerned, these would have too brief an existence to warrant investigation. However, some work was done later by Peppler and Wells [34]. They held a series of mixed calcium aluminate and lime solutions at 90 °C for one hr, before filtration and analysis. The time taken to raise the temperature to 90 °C was not stated. The solid phases contained alumina gel and hexagonal phases together with larger amounts of $C_3A{\cdot}6H_2O$. The authors state that the curve defined by the solution data "is considered to represent a metastable region rather than to define a metastable equilibrium. The metastable hexagonal hydrate equilibrium curve would lie above this curve and to the right of it". If one compares the position of the curve after 1 hr at 90 °C with that for the curves for 50 °C and lower temperatures as drawn in figure 13 of the present paper, it will be seen that it falls even below those for 25 °C or 21 °C. This is apparently due to a more rapid approach to the stable equilibrium at 90 °C. The actual position for a hexagonal plate-phase curve at 90 °C, if it could be determined at very short periods, must of course be to the right of and above the curve for 50 °C in figure 13.

Wells, Clarke, and McMurdie, in their investigations, did not find it feasible to determine equilibria at 90 °C by an approach from supersaturation, in spite of the more rapid approach noted above, because of persistence of some of the hexagonal phase. They therefore determined the stable equilibria by heating, on a steam bath for 4 to 5 days, mixtures of lime solutions and $C_3A{\cdot}6H_2O$ or gibbsite at 90 °C. Glass vessels were used, and some silica was found in solution as a result of attack of the glass by lime at this temperature. How far this or entry of silica into the $C_3A{\cdot}6H_2O$ structure may have had an effect on the equilibria is uncertain. A further point which seems uncertain to the present author is the precise location of the invariant point

$Al_2O_3 \cdot 3H_2O$ (gibbsite)–$C_3A \cdot 6H_2O$. Wells, Clarke, and McMurdie drew their curve for solubility of gibbsite through only three points, and appear to have ignored a group of five points apparently defining the invariant point. Had these been considered, and, on their data, the curve been drawn with a curvature towards the Al_2O_3 axis, the position of the invariant point might well have been placed somewhat higher. However, the stable curves as concluded by Wells, Clarke, and McMurdie are included in figure 16, with some reservation by the present author as to the correctness of the precise location of invariant points.

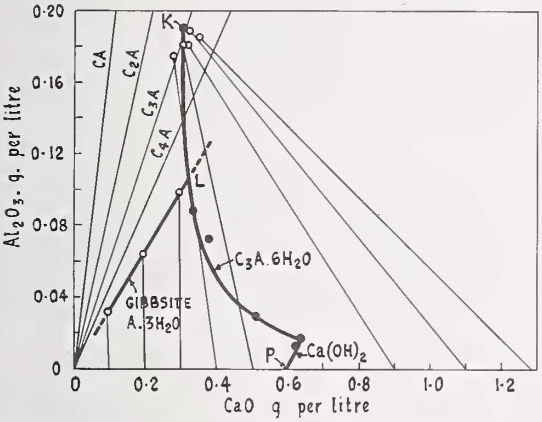


FIGURE 16. *System* CaO-Al_2O_3-H_2O *at 90 °C.*
Stable equilibria. (Wells, Clarke, and McMurdie [22], 1943.)

This survey of equilibria in the range 25 °C to 100 °C indicates that the stable phases are still gibbsite, $C_3A \cdot 6H_2O$ and $Ca(OH)_2$ and that unstable or metastable phases are still probably forms of hydrated alumina in the alumina gel→gibbsite range, $C_2A \cdot 8H_2O$, a limited solid solution between the C_2A·aq. and C_4A·aq. structures, and $C_4A \cdot 19H_2O$ (or possibly $C_4A \cdot 13H_2O$ at some higher temperature than 50 °C).

Range Above 100 °C

The system above 100 °C, involving pressures above atmospheric, has less interest for hydrated cement chemistry except in relation to steam curing, and will only be considered briefly.

From the present point of view, it is of chief interest for the preparation by Thorvaldson and coworkers of a calcium aluminate hydrate of formula $C_4A_3 \cdot 3H_2O$ [36]. As previously prepared by Harris, Schneider, and Thorvaldson [35] the exact composition was unknown, and the lime/alumina ratio was simply stated to be probably lower than 1.5. It was however found at 250 °C and above, when C_3A, $C_3A \cdot 6H_2O$, or "hexagonal C_3A·aq." were autoclaved at 250 °C, that rectangular, elongated. prismatic plates of low birefringence and R.I.=1.627 were formed. The compound was more precisely defined by Johnson and Thorvaldson by treating C_3A in saturated steam at 250 °C, and the formula $C_4A_3 \cdot 3H_2O$ was assigned, with a density of 2.71 at 20 °C. The crystals were described as probably orthorhombic. The water content was determined after drying over CaO. An older preparation of a $C_4A_3 \cdot 3H_2O$ compound is mentioned by the authors as that of Friedel, which may have been the same compound.

According to the work of Thorvaldson and coworkers also, a new hexagonal anisotropic calcium aluminate hydrate can be formed on autoclaving the lower calcium aluminates at 105–150 °C [46]. The average refractive index of this new hydrate was given as 1.58, or later, 1.576 with some grains of ϵ=1.589, birefringence about 0.013, optically positive. The composition was not determined. Spangenberg [47] later considered the behavior of cement mortars during steam hardening at higher pressures with temperatures in the range 100–200 °C. Referring to the work of Thorvaldson, this author suggested that the hexagonal-plate phase possibly had a composition $C_2A \cdot H_3$, and wrote it as $2(Ca(OH)_2 \cdot AlO(OH))$, indicating a layer lattice in which boehmite layers occur instead of $Al(OH)_3$. This suggested composition was based on the fact that hydrargillite ($=2Al(OH)_3$) is converted on raising the temperature to boehmite ($=2AlO(OH)$). Spangenberg suggests that both the $Al(OH)_3$ layers of hexagonal hydrated calcium aluminate and isolated $Al(OH)_6$ groups in C_3AH_6 are unstable above 150 °C and pass into the boehmite layers of the new hexagonal phase or, above 250 °C, into $C_4A_3H_3$. For the latter phase, the formula $2CaO \cdot 3AlO(OH)$ was suggested. There is no space in this review to offer any detailed discussion of these suggestions, though the layer lattices appear to conflict with the views on the structure of the hexagonal-plate tetracalcium aluminate hydrate recently put forward by Buttler, Dent Glasser, and Taylor. However, reconsideration of the structural ideas of these various authors would help to clarify the problem.

Assuming, tentatively, that a high-temperature form of C_2A·aq. does exist, as indicated above, then there appear to be two high-temperature calcium aluminate hydrates, which we may write as $C_2A \cdot H_3$(?) and $C_4A_3 \cdot H_3$, the latter appearing at higher temperatures.

Peppler and Wells [34] have carried out work at 120°, 150°, 200°, and 250 °C, using stainless-steel pressure vessels. Representation of equilibria was as commonly used for low temperatures. It is possible here only to summarize their main conclusions.

At 120 °C, gibbsite was again the stable hydrated alumina phase, with a straight-line solubility curve, congruently soluble in limewater up to an invariant point with $C_3A \cdot 6H_2O$. The equilibrium curve for $C_3A \cdot 6H_2O$ (also a straight line) was determined up to the invariant point with $Ca(OH)_2$.

At 150 °C, boehmite ($Al_2O_3 \cdot H_2O$) was now the stable phase. Transformation of gibbsite to boehmite was very slow and it was found possible to determine a metastable curve for gibbsite.

At 200 °C there was rapid conversion of gibbsite to boehmite. Attack on the bomb was stated to be very severe, while the bomb absorbed lime from solution. Only approximate positions for solubility curves could be assigned. When $C_4A_3 \cdot H_3$ was added to saturated limewater at 200 °C, $C_3A \cdot 6H_2O$ and boehmite were found as final phases; $C_3A \cdot 6H_2O$ was unchanged. In tests to locate the transition temperature $C_3A \cdot 6H_2O \rightarrow C_4A_3 \cdot H_3$ in the range 200–250 °C, microscopically detectable amounts of $C_4A_3 \cdot H_3$ were first found between 210 and 220 °C. At times, however, $C_3A \cdot 6H_2O$ persisted up to 250 °C below times of 4 days.

At 250 °C, $C_3A \cdot 6H_2O$ was quantitatively converted to $C_4A_3 \cdot H_3$ at initial lime concentrations from 0.1 g per liter up to saturation. Lime solubility at 250 °C is actually given by the authors as approximately 0.02–0.03 g per liter (their solubility curve for $Ca(OH)_2$ at various temperatures).

Other work by Majumdar and Roy [37] lay in a range 100 °C to 1,000 °C, involving extremely high pressures. Results could be expressed as a series of compatibility triangles within triangular coordinates. There is no space to discuss this work in detail, but again it was concluded that only three stable hydrated phases are formed in the system, namely $Ca(OH)_2$, $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$.

It may be noted here that Peppler and Wells have drawn a series of curves at different temperatures showing stable equilibria throughout the range they examined, somewhat parallel to those shown for metastable equilibria in figure 13.

(b) Compounds or Solid Solutions

The various hydrated compounds which can be formed in the system $CaO\text{-}Al_2O_3\text{-}H_2O$ have been discussed fairly fully in the preceding, both in the light of phase-rule equilibria studies and of structural considerations. It is concluded that compound or solid-solution formation within the ternary system is restricted to those given in table 7. It should be particularly noted that

(a) It is concluded that no metastable hexagonal-plate tricalcium aluminate hydrate exists, while the existence of a needle-form $C_3A \cdot 18H_2O$ is doubtful.

(b) The only mutual solid solution amongst the calcium aluminate hydrates appears to be between $C_4A \cdot 19H_2O$ and $C_2A \cdot 8H_2O$. It is suggested that the solid solution may be derived from $C_2A \cdot 8H_2O$ by loss of Al_2O_3 and replacement by H_2O ($Al(OH)_3 \equiv 3H_2O$ or Al^{3+} replaced by $3H^+$) up to one-sixth of the A content, following which the $C_4A \cdot 19H_2O$ structure is formed.

(c) A compound $CA \cdot 10H_2O$ is formed only below about 22 °C. Above this temperature, the metastable structure formed is that of $C_2A \cdot 8H_2O$.

(d) Although $C_2A \cdot 8H_2O$ or its solid solution with $C_4A \cdot 19H_2O$ is formed above 22 °C, it is metastable with respect to $C_3A \cdot 6H_2O$.

(e) A possible lower hydrate of dicalcium aluminate of formula $C_2A \cdot 3H_2O$ may be formed above about 100 °C, in which Al is linked with O and OH as in the boehmite structure.

(f) $C_3A \cdot 6H_2O$ is fundamentally stable up to over 215 °C.

(g) $C_4A_3 \cdot 3H_2O$ is formed at over 215 °C.

TABLE 7. *Hydrated calcium aluminates*

(a) Aqueous equilibria up to 100 °C	
α_1-$C_4A \cdot 19H_2O$ [a]	Unstable or "disordered" layer structure. Formed from supersaturation and converts to α_2-$C_4A \cdot 19H_2O$
$\downarrow$	
α_2-$C_4A \cdot 19H_2O$ [a]	Layer structure, satisfactorily indexed on hexagonal unit cell: $a=5.77$ A, $c=21.37$ A.
Solid solution $C_{2\text{-}2.4}$ $A \cdot 8-10.2H_2O$	
β-$C_2A \cdot 8H_2O$	A new form of $C_2A \cdot 8H_2O$ formed from supersaturation as an unstable or "disordered" layer structure which converts to $\alpha_1 = C_2A \cdot 8H_2O$.
$\downarrow$	
α_1-$C_2A \cdot 8H_2O$	The previously known $C_2A \cdot 8H_2O$. Unstable, when passed through a dehydration and rehydration cycle, with respect to a new $\alpha_2 = C_2A \cdot 8H_2O$.
$\downarrow$	
α_2-$C_2A \cdot 8H_2O$	Not so far found in the aqueous equilibria but may be formed after long periods. Most stable structure of the three $C_2A \cdot 8H_2O$ structures. and one which can be satisfactorily indexed on a hexagonal unit cell; $a=5.80$ A, $c=21.59$ A.
It is concluded that no hexagonal tricalcium aluminate hydrate $C_3A \cdot 12H_2O$ exists. A form $C_3A \cdot 18H_2O$ which has occasionally been reported as occurring in long needles may possibly have a fleeting existence.	
$CA \cdot 10H_2O$	Formed below 22 °C, above which $C_2A \cdot 8H_2O$ is formed. 22 °C is a transition temperature for the change $2\,CA \cdot 10H_2O \rightleftarrows C_2A \cdot 8H_2O + A \cdot aq$. Hexagonal(?) crystal structure. Brocard's work suggests may have $a=9.45$A(?), $c=14.6$ A(?).
$C_3A \cdot 6H_2O$	The only stable phase. Cubic crystal structure $a=12.56-12.59$ A.
(b) At high temperatures (>100 °C) and pressures	
$C_2A \cdot 3H_2O$?	Formed at 105–150 °C (Thorvaldson). Spangenberg suggested the composition C_2AH_3 with a layer lattice structure in which Al is linked with O and OH as in the boehmite structure.
$C_4A_3 \cdot 3H_2O$	Formed only at high temperatures (over 215 °C) and pressures. Not relevant therefore in cement-water system up to 100 °C. Probably orthorhombic (Johnson and Thorvaldson).
(c) After dehydration	
Various. Not relevant to aqueous system, but their study may throw light on structure of the fully hydrated compounds and on behavior of cement pastes mortars, and concrete on drying.	

[a] Observed only up to 50 °C.

When consideration of hydrated aluminates is extended to the effect of gypsum, added as retarder, or calcium chloride, added to accelerate hardening, structures based on the metastable lattice (1) or (2) may be obtained, depending on the nature and amount of the additional anions present, and the temperature. The present position is summarized in table 8.

So far as appears to be known at present, no substitution in the stable cubic lattice by such ions as SO_4^{2-}, Cl^-, etc., appears to be possible. Thus when a metastable structure such as the low form of chloro- or sulfoaluminate reverts to a cubic $C_3A{\cdot}6H_2O$ lattice, chloride or sulfate should be freed. This release may be important; e.g., in considering the effect of calcium chloride additions to concrete on possible corrosion of reinforcement. Thus calcium chloride originally taken up into a solid solution and so originally removed as a factor in possible corrosion may, if a stable cubic lattice structure is subsequently formed, be freed again.

TABLE 8. *Hydrated calcium sulfo- and chloroaluminates and ferrites*

<table>
<tr><th>Sulfoaluminates</th><th>Sulfoferrites</th></tr>
<tr><td>$C_3A{\cdot}3CaSO_4{\cdot}32H_2O$</td><td>$C_3F{\cdot}3CaSO_4{\cdot}32H_2O$</td></tr>
<tr><td>Hexagonal needles. Slight birefringence. Uniaxial negative, $\omega=1.464$, $\epsilon=1.458$.</td><td>"Hexagonal" needles: Slight birefringence.
Mean R.I=1.49.
Uniaxial positive?, $\omega=1.486$, $\epsilon=1.490$</td></tr>
<tr><td>$C_3A{\cdot}CaSO_4{\cdot}12H_2O$</td><td>$C_3F{\cdot}CaSO_4{\cdot}12H_2O$</td></tr>
<tr><td>"Hexagonal" plates, uniaxial negative. $\omega=1.504$, $\epsilon=1.488$</td><td>Uniaxial negative, $\omega=1.564$, $\epsilon=1.539$.</td></tr>
<tr><td colspan="2">Solid solution—$C_3A(F){\cdot}3\ CaSO_4{\cdot}32H_2O$ in limited degree (up to ¼A and ¾F approx). May be more extensive.
Solid solution—$C_3A(F){\cdot}CaSO_4{\cdot}12H_2O$. Little evidence in literature for such a solid solution, but it appears likely, and one typical solid solution of this general composition with A/F=2 has been prepared at Building Research Station with $\omega=1.520$, $\epsilon=1.505$.</td></tr>
<tr><th>Chloroaluminates</th><th>Chloroferrites</th></tr>
<tr><td>$C_3A{\cdot}3CaCl_2{\cdot}30H_2O$</td><td>$C_3F{\cdot}3CaCl_2{\cdot}xH_2O$</td></tr>
<tr><td>Formed preferentially below 0 °C by hydration of C_3A in 23% $CaCl_2$ solution.</td><td>Existence not yet established.</td></tr>
<tr><td>$C_3A{\cdot}CaCl_2{\cdot}10H_2O$</td><td>$C_3F{\cdot}CaCl_2{\cdot}10H_2O$</td></tr>
<tr><td>Hexagonal plates $\omega=1.550$, $\epsilon=1.535$. Uniaxial negative.</td><td>Biaxial negative, $\alpha=1.600$, $\gamma=1.605$</td></tr>
<tr><td colspan="2">Solid solution—$C_3A(F){\cdot}3CaCl_2{\cdot}aq.$ Presumably possible, but no evidence.
Solid solution—$C_3A(F){\cdot}CaCl_2{\cdot}10H_2O$. Stated to be obtained, but no details.</td></tr>
</table>

(c) Hydration of Anhydrous Compounds

A good deal of work has been done in the past on the behavior of various anhydrous aluminates when treated with water in various ways. It is however not proposed to examine this older work in detail. Space does not permit more than a brief reference, nor indeed does it appear for this system, where so much work has been done in phase-rule studies, to be essential to the present purpose. It is thought that the more recent knowledge of phase-rule equilibria will contribute to an understanding of many of the results described in the older literature. The position is reversed in considering the system $CaO\text{-}Fe_2O_3\text{-}H_2O$, where little has been possible as yet on a phase-rule approach, and results obtained on treating anhydrous iron compounds with water, or lime, etc., solutions are correspondingly more important.

The System $CaO–Fe_2O_3–H_2O$

(a) Introduction and Review of Phase-Rule Equilibria Possibilities

Malquori and Caruso [48] pointed out in 1938 the limited knowledge available of the system $CaO\text{-}Fe_2O_3\text{-}H_2O$ or related quaternary systems with calcium salts, and in this and later papers [49–52] described the preparation of such compounds as hexagonal $C_4F{\cdot}14H_2O$ (after Hoffmann) cubic $C_3F{\cdot}6H_2O$, hexagonal $C_3F{\cdot}CaSO_4{\cdot}10H_2O$, and $C_3F{\cdot}CaCl_2{\cdot}10H_2O$ and their solid solutions and also partial replacement of Al by Fe in $C_3A{\cdot}3CaSO_4{\cdot}31\text{–}33H_2O$.

It has been independently suggested by Jones [27] in 1945 that for this and related systems, equilibria somewhat similar to those found for Al_2O_3 may exist, though the possibilities of compound and solid-solution formation (of the type found in the $CaO–Al_2O_3–H_2O$ system) may be much more limited. This suggestion has received support from Steinour [32]. Very little work has been done on this system, partly owing to the need for further clarification of the more important $CaO–Al_2O_3–H_2O$ system and partly owing to the practical difficulties involved. Yet there seems little doubt that the variety of hydrated compounds containing iron, analogous to corresponding alumina compounds, and which can be formed in cement hydration, demands sooner or later a radical study of this system and of more complex quaternary and quinary systems involving additionally sulfate, chloride, and alkali (Na_2O and K_2O).

The main difficulty in studying the ternary system is the fact that an approach to equilibrium is difficult from supersaturation since no metastable calcium ferrite solutions are formed analogous to the metastable calcium aluminate solutions. However, it may be possible in the way adopted by Schippa [9] (1958) in his study of calcium sulfoferrite hydrates, using a ferric hydroxide sol prepared from ferric sulfate. Further, the solubilities of corresponding or related iron compounds appear to be very much less, only extremely small amounts of iron being found in solution. However, hydration of cement involves not only the intermediate formation of metastable supersaturated solutions of calcium aluminates from which metastable and ultimately stable solid phases may be formed in an approach to equilibrium, but also a hydration process in which substantially no intermediate metastable supersaturated solution is formed. The latter appears to be the case with the iron-containing compounds of portland cement, so far as the iron component is concerned. The reason for nonformation of a metastable supersaturated calcium ferrite solution cannot be clearly stated. That it is connected with the difference in properties of the Al and Fe atoms is obvious. It may perhaps be sufficient to say that this difference involves a very high instability of a postulated calcium ferrite solution or (saying the same thing in another way) that the hydrated calcium ferrites are very much less soluble than even the calcium aluminates. For a study of the system $CaO–Fe_2O_3–H_2O$ it appears that it is necessary in the first place to rely on an approach from undersaturation and on analogy with the compounds formed in the system $CaO–Al_2O_3–H_2O$ and other more complex systems.

A cubic $3CaO \cdot Fe_2O_3 \cdot 6H_2O$ (the precipitate was stated to contain some "calcium silicate") was prepared originally by Eiger [53] (1937). It is isomorphous with cubic $3CaO \cdot Al_2O_3 \cdot 6H_2O$. Physical properties are given in table 9. At about 400 °C the hydrate loses $4.5H_2O$, showing similar behavior to that of the corresponding aluminate.

TABLE 9. *Hydrated calcium ferrites*

$C_4F \cdot 14H_2O$	Hexagonal plate hydrated calcium ferrite analogous to $C_4A \cdot 13H_2O$. No satisfactory evidence that this exists without some Si or Cl or both in the structure. Apparently lattice similar to $C_4A \cdot 13H_2O$. $\omega=1.59$ A (Malquori & Cirilli [52] 1943). Feitknecht [62] (1942) proposed hexagonal or pseudo hexagonal parameters $a=3.42$, $c=8.0$ A, compared with (Feitknecht and Gerber [63] 1942) $a=3.36$, $c=7.9$ A for the corresponding $C_4A \cdot 13H_2O$.
$C_2F \cdot aq$	No satisfactory evidence for the existence of a hexagonal layer structure corresponding to $C_2A \cdot 8H_2O$.
$CF \cdot aq$	No satisfactory evidence for the existence of a structure corresponding to $CA \cdot 10H_2O$.
$C_3F \cdot 6H_2O$	May be formed as a pure phase, but difficult to prepare free from contamination with other phases, possibly due to formation of protective films, or to carbonation. Also, a pure $C_3F \cdot 6H_2O$ may be an unstable structure with respect to a solid solution containing, e.g., Al or Si or both. $n=1.72$. Cubic cell, $a=12.76$ A

It appears therefore that we may expect stable equilibria in the system $CaO–Fe_2O_3–H_2O$ involving solubility curves for $Ca(OH)_2$, "$C_3F \cdot 6H_2O$" (which may contain SiO_2), and hydrated ferric oxide with corresponding invariant points. We may expect solubilities of both "$C_3F \cdot 6H_2O$" and hydrated ferric oxide to be much lower than for the corresponding alumina phases, but there appear to be no data available from which a precise diagram may be constructed. However, a theoretical scheme is given in figure 17, based on analogous equilibria in the $CaO–Al_2O_3–H_2O$ system. No trihydrates of ferric oxide similar to $Al_2O_3 \cdot 3H_2O$ appear to exist, and the stable ferric-oxide hydrate would seem to be either α-$Fe_2O_3 \cdot H_2O$ (goethite) with a crystal structure similar to that of naturally occurring α-$Al_2O_3 \cdot H_2O$ (diaspore), or γ-$Fe_2O_3 \cdot H_2O$ (lepidocrocite) with a crystal structure similar

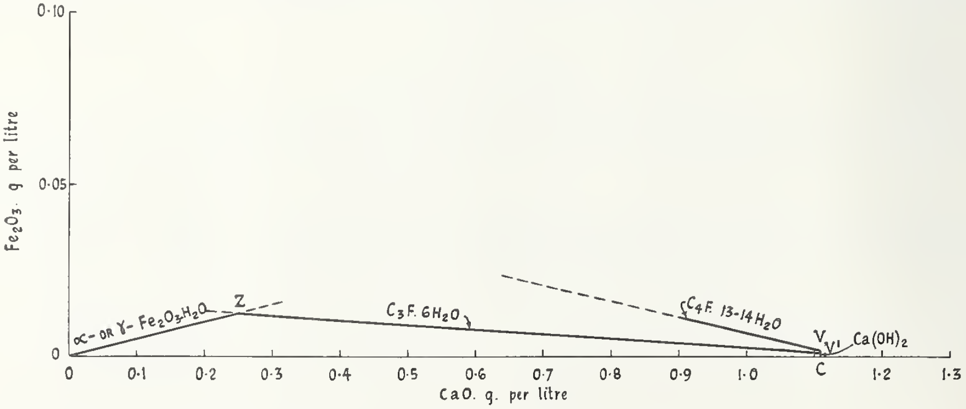


FIGURE 17. *Tentative approach to representation of system $CaO–Fe_2O_3–H_2O$ at room temperature, 25 °C.*

to that of γ-$Al_2O_3 \cdot H_2O$ (boehmite). (An interesting point is that Hoffmann [54] states that γ-$Fe_2O_3 \cdot H_2O$ easily changes to α-$Fe_2O_3 \cdot H_2O$ on crushing in an agate mortar.)

Besides the $C_3F \cdot 6H_2O$ compound which now appears to be established as the "stable" analog of $C_3A \cdot 6H_2O$, a hexagonal-plate tetracalcium ferrite hydrate is also formed. Following Pelouze [55] (1851), Hoffmann [54] (1935) prepared a hydrate which was assigned the formula $4CaO \cdot Fe_2O_3 \cdot 14H_2O$. This was also prepared by Malquori and Cirilli [49] (1940), who got a similar X-ray pattern. Hoffmann had also claimed the existence of a $4CaO \cdot Fe_2O_3 \cdot 7H_2O$ hydrate said to be formed at 50–60 °C, but Malquori and Cirilli did not confirm this, saying that the latter was really the cubic $C_3F \cdot 6H_2O$ compound.

Eiger has stated that $C_3F \cdot 6H_2O$ is not stable below a lime concentration of 0.25 g CaO per liter, but then changes to a dicalcium ferrite hydrate $2CaO \cdot Fe_2O_3 \cdot 5H_2O$, of orange color, which is stable down to a concentration of 0.15 g CaO per liter. This compound was stated to be further hydrolyzed to give "$Fe_2O_3 \cdot 3H_2O$".

Bogue and Lerch [56] and Yamauchi [57] have also considered that a hydrated dicalcium ferrite is formed, while the former authors also cite the possible formation of an amorphous hydrated monocalcium ferrite. The evidence for hydrated di- and monocalcium ferrites is however indecisive, as discussed later. If formed, it is possible that they are similar in structure to the hexagonal di- and monocalcium aluminates.

Brocard [19] (1948) concluded that in hydration of C_4AF with water at 15 °C there is first produced (besides hydrated hexagonal dicalcium aluminate hydrate and cubic $C_3A \cdot 6H_2O$) an iron-containing amorphous gel which gradually decomposes into Fe_2O_3 and lime. At 50–100 °C, cubic $C_3A \cdot 6H_2O$ was stated to be formed, together with a gel and Fe_2O_3. Malquori and Cirilli [52] (1943) found that by hydration of C_4AF in saturated lime solution at 0 °C, a solid solution of C_4A·aq. and C_4F·aq. with an Al_2O_3/Fe_2O_3 molar ratio of one is formed. At room temperature, the same phase appeared to have formed first and then to convert to a solid solution $C_3A \cdot 6H_2O$–$C_3F \cdot 6H_2O$.

Returning to figure 17, the schematic tentative indication of stable equilibria is based on corresponding equilibria in the CaO–Al_2O_3–H_2O system. The solubility of lime at 25 °C is given at point *C*, while on the basis of a statement by Eiger, a possible invariant point for "$C_3F \cdot 6H_2O$" with, it is thought, α- or γ-$Fe_2O_3 \cdot H_2O$ rather than a compound $C_2F \cdot 5H_2O$ is indicated at *Z*. The Fe_2O_3 concentration at *Z* is indicated quite arbitrarily (for want of a precise value) as half that for the $C_3A \cdot 6H_2O$–$A \cdot 3H_2O$ (gibbsite) invariant point at 25 °C. Eiger's statement of decomposition of $C_3F \cdot 6H_2O$ at 0.25 g CaO per liter to give a $C_2F \cdot 5H_2O$ compound, stable down to 0.15 g CaO per liter, is not supported by experimental detail. No statement is made as to crystal structure of the supposed $C_2F \cdot 5H_2O$ compound. If, by analogy, it was a hexagonal-plate phase, it appears more probable that it forms part of metastable equilibria linked with a hexagonal "$C_4F \cdot 14H_2O$" curve. On the whole, and on present inadequate evidence, it appears preferable to reject this supposed compound $C_2F \cdot 5H_2O$ as part of the stable equilibria. It may however form part of metastable equilibria analogous to the $C_{2-2.4}A \cdot 8\text{–}10.2H_2O \rightarrow C_4A \cdot 19H_2O$ equilibria of the corresponding CaO–Al_2O_3–H_2O system. In the light of this discussion, the establishment of the stable equilibria from undersaturation would seem to be reasonably practicable. No one so far appears, however, to have undertaken it, or if so, has been able to carry it to completion.

At present, also, work designed to clear up the existence and solubility relations and transformations of possible metastable hexagonal-plate phases in the system appears to be making very slow progress.

However, the preparation of a C_4F hydrate by Hoffmann indicates that we should expect a curve starting from a "C_4F·aq."–$Ca(OH)_2$ invariant point denoted by V in figure 17, at a lime concentration near the saturation concentration of lime. Theoretically, following a similar curve for $C_4A \cdot 19H_2O$ in the CaO–Al_2O_3–H_2O system a curve for "C_4F·aq." should proceed from this invariant point in the direction of lower lime and higher ferric oxide concentrations. This line presumably may terminate in an invariant point for a C_4F·aq.-$C_{<4}F$·aq. structure.

To proceed with a study of the system CaO–Fe_2O_3–H_2O from undersaturation it is first desirable to consider the preparation of $C_3F \cdot 6H_2O$ or C_4F·aq., or if it exists, a C_2F·aq. in the pure state. It is to a consideration of this that we must now turn.

(b) Compounds or Solid Solutions

1. *Cubic $C_3F \cdot 6H_2O$ or solid solutions.* As stated, $C_3F \cdot 6H_2O$ was originally prepared by Eiger [53]. The method was to place a quantity of "colloidal iron hydrate" in a large volume of supersaturated lime solution at room temperature and shake several times a day. A clear brown deposit formed which in the course of some days showed a silky appearance similar to that of the aluminate observed by Hoffmann. At the end of 6 weeks, the residue, now become white, was separated by filtration and dried, first over calcium chloride and then at 100 °C. Eiger reports that it contained some calcium silicate "owing to the action of lime on the glass". After correcting for the silica (how is not stated, but it is here assumed that it was considered to be present as a second phase CS·aq.), the composition was stated to be $3.01CaO \cdot Fe_2O_3 \cdot 6H_2O$. Optical examination of Eiger's preparation by Lea and Bessey (see ref. [53]) showed that it consisted of cubes of R.I.=1.710, and birefringent hexagonal plates of indexes 1.61–1.66. There is little doubt, in the light of further experience, that the first result of interaction was to produce a C_4F·aq.

hydrate as a hexagonal plate phase, giving the silky appearance noted, followed later by its partial transformation to cubic $C_3F\cdot6H_2O$. This transformation was evidently not entirely complete. Furthermore, later work by others indicates that silica can enter the crystal structure of $C_3F\cdot6H_2O$ and may therefore not have been present as a separate CS·aq. phase, but as part of the lattice structure of $C_3F\cdot6H_2O$ and possibly $C_4F\cdot$aq.

Malquori and Cirilli [49] (1940) reported preparation (apparently in glass vessels) by precipitating a mixed solution of $CaCl_2$ and $FeCl_3$ in the molar proportions of 3 to 1, by sodium hydroxide. The precipitate was left in contact with the markedly alkaline mother-liquor for about a month at 50–60 °C, when it was observed that the preparation appeared to consist entirely of octahedral crystals of R.I. very nearly 1.72. The water retained after drying *in vacuo* over $CaCl_2$ or P_2O_5 corresponded to $6H_2O$. X-ray examination showed a pattern similar to that of $C_3A\cdot6H_2O$, while the dehydration curves of the two hydrates were also similar. No examination appears to have been made for SiO_2.

Flint, McMurdie, and Wells [30] (1941) included tests in which mixtures of dilute acidified iron and aluminum chloride were added very slowly to a large volume of boiling lime solution in a glass flask. The resultant crystals were filtered at room temperature, washed with alcohol and ether, and dried over $CaCl_2$. It was found that they consisted of a series of solid solutions between $C_3A\cdot6H_2O$ and $C_3F\cdot6H_2O$ and they all contained SiO_2 (usually about 5 to 6 percent). Attempts were made to avoid SiO_2, using copper and iron vessels and a silver-lined glass flask. In these experiments, however, the products were all badly contaminated with hydrous iron oxide. It was concluded that SiO_2 helps to stabilize the calcium aluminoferrite hydrates.

Burdese and Gallo [58] (1952) reported a "similar" method of preparation, though actually the details were not identical. Thus it is stated that ferric chloride solution in amount sufficient to produce 4 g of $C_3F\cdot6H_2O$ was slowly added to 6 liters of a saturated lime solution. The solution, contained in a "Pyrex" glass vessel, was kept at 80 °C for 3 to 4 days, and the precipitate then filtered off, washed with alcohol and ether, and dried over $CaCl_2$. Analysis showed the presence of SiO_2, though this was considerably less than found by Flint, McMurdie, and Wells, 0.1–0.15 mole instead of 0.4–0.5 mole. Similar preparations, using a platinum vessel of 2 liters capacity (to yield about one gram $C_3F\cdot6H_2O$), gave preparations near the theoretical composition, with no SiO_2. From these authors' experiments therefore it appears to be practicable to obtain a $C_3F\cdot6H_2O$ free from SiO_2, with refractive index 1.74. They do not however report any examination for chloride.

The reason why Burdese and Gallo were able to get the cubic compound pure and free from SiO_2 is not at first sight clear. Thus it might perhaps lie in the different temperatures used and the difference in the mechanisms involved. These are actually quite distinct. Flint, McMurdie, and Wells used boiling saturated lime solution, the concentration of lime therefore being 0.53 g CaO per liter, and the temperature 100 °C, while the dropwise addition of ferric chloride solution (or mixed ferric and aluminum chlorides) means that the temperature is maintained at 100 °C, and the product or products expected are those in stable equilibrium at 100 °C. These could well be therefore, as found, a mixture of ferric hydroxide and $C_3F\cdot6H_2O$ at 100 °C. In Burdese and Gallo's preparation, the two solutions were first mixed cold. This procedure results in the formation of a hexagonal-plate phase which may be $C_3F\cdot CaCl_2\cdot10H_2O$ or a solid solution of this with $C_3F\cdot Ca(OH)_2\cdot$aq. The temperature was then raised to 80 °C, at which the lime solubility is 0.68 g CaO per liter. It might thus be that at 80 °C, $C_3F\cdot6H_2O$ produced by decomposition of the $C_3F\cdot CaCl_2\cdot10H_2O$ or solid solution is congruently soluble in the solution formed.

Flint, McMurdie, and Wells had in fact reported that when ferric chloride solution is added to limewater at room temperature, the compound $C_3F\cdot CaCl_2\cdot10H_2O$ is formed, and that, at room temperature, this changes slowly to $C_3F\cdot6H_2O$. Thus a sample kept at room temperature in contact with the solution was 50 percent changed and contained 0.83 percent SiO_2. Another preparation of chloroferrite with negligible silica (since it was filtered shortly after precipitation) was placed at 60 °C in contact with a lime solution containing 0.626 g CaO per liter (saturation concentration = 0.84 g CaO per liter at 60 °C), with frequent shaking. After two weeks it was stated to have completely transformed to the isometric $C_3F\cdot6H_2O$, which however now contained 6.85 percent SiO_2 taken up from the glass container.

There is of course a close parallelism between Eiger's mixture of colloidal iron hydrate and lime solution at room temperature yielding hexagonal C_4F hydrate initially, followed by transformation to $C_3F\cdot6H_2O$ hydrate, and Flint, McMurdie, and Wells' mixtures of ferric chloride and lime solution, also at room temperature, yielding hexagonal $C_3F\cdot CaCl_2\cdot10H_2O$ followed by change to $C_3F\cdot6H_2O$. There is, for example, clearly an initial formation of the appropriate metastable hexagonal-plate structure, followed by transformation to the stable $C_3F\cdot6H_2O$. There is also a further parallelism to be drawn between the CaO–Fe_2O_3–H_2O and CaO–Al_2O_3–H_2O systems. In the latter, from metastable calcium aluminate solutions plus lime (cf., colloidal iron hydroxide plus lime), the metastable $C_4A\cdot$aq. hexagonal-plate phase is precipitated at higher lime concentration and slowly transforms to $C_3A\cdot6H_2O$.

Attempts have been made at the Building Research Station (M. H. Roberts [15]) using polyethylene vessels to obtain pure $C_3F\cdot6H_2O$ free from contamination with other material, so far without success, though it appears that in some cases the $C_3F{\cdot}6H_2O$ found in the admixtures produced is in itself a pure phase.

Only a brief indication of some of the tests made can be given here. Addition of ferric chloride solution, dropwise with continuous stirring, to saturated lime solution at 90 °C and at 50 °C produced brown material. At 50 °C some isotropic grains were found with R.I.=1.71. Modification of conditions by adding at room temperature, then heating at 50 °C, or by shaking cold for 2 days until white, and then heating at 60 °C, merely gave brown material in which no cubic grains could be detected, in one case up to 4 months.

Attempts were made to convert calcium chloroferrite to $C_3F{\cdot}6H_2O$. In lime solutions at 60 °C, only a deep red-brown solid phase was obtained. In N NaOH solution, however, at 60 °C, the solid was cream-colored after 3 days, and microscopic examination showed some cubic grains. After 5 months the mix was filtered. X-ray examination of the solid after washing with alcohol and ether and drying at 81 percent R.H. indicated the presence of much $C_3F{\cdot}6H_2O$ and much $C_4F{\cdot}aq.$—or more probably $C_4F{\cdot}aq.\text{-}C_3F{\cdot}CaCl_2{\cdot}aq.$ solid solution, plus a little $Ca(OH)_2$. The $C_3F{\cdot}6H_2O$ pattern gave $a=12.76$ A±.01 A, indicating a pure $C_3F{\cdot}6H_2O$.

Somewhat similar tests in stainless steel tubes at 50 °C and 90 °C have given either, at 50 °C, some conversion of calcium chloroferrite to $C_3F{\cdot}6H_2O$ or, at 90 °C, a brown phase indicating further decomposition with production of ferric oxide. The presence of $C_3F{\cdot}6H_2O$ was indicated by X-ray examination of moist solids. Visual comparison indicated identity of the patterns with that referred to above.

These results and those of Burdese and Gallo are at first sight rather contradictory, and it is not known clearly as yet why in Burdese and Gallo's work, a chloroferrite precipitate held with its mother-liquor at 80 °C should transform to $C_3F{\cdot}6H_2O$, while in the above work a similar precipitate held with its mother-liquor at 60 °C should decompose. Clearly work is required in particular on the system $CaO\text{-}Fe_2O_3\text{-}CaCl_2\text{-}H_2O$ to try and solve this problem, while the possibility of sufficient carbon dioxide penetration through the walls of polyethylene vessels to cause decomposition also needs further examination.

Flint, McMurdie, and Wells have however apparently already found that a pure $C_3F{\cdot}6H_2O$ structure may sometimes be obtained in the presence of other phases. Thus sample 10 of their table 10, in their series of precipitated solid solutions was prepared in a vessel of dense unglazed porcelain. No alumina appeared to be present, though it was not apparently analyzed for, so that apart from SiO_2 (and possibly alumina) taken up from the porcelain, only calcium ferrite hydrate was expected. The preparation actually contained 6.34 percent SiO_2. It was stated however to show "considerable contamination by fine-grained material of low birefringence, which may have been calcium silicate." Excess lime was present, since the molar ratio in the whole product was calculated to be $3.54CaO{\cdot}0.52SiO_2{\cdot}Fe_2O_3{\cdot}6.01H_2O$. It was concluded possible therefore that the silica was combined with the excess lime and that the $C_3F{\cdot}6H_2O$ was free from SiO_2. This conclusion received confirmation from the fact that the X-ray pattern indicated a cell size of 12.74 A, equal to that deduced by McMurdie in his discussion of the X-ray data obtained by him on the garnet-hydrogarnet series.

Thus it appears that a pure $C_3F{\cdot}6H_2O$ may sometimes be realized, though the precise conditions are not clearly known, and the structure seems to be unstable.

However it is also evident that the presence of silica in the structure of $C_3F{\cdot}6H_2O$ will stabilize it. Flint, McMurdie, and Wells concluded, in fact, that solid solutions could be formed between $C_3A{\cdot}6H_2O$, $C_3F{\cdot}6H_2O$, $C_3A{\cdot}3SiO_2$, and $C_3F{\cdot}3SiO_2$, each being capable of forming complete mixed crystals with the other three, Fe_2O_3 and Al_2O_3 (Fe^{3+} and Al^{3+}) being mutually replaceable, while one part of SiO_2 substitutes for two parts of H_2O (1 Si^{4+} for 4 H^+). They were unable to obtain $C_3F{\cdot}6H_2O$ free from SiO_2 except exceptionally, and concluded that $C_3F{\cdot}6H_2O$ or the aluminoferrite hydrates are unstable in the absence of a certain amount of SiO_2 in solid solution. This conclusion to a limited degree contradicts the statement of complete miscibility between each member of the solid solution series including $C_3A{\cdot}6H_2O$ and $C_3F{\cdot}6H_2O$.

Zur Strassen [20] (1958) has recently discussed work on the garnet-hydrogarnet series, including investigations by Dörr, Zeeh, and Schmitt. He concludes that a pure $C_3F{\cdot}6H_2O$ does not exist, and that there is not complete miscibility between $C_3A{\cdot}6H_2O$ and $C_3F{\cdot}6H_2O$. In other words, it is not possible to replace Al wholly by Fe. A point is reached when the structure becomes unstable.

Figure 18 shows a garnet-hydrogarnet solid-solution identification chart as given by zur Strassen. This was prepared on the basis of a repetition, to some extent, of the work of Flint, McMurdie, and Wells. The figure shows the mixed crystal system with the positions of prepared mixes plotted therein. The entire field could not be covered owing to various experimental difficulties. From the data obtained, a series of

TABLE 10. *Solid solutions of calcium aluminates and ferrites*

$C_3A{\cdot}6H_2O-C_3A{\cdot}3SiO_2$ $C_3F{\cdot}6H_2O-C_3F{\cdot}3SiO_2$	The garnet-hydrogarnet series. See also figure 18.
$C_4A{\cdot}aq-C_4F{\cdot}aq$	No definite evidence as yet that a *pure* $C_4F{\cdot}aq.$ structure exists.
$C_3A{\cdot}6H_2O-C_3F{\cdot}6H_2O$	Doubtful if can be formed stably entirely free from silica, at least at iron-rich end.

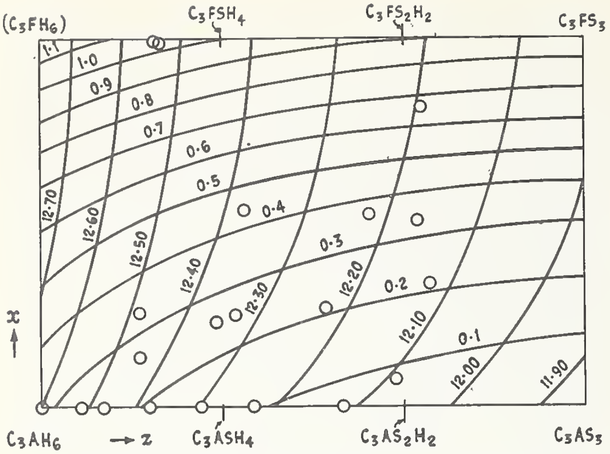


FIGURE 18. *The garnet-hydrogarnet solid solutions.*

(Identification chart—H. zur Strassen [20], 1958.) (Used by permission, Zement-Kalk-Gips.)

curves for constant cell dimensions, 11.90 A to 12.70 A, were drawn as the content of Al_2O_3 and Fe_2O_3, SiO_2 and H_2O, varied. A second value, necessary to determine the position of a solid solution in the series was based on the finding that the 220 reflection shows marked differences in intensity in relation to composition, whereas other reflections such as 611 are almost independent of composition. Thus the intensity ratio 220/611 can be used with the cell size to determine composition. Intensity-ratio curves from 0.1 to 1.1 are also plotted in the figure. It will be seen that according to the diagram a pure $C_3F\cdot 6H_2O$ should have $a=12.76$ A, intensity ratio=1.2. The Building Research Station preparation of $C_3F\cdot 6H_2O$ (Roberts) obtained from hexagonal chloroferrite in N NaOH solution at 60 °C had $a=12.76$ A, intensity ratio 1.3. It appears, therefore, that a pure $C_3F\cdot 6H_2O$ can be obtained, although unstable. A high OH^- concentration in solution may assist in preventing breakdown. (Note that the ratio 1.3 was obtained [15] from measurements of intensities on a powder pattern obtained with an 18-cm-diam cylindrical camera. With a focusing camera the value obtained was 1.7. The discrepancy between these values and that given by zur Strassen (1.2) is probably due to differences in experimental technique.)

2. *Hexagonal $C_4F\cdot 14H_2O$ or Solid Solutions.* As previously stated, Hoffmann claimed to have prepared a hydrate to which he assigned the formula "$4CaO\cdot Fe_2O_3\cdot 14H_2O$". The method used was to add a mixed solution of calcium chloride and ferric chloride in the molar ratio $CaO/Fe_2O_3=5$ to a large volume of sodium hydroxide solution. Amounts were arranged so as to leave an $N/4$ NaOH solution after reaction. The filtered product was washed with methyl alcohol and ether, and dried *in vacuo* for several days over $CaCl_2$. Precipitates were obtained at 20 °C and 50–60 °C. In both cases it was noted that the initial precipitate contained a little free ferric hydroxide. At 20 °C, the precipitate soon became white, while at 50–60 °C, it remained very slightly brown. Analysis of the products indicated "$C_4F\cdot 14H_2O$" at 20 °C and "$C_4F\cdot 7H_2O$" at 50–60 °C. Hoffmann does not indicate whether silica or chloride was looked for. So far as can be ascertained, glass vessels were used, both in the actual preparation of the $C_4F\cdot$aq., and probably in the initial preparation of CO_2-free NaOH by allowing a saturated solution of NaOH to stand for some weeks. If this is the case, silica would be taken into solution, and as other work shows, may be expected in the precipitated $C_4F\cdot$aq. Chloride also may have been present, as found in later work at the Building Research Station. The accuracy of the analysis for a supposed $C_4F\cdot 7H_2O$ also appears to be doubtful. As discussed later, the "$C_4F\cdot 7H_2O$" was almost certainly cubic $C_3F\cdot 6H_2O$ together with free $Ca(OH)_2$.

Malquori and Cirilli [49] (1940) also prepared $C_4F\cdot 14H_2O$ in the same way and stated that for the degree of dilution used by Hoffmann, the resulting solid does not contain any chloroferrite, but that with higher concentrations, this forms as impurity. The authors do not say so, but it is presumed that glass vessels were also used, with at least the possibility of silica contamination. They indicate that their products did not contain chloroferrite. This result is contrary to later findings on similar preparations at the Building Research Station. The hydrated calcium ferrite is described as pure white in color, retaining $14H_2O$ when dried *in vacuo* over $CaCl_2$ and $12H_2O$ over P_2O_5. The X-ray pattern found was similar to that obtained by Hoffmann.

In another method of preparation, gradual addition of 20 ml $FeCl_3$ solution containing 0.04 g Fe_2O_3 per ml to 20 liters of saturated lime solution, hexagonal plates were obtained. Results of analysis were stated to point to the formula $C_4F\cdot$aq.

The authors draw attention to behavior similar to $C_4A\cdot 12H_2O$ when the $C_4F\cdot 14H_2O$ was dehydrated.

Early work at the Building Research Station (Roberts) [15] on the preparation of $C_4F\cdot$aq., using glass vessels, has confirmed Malquori and Cirilli's observation that with high concentration of reactants in Hoffmann's method of preparation, $C_3F\cdot CaCl_2\cdot$aq. is formed. In fact, with an initial chloride concentration in solution of about 8–9 g Cl per liter, the composition of the product approached very closely to that of $C_3F\cdot CaCl_2\cdot$aq. Even at much lower initial chloride concentration of about 1 g Cl per liter, as used by Hoffmann, there was still appreciable contamination with the chloroferrite, and the products were not white, but cream-colored, suggesting incomplete reaction and the presence of free ferric hydroxide. Further experiments were made, varying the CaO/Fe_2O_3 ratio in the mixed chloride solutions, and the amount of NaOH, to give varied final NaOH concentrations. The results indicated the NaOH concentration to be more important than the CaO/Fe_2O_3 ratio in the mixed chloride solutions in producing a white precipitate free from ferric hydroxide. However, as stated, these early experiments were carried out in glass vessels, and it was found that most of the products contained from 1 to 8 percent of SiO_2, depending upon the strength of the alkali solution and the time in contact with the glass. Further attempts were made in polyethylene bottles to avoid silica contamination. Also, in order to minimize contamination by chloride, the precipitate was extracted first with one liter of $N/10$ NaOH (to remove excess solid $Ca(OH)_2$) and then with two lots, each of one liter, of nearly saturated lime solution (1.10 g CaO per liter). However, even with a molar ratio $CaO/Fe_2O_3=5$ in the mixed chlorides and a final NNaOH concentration in solution, a deep cream or buff-colored precipitate was obtained containing 2.2 percent of Cl, equivalent to about 19 percent of $C_3F{\cdot}CaCl_2{\cdot}aq$. In order to reduce the Cl further, the initial chloride concentration was reduced from about 1.0 to about 0.05 g Cl per liter, giving products containing 1 to 5 percent of Cl. X-ray and microscopic examination indicated that the products consisted of a single solid phase of the solid solution series $C_4F{\cdot}aq.$-$C_3F{\cdot}CaCl_2{\cdot}aq$. An attempt to replace Cl^- by OH^- in the product obtained, by repeated extraction with one-liter lots of saturated lime solution, produced at best, after five extractions, a minimum content of 1.2 percent of Cl, corresponding to about 10 percent of $C_3F{\cdot}CaCl_2{\cdot}aq$.

From this later experimental evidence, therefore, the author cannot feel convinced that either Hoffmann or Malquori and Cirilli obtained a pure tetracalcium ferrite hydrate free from either silica or chloride or both. The possibility that the crystal lattice structure of the $C_4F{\cdot}aq.$ compound is not stable without the presence of silica is implicit in the findings of Flint, McMurdie, and Wells [30] (1941) with regard to the cubic $C_3F{\cdot}6H_2O$, which they could not prepare free from SiO_2 (with one possible exception). It seems possible also that the apparently strong tendency of Cl^- to substitute for OH^- in the structure "$C_4F{\cdot}aq.$" is partly bound up with spatial considerations concerned with the relative sizes of the ions involved. Thus it may be speculated that since the chloride ion is slightly larger than OH^-, it will partly conform to slight increase in size of Fe^{3+} substituting for Al^{3+} and result in less instability than where Fe^{3+} and OH^- are associated alone in the structure. There may however be other factors. Thus it seems possible that where two or more anions are available for entry into a crystal structure, that ion is preferred which confers greatest insolubility, or relative concentrations in solution may play some part. The factors at work and their relative importance in this structure are however not yet clear.

3. *$C_2F{\cdot}xH_2O$ or Solid Solutions.* Following the analogy of the hexagonal-plate hydrated calcium aluminates, it would seem possible at first sight that a hexagonal plate $C_2F{\cdot}xH_2O$ compound may exist. However, the apparent difficulty of preparing pure $C_4F{\cdot}aq.$ because of instability of structure when too much iron is present suggests that it may never be possible in a structure analogous to $C_2A{\cdot}8H_2O$. It seems more likely that a limited replacement of Al by Fe in the $C_2A{\cdot}8H_2O$ compound may occur before the structure becomes unstable.

There appears to be no reported preparation by a precipitation method. Nor has any satisfactory evidence been reported of preparation in any other way. As previously indicated, it is concluded that a dicalcium ferrite hydrate probably does not exist, though it must be accepted as a possibility.

(c) Hydration of Anhydrous Compounds

1. *Hydration of C_2F.* Besides precipitation experiments, Hoffmann examined the effect of shaking more or less finely crushed C_2F with water or lime solutions at 20 °C for various times (CF gave practically no reaction). In this first series he used C_2F crushed to pass a sieve of 10,000 meshes per sq cm in admixture with a standard sand (1 g C_2F with 10 g sand and 75 ml water or lime solution), shaking for periods up to 6 days. No iron was found in the filtrate. Depending on the initial concentration of lime, lime was either released from or taken up by the solid phase to give a final lime concentration of 1.06 g CaO per liter. (The sand appears to have been used in an attempt to prevent interference of protective films forming on the surface of the C_2F particles.)

Another series was carried out with a rather more coarsely crushed C_2F (2,500–4,900 meshes per sq cm; diam 88–120 μ). This was shaken (10 g C_2F with 20 g sand and 300 ml saturated or half-saturated limewater) at 20 °C for 150 days. It was stated that after the sand and (residual) C_2F had settled, the hydrated calcium ferrite was found as a rather heavy suspension of light brown color in the solution. This was white after a week (presumably due to further settling of the brown material). The white suspension was analyzed on a 50 ml sample, apparently including both solid and solution, while lime in solution was determined on a 25 ml sample of suspension after filtration. In this way, final lime concentrations were found to be 1.005 g CaO per liter, starting with 1.239 g CaO per liter, and 1.100 g CaO per liter, starting with 0.600 g CaO per liter. The CaO/Fe_2O_3 ratios in the calcium ferrite hydrate were stated to be 3.4 and 2.9, respectively.

From the above, Hoffmann concluded that two calcium ferrite hydrate phases, $C_4F{\cdot}aq.$ and another phase with a lower CaO/Fe_2O_3 ratio were present in equilibrium with a solution containing 1.06 g CaO per liter. This conclusion however appears open to question. Hoffmann compared the X-ray patterns of the product obtained with an initial half-saturated lime solution of final CaO/Fe_2O_3 molar ratio 2.9 and the compound "$C_4F{\cdot}7H_2O$" thought by Hoffmann to have been obtained by him by precipitation at 60 °C, and stated that they showed agreement. Malquori and Cirilli [49] however could not confirm the existence of such a compound. Repetition of

Hoffmann's experiments, at 50–60 °C, produced cubic $C_3F{\cdot}6H_2O$, and Malquori and Cirilli concluded that at this temperature there is fairly rapid conversion of $C_4F{\cdot}14H_2O$ to $C_3F{\cdot}6H_2O$. They point out too that the pattern given by Hoffmann for his supposed "$C_4F{\cdot}7H_2O$" is similar to that for $C_3F{\cdot}6H_2O$. On the whole, it seems very probable (and this is supported by later work) that Malquori and Cirilli are correct and that Hoffmann really got partial transformation of $C_4F{\cdot}$aq. to $C_3F{\cdot}6H_2O$ at 50–60 °C, and also in the above shaking experiments at 20 °C. Thus it appears that Hoffmann, by hydration of C_2F, produced $C_3F{\cdot}6H_2O$, thus:

$$C_2F+C{\cdot}\text{aq.}\rightarrow C_3F{\cdot}6H_2O,$$

or

$$2C_2F+H_2O\rightarrow C_3F{\cdot}6H_2O+C+F.$$

Hoffmann, further, appears not to have considered the significance of the brown iron-rich solid phase present (apart from residual C_2F). If no lower hydrates than $C_4F{\cdot}$aq. or $C_3F{\cdot}6H_2O$ were formed, this solid phase would be iron hydroxide (or Fe_2O_3). In this case it would appear that Hoffmann obtained an approximation to an invariant point for iron hydroxide–$C_4F{\cdot}$aq. or iron hydroxide–$C_3F{\cdot}6H_2O$. This would suggest only a short curve for $C_4F{\cdot}$aq. or $C_3F{\cdot}6H_2O$ in the system, since the apparent "equilibrium" lime concentration is 1.06 g CaO per liter compared with (at 20 °C) a saturation concentration of 1.24 g CaO per liter. Such speculations are of course subject to other possibilities for calcium ferrite hydrate formation yet to be discussed.

Bogue and Lerch [56] had previously attempted to hydrate C_2F. The compound was stated to require about 30 percent of water to form a plastic paste. No stiffening or temperature changes were observed. Hydration was found to be very slow, combined water amounting to only 7 percent by weight of C_2F after 2 years. It was stated that the hydrate formed was amorphous, with a refractive index of about 1.70. The authors suggested that it was a dicalcium ferrite hydrate, but no direct evidence was offered.

In the light of the evidence provided by later work (e.g., Eiger, Hoffmann, and Malquori and Cirilli), it would appear that treatment of C_2F with water results first in extraction of lime leaving an iron-rich surface residue, which later reacts with the lime solution producing $C_3F{\cdot}6H_2O$ (or possibly first $C_4F{\cdot}$aq., this transforming to $C_3F{\cdot}6H_2O$), so producing, under the conditions used by Bogue and Lerch, a protective coating. The product of partial hydration may thus be an outer skin of $C_3F{\cdot}6H_2O$, over a shell from which some lime has been extracted, leaving a shell of composition $C_{<2}{\cdot}F$, and within this, unaffected C_2F. It has been shown by Malquori and Cirilli that dehydration of both $C_3F{\cdot}6H_2O$ and $C_4F{\cdot}14H_2O$ results eventually in breakdown to C_2F and lime, in agreement with Bogue and Lerch's assumption for the behavior of calcium ferrite hydrate with $C/F>2$. It will be seen that on the mechanism of hydration now suggested, not only is the amount of $C_3F{\cdot}6H_2O$ probably small, but free lime liberated on complete dehydration may react with the lime-poor shell to produce further C_2F. Thus, either no free lime may be left or it may be present in too small amount for detection. This may well explain the fact that Bogue and Lerch could not detect free lime in the dehydrated product.

Bogue and Lerch considered also the possible formation of a less basic hydrated compound such as $CF{\cdot}$aq. This is at first sight in line with the fact that lime is extracted from the C_2F. However no $Ca(OH)_2$ could be found either by microscopic or by X-ray examination.

It seems clear that there is no evidence for either a di- or monocalcium ferrite hydrate in these experiments. It should be noted that at the time of Bogue and Lerch's experiments, neither $C_3F{\cdot}6H_2O$ nor $C_4F{\cdot}14H_2O$ was known, except, in the latter case, for the very old work (1851) by Pelouze [55].

The author regrets that the length of this paper precludes consideration of the relatively small amount of work relevant to hydration of C_2F by other authors at this time. It does not appear that such work modifies the conclusions now reached on the calcium ferrites which can be formed.

2. *Hydration of C_4AF.* Hydration of C_4AF, which later work has shown to be not a compound, but a solid solution of this composition in anhydrous cement, has been studied by several authors. Brief summaries have been published by Steinour [32], Bogue [59], and Lea [26]. The results of experimental studies are now described and discussed, not in chronological order, but in an order which seems best to explain behavior.

Malquori and Cirilli [52] (1943) found that on shaking C_4AF with "constantly saturated limewater" at about 0 °C (in order to prevent transformation to the cubic phase) a "perfectly white" product was obtained, consisting of hexagonal plates of refractive index 1.57, corresponding to that of a 50 percent solid solution between $C_4A{\cdot}$aq. and $C_4F{\cdot}$aq. The X-ray pattern was also stated to be similar to that of the product obtained by precipitation from solution when equimolar amounts of $AlCl_3$ and $FeCl_3$ were added to sodium hydroxide solution. At 20–25 °C, the same hexagonal-plate crystals plus cubic crystals of index 1.66–1.67 were obtained, corresponding to the 50–50 percent solid solution of $C_3A{\cdot}6H_2O$ and $C_3F{\cdot}6H_2O$.

These experiments appear to lead quite definitely to the conclusion that the hydration of C_4AF in limewater maintained in the saturated condition leads initially at lower temperatures to formation of a one-to-one molar solid solution of $C_4A{\cdot}$aq. and $C_4F{\cdot}$aq., this gradually transforming to the corresponding C_3A·aq.-C_3F·aq. solid solution at higher temperatures.

In Hoffmann's prior tests at 20 °C, for times up to 270 days, it had been found that, whether starting with saturated limewater, half-saturated limewater, or water, using initially 1 g C_4AF with 75 ml water or solution, the lime concentration, subject to some fluctuation, approached a final value of 0.63–0.64 g CaO per liter. The hydrated product produced was light brown in color, while a little unreacted C_4AF was stated to remain. Hoffmann argues that three hydrated phases must be formed in the hydration of C_4AF, either two hydrated calcium aluminate phases and one ferrite hydrate or vice versa. This conclusion would follow if the alumina and ferric oxide components behaved independently, but the mutual replacement of Al and Fe in solid solution suggests that the system $CaO–Al_2O_3–Fe_2O_3–H_2O$ may be effectively ternary in part. (The same conclusion may also be made where SiO_2 additionally forms part of the solid-solution equilibrium). Further, Hoffmann accepts an earlier conclusion by von Polheim on the $CaO–Al_2O_3–H_2O$ system that the solid phase in equilibrium in this system at a lime concentration of 0.64 g CaO per liter is C_3A·aq. This conclusion of course is in conflict with the results of later work. The argument developed by Hoffmann that the phases formed are C_3A·aq., iron hydroxide, and a mono- or more probably a dicalcium ferrite hydrate C_2F·aq. thus hardly seems valid. However, Hoffmann states that the hydrated products obtained with an initial saturated lime solution (final concentration, 0.64 g CaO per liter, nil Fe_2O_3) and water (final concentration 0.64 g CaO per liter, nil Fe_2O_3) gave on analysis compositions corresponding respectively to $7.26\,CaO{\cdot}2.3Al_2O_3{\cdot}1\,Fe_2O_3$ and $6.93CaO{\cdot}2.3Al_2O_3{\cdot}1Fe_2O_3$.

Flint, McMurdie, and Wells [30] hydrated C_4AF by shaking with water in the proportion of 100 g C_4AF to 2 liters water, presumably at room temperature, filtering after various times, and analyzing the filtrates. Only CaO and Al_2O_3 passed into solution, concentrations of about 0.55 g CaO and 0.32 g Al_2O_3 per liter being reached in about one-half hr, then decreasing slowly and asymptotically to about 0.45 and 0.05 g per liter respectively after about a week. The metastable solutions precipitated "silky" precipitates (indicating formation of a hexagonal-plate phase) on standing after various indicated times of shaking, ½, 1, 2, 4, 6, 24 hr; 3 and 7 days. After 3 months, mixtures of hexagonal calcium aluminate hydrate and $C_3A{\cdot}6H_2O$ of R.I.=1.605 were formed. The residual iron-containing material after filtration was not further considered.

This method of experiment clearly separates the iron-containing residue from the metastable solution containing lime and alumina at an early stage, and the subsequent precipitation from the solution on standing may be expected to yield (from the work of Jones and Roberts) initially hexagonal plates of solid solution in the range $C_{2-2.4}A{\cdot}8–10.2\,H_2O$, possibly accompanied by alumina gel. There appears then to be a further conversion to the stable cubic hexahydrate $C_3A{\cdot}6H_2O$ and hydrated alumina at the invariant point $A{\cdot}3H_2O–C_3A{\cdot}6H_2O$. No iron would of course be expected in the solid phases under these conditions.

Another identical mix was allowed to stand for 10 yr at room temperature with occasional shaking. Under these conditions, several processes are or may be proceeding side by side or consecutively with overlapping:

1. Precipitation from the extracted solution of hexagonal-plate hydrated aluminates and possibly alumina gel as described above.
2. Removal of further lime from the iron-containing residue, leading to increase in lime concentration of the solution.
3. Formation of crystals of $C_3A{\cdot}6H_2O–C_3F{\cdot}6\,H_2O$ solid solution from the iron-containing residue, presumably preceded by a hexagonal-plate solid solution of C_4A·aq.–C_4F·aq.
4. Formation of a residue of iron hydroxide.

The above suggested mechanism appears to fit the description given by the authors, viz: "Analysis of this solution (i.e., after 10 yr) showed but a trace of alumina. The lime in solution was 1.087 g CaO per liter, slightly less than that of a saturated lime solution. This increase in concentration of lime was accompanied by the disappearance of the hexagonal forms of hydrated calcium aluminate, and of the anhydrous phase. The solid residue was a mixture of isometric crystals and finely divided reddish material. The bulk of the isometric crystals had the normal refractive index of $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$. A relatively small proportion possessed a higher index of refraction with a maximum value of about 1.637."

In the present author's view, the results of this experiment may be reasonably interpreted on the basis that the initial extraction in effect produces two experiments proceeding side by side in the same reaction vessel, with relatively little mutual interaction:

(a) Precipitation from a metastable solution containing lime and alumina in molar ratio.

(b) Reaction of the partly hydrated solid phase from the extraction containing CaO, Al_2O_3, and Fe_2O_3 in molar ratio with a lime solution.

Thus (a) may be expected to give the equilibrium of the system $CaO–Al_2O_3–H_2O$ and (b), that of $CaO–Fe_2O_3–H_2O$, finally ending with, for (a), an invariant point $C_3A{\cdot}6H_2O$-hydrated alumina, and for (b) an invariant point for a solid solution "$C_3F{\cdot}6H_2O–C_3A{\cdot}6H_2O$"–ferric hydrate. The final lime concentration appears to be common to both equilibria. It seems probable that the high degree of insolubility of ferric hydroxide (or oxide) prevents any attainment of equilibria between the $C_3A{\cdot}6H_2O$ obtained by precipitation from supersaturation, and the solid solution "$C_3F{\cdot}6H_2O–C_3A{\cdot}6H_2O$" obtained from the iron-rich residual solid phase. If these conclusions are correct, no hydrated hexagonal calcium ferrite phase with a CaO/Fe_2O_3 ratio less than 3 could be expected in these experiments.

Flint, McMurdie, and Wells apparently used glass vessels. There is therefore a possibility that some silica was removed from the glass and entered into the structures of the hexagonal and cubic phases formed.

The authors finally examined behavior in a paste made from 10 g C_4AF and 5 g water, stored in a glass vessel for 6 days. There will be an appreciable evolution of heat in a paste of this composition and the temperature will therefore be somewhat above room for some time. We may however assume that the general form of the equilibria to be expected in extracted solution and residue will be as given above. Microscopic examination of the mixture "showed the presence of about 20 percent of unhydrated $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ with the alteration products consisting of a mixture of reddish amorphous material and of isometric crystals with index of 1.63 to 1.64." The authors concluded that the increase in index was due to the presence of Fe_2O_3 in solid solution. This is clearly so, while the fact that the observed crystals are now solid solution and not pure $C_3A \cdot 6H_2O$ appears to be due to the large solid-to-solution ratio, little lime-alumina solution being produced from which $C_4A \cdot aq. \rightarrow C_3A \cdot 6H_2O + C$ could precipitate. The intimate association of alumina and ferric oxide in the relatively large body of hydrating C_4AF then leads to solid-solution formation. For this paste therefore, under the conditions and for the time tested, it is concluded that the final solid phases, excluding unhydrated material, consisted of cubic solid solution $C_3A(F) \cdot 6H_2O$ and a mixture or possibly solid solution of ferric and alumina hydrates.

Work had been carried out previously by Bogue and Lerch [56] (1934). These authors stated that the anhydrous phase had disappeared after one month. The isotropic crystalline phase had an index of 1.640, as later confirmed by Flint, McMurdie, and Wells. Bogue and Lerch could not however at the time distinguish the X-ray pattern from that of $C_3A \cdot 6H_2O$. The reddish-brown amorphous phase was not identified. It was suggested as "probable" that it was a hydrated calcium ferrite, but in the light of the discussion given in the present paper, this suggestion seems untenable.

Brocard [19] (1948) carried out similar though not identical shaking tests, with analyses of solutions, to those of Flint, McMurdie, and Wells. Instead of using 100 g C_4AF to 2 liters of water, he used 30 g C_4AF, and instead of using separate mixes for each time period, filtering and analyzing, he withdrew 50 ml aliquots after various times, thus gradually decreasing the amount of liquid present by 450 ml in 9 withdrawals over a period of 3 days. He carried out tests at various temperatures also, 15°, 30°, 50°, 70°, and 100 °C. Considering his results at 15 °C in comparison with those of Flint, McMurdie, and Wells, the initial maximum content of CaO is much the same in both cases, but Brocard found a much higher content of alumina than did Flint, McMurdie, and Wells at their room temperature and therefore a much lower lime/alumina ratio. No iron was found in solution, confirming Flint, McMurdie, and Wells' finding. Hexagonal-plate crystals first precipitated, later converting into cubes. There was also left a brownish amorphous gel. X-ray examination of the hydrated product after 3 days indicated the presence of hexagonal "$C_2A \cdot 7H_2O$" and cubic $C_3A \cdot 6H_2O$. Brocard wrote the reaction as $2C_4AF + aq. \rightarrow C_3A \cdot 6H_2O + C_2A \cdot 7H_2O + 2C_xF$ and considered that an amorphous calcium ferrite gel was present.

When the reaction was allowed to proceed at room temperature (15°–18 °C), it was noted that the lime concentration reached a minimum of 0.29 g CaO per liter after 8 days, and then increased slowly, becoming 0.41 g at 6 months. X-ray examination at 6 months showed a preponderance of cubic aluminate.

In the light of the present discussion and of the work of Jones and Roberts, it seems clear that the lime-alumina solution of relatively low CaO/Al_2O_3 molar ratio obtained by Brocard can be expected to precipitate dicalcium aluminate hydrate, with possibly alumina gel, in contrast to higher calcium aluminate hydrates expected from Flint, McMurdie, and Wells' solution. The conversion to $C_3A \cdot 6H_2O$ can then be expected to follow, the final equilibria ending up as described above.

At higher temperatures, Brocard found precipitation of $C_2A \cdot 7H_2O$ followed by more and more rapid transition to cubic $C_3A \cdot 6H_2O$, while in X-ray examination the presence of hematite (α-Fe_2O_3) was evident. To the present author, this lends support to the view that the final products of hydration of C_4AF with water in the relative amounts used by Flint, McMurdie, and Wells, or Brocard, in their shaking tests, are those indicated above for the various conditions of experiment, with the evidence pointing to the iron being present partly as a solid solution "$C_3A \cdot 6H_2O$–$C_3F \cdot 6H_2O$" and partly as a hydrated (or hydrous) iron phase. There is no satisfactory evidence of a $C_2F \cdot aq.$ or $CF \cdot aq.$ compound.

There are two further points on which it seems desirable to comment. One is concerned with the actual constitution of the residual "amorphous" material produced in the process of hydration of C_4AF, the other with the formation of hematite.

As the present author sees it, when a particle of "C_4AF" is placed in contact with water, Ca and Al pass into solution from the crystal lattice, first from the surface layer, as "$Ca(OH)_2$" and "$Al(OH)_3$", with possibly some replacement by H_2O and the immediate formation of a more or less structureless "gel". This is a continuous process, as water penetrates into the crystal lattice of C_4AF, and the initially formed hydrated material remaining *in situ* will exercise a protective effect on the underlying residual unaffected C_4AF structure, as visualized by Brocard. In the present author's view, however, it is not possible at any stage to regard the external initially "gelatinous" residue as a definite calcium ferrite hydrate. Perhaps this is more a matter of words than anything else, and the author is otherwise in substantial agreement with Brocard's conclusions. It is not thought however that one can speak in too rigid terms about the change from the initially formed gel to "hematite". The whole is a gradual process in which the gradual extraction of lime and alumina from the C_4AF lattice and the increasing rapidity of building the residual disordered "micro-lattices of hematite" into larger units are essential features.

The second point is concerned with the structure of the final iron-containing phase. Although Brocard states that he found the lines of hematite (α-Fe_2O_3) in the X-ray powder patterns of the hydrated products, he nevertheless states in a footnote that the pattern of hematite is identical with that of hydrous or hydrated hematite "$Fe_2O_3 \cdot nH_2O$" and appears to conclude that the iron phase is really in a hydrated condition. There seems to be some doubt about this, since in work at the Building Research Station (Roberts), only α-Fe_2O_3 (hematite) has been identified on X-ray examination of mixes in which calcium chloroferrite, $C_3F \cdot CaCl_2 \cdot aq.$ was treated at 90 °C with water, saturated limewater, or 0.5 percent and 1.0 percent NaOH and KOH solutions saturated with lime. This result of course confirms Brocard's actual observations.

In view of these findings on the ferric oxide formed, and the bearing which the phase has in the CaO-Fe_2O_3-H_2O equilibria, it seems desirable to discuss very briefly the position with regard to anhydrous and hydrated oxides of iron insofar as this is relevant. Rooksby [60] has discussed these oxides (1951) and summarized the position at that time.

The only anhydrous oxides which need concern us here are α-Fe_2O_3, which occurs naturally as hematite, and γ-Fe_2O_3, found naturally as a comparatively rare mineral maghemite. The γ-Fe_2O_3 is metastable with respect to α-Fe_2O_3, rapid conversion occurring at about 400 °C, while the color changes with the change in structure from light brown to a "turkey-red".

Of the hydrates, α-, β-, and γ-$Fe_2O_3 \cdot H_2O$, only the α- and γ- forms occur naturally, as goethite and lepidocrocite respectively. The crystal structures of these two forms are similar to those of α-$Al_2O_3 \cdot H_2O$ (diaspore) and γ-$Al_2O_3 \cdot H_2O$ (boehmite), respectively. So-called limonite appears to be poorly crystallized goethite. The third form, β-$Fe_2O_3 \cdot H_2O$, can be obtained from ferric chloride as an orange-yellow precipitate by "heating a solution of moderate concentration to 60 °C for 45 min". Rooksby comments that in natural bauxite, in which the main constituent has the boehmite crystal structure, iron, if present, may replace the aluminum isomorphously. It may here further be remarked that this observation may also apply to the system CaO–Al_2O_3–H_2O, where initial precipitation of hydrated alumina may be as a boehmite structure.

The colors of the hydrated iron oxides are respectively yellow, orange, and brown, apparently related to the changes in structure. Both α-' and γ-hydrated oxides are comparatively easily decomposed to the corresponding α- and γ-anhydrous oxides by heating in air for one hr at 300 °C. As stated, heating of the γ-Fe_2O_3 above 400 °C then causes transformation to α-Fe_2O_3. It is of interest to recall that Hoffmann [54] found a change of structure of γ-$Fe_2O_3 \cdot H_2O$ to α-$Fe_2O_3 \cdot H_2O$ on grinding in an agate mortar.

We can now return to Brocard's observation on the iron-oxide phase produced in the hydration of C_4AF. He states that the X-ray pattern of hematite is identical with that of hydrated hematite "$Fe_2O_3 \cdot nH_2O$." It is not clear precisely what this "$Fe_2O_3 \cdot nH_2O$" material was. From the data presented by Rooksby [60], the structure and X-ray pattern of hematite is substantially different from those of α-$Fe_2O_3 \cdot H_2O$ or the β- and γ- forms. If Brocard's material was really a limonite, assigned a formula such as $2Fe_2O_3 \cdot 3H_2O$, Rooksby comments that X-ray examination of "limonite" shows it to be generally composed of goethite, i.e., α-$Fe_2O_3 \cdot H_2O$. It is difficult to reconcile these apparently conflicting data about the identity of hematite and hydrated iron oxide.

Replacement of Al by Fe in Hydrated Calcium Aluminates, and Calcium Chloro- and Sulfoaluminates

Owing to the length of this paper, only a brief and somewhat incomplete discussion can be given here.

Following their experiments on the preparation of hexagonal $C_4F \cdot 14H_2O$ and cubic $C_3F \cdot 6H_2O$, Malquori and Cirilli [52] (1943) investigated the possibility of solid solution formation between these compounds and the corresponding aluminates.

For the hexagonal-plate structures the method used was still that of adding a mixed solution of chlorides to sodium hydroxide solution. The precipitate obtained under the conditions used, after drying over $CaCl_2$ and KOH, was stated to contain (as determined by analysis) a Cl content always below one percent, based on the anhydrous compound. It is evident from this statement that the product contained some chloroaluminate and/or chloroferrite in the hexagonal-plate solid solutions. It appears also that the authors worked throughout with glass vessels, so that the presence of silica in the structures is probable. Precipitates obtained in this way, with compositions (neglecting the possible presence of Si and of Cl) of C_4A·aq.; $4CaO \cdot 0.33Fe_2O_3 \cdot 0.67Al_2O_3$·aq.; $4CaO \cdot 0.5Fe_2O_3 \cdot 0.5Al_2O_3$·aq.; $4CaO \cdot 0.67Fe_2O_3 \cdot 0.33Al_2O_3$·aq.; and C_4F·aq. showed X-ray patterns indicative of solid-solution formation. It appears that Malquori and Cirilli did not use in their mixed precipitates a higher proportion of Fe to Al than 2:1 (molar).

Tests were also carried out to investigate the possibility of solid solutions between $C_3A \cdot 6H_2O$ and $C_3F \cdot 6H_2O$, though it was stated that since the X-ray patterns and spacings are very similar, comparison of these is not a suitable criterion. Reliance was placed on refractive-index determinations. The method of preparation was to heat solid solutions of C_4A·aq. and C_4F·aq. in lime solutions at about 70 °C for several days. The cubes obtained, of composition C_3A·aq.; $3CaO \cdot 0.25Fe_2O_3 \cdot 0.75Al_2O_3$·aq.; $3CaO \cdot 0.33Fe_2O_3 \cdot 0.67Al_2O_3$·aq.; $3CaO \cdot 0.5Fe_2O_3 \cdot 0.5Al_2O_3$·aq.; $3CaO \cdot 0.67Fe_2O_3 \cdot 0.33Al_2O_3$·aq.; and C_3F·aq. showed a continuous variation of index, indicating solid solution. Again it is to be noted that Malquori and Cirilli did not work with a higher molar proportion of Fe to Al than 2:1.

It seems possible therefore that silica was present in both the above cases, while some Cl was present in the $C_4A(F)$·aq. structure. While Cl would not be expected in the cubic $C_3A(F)$·aq. structure, analysis does not appear to have been carried out to confirm its absence.

The "low" form of calcium chloroaluminate has long been known. A corresponding ferrite compound was obtained by Malquori and Caruso [48] (1938). Malquori and Cirilli [61] (1952) state that solid solution of the two compounds can be obtained, but few details are given.

Only recently has there been evidence of a "high" chloride calcium chloroaluminate [24] (1956), and the existence of a corresponding ferrite or of solid solution with $C_3A \cdot 3CaCl_2$·aq. does not yet appear to have been established.

Corresponding to the "low" sulfoaluminate, the "low" sulfoferrite was prepared by Malquori and Caruso [48] (1938). Evidence for the existence of a $C_3A(F) \cdot CaSO_4$·aq. solid solution does not appear to be available in the literature. However, one solid solution within this general composition has been prepared at the Building Research Station (Roberts [15]). Analysis gave $2.99CaO \cdot 0.63Al_2O_3 \cdot 0.37Fe_2O_3 \cdot 0.94CaSO_4 \cdot 13.7H_2O$, with refractive indices intermediate between those of $C_3A \cdot CaSO_4$·aq. and $C_3F \cdot CaSO_4$·aq.

Limited solid solution between a "high" sulfoferrite and the corresponding high-sulfate sulfoaluminate was reported by Cirilli [28] (1943), up to about 75 percent Al_2O_3 being replaced by Fe_2O_3.

Malquori and Cirilli [61] (1952) have discussed the calcium aluminate complex salts and summarized the evidence obtained by them for the close analogy between hydrated calcium ferrites and aluminates and among the salts derived from them.

Generally, it appears likely that the existence of a complete series of corresponding "low" and "high" forms of chloro- and sulfoaluminates and ferrites will eventually be established and partial or full solid solution shown between corresponding structures, depending on the effect of replacement of Al by Fe in the particular type of structure concerned.

Conclusions

On the basis of the preceding discussions, it seems possible to attempt some unifying picture of at least one portion of the cement-hydration field, which, however inadequate, may serve to stimulate discussion helpful to further investigation. The picture thus drawn must inevitably be a mixture of what is proven and what is more or less conjectural.

The simplest conception, on present evidence, appears to be that hydrated calcium aluminates formed within the portland cement-water system, before any dehydration occurs, are restricted, within the range 22 °C–100 °C, to $C_4A \cdot 19H_2O$ and $C_2A \cdot 8H_2O$, metastable however with respect to $C_3A \cdot 6H_2O$, while below 22 °C, $C_2A \cdot 8H_2O$ is replaced by $CA \cdot 10H_2O$. Above about 100 °C, the metastable $C_4A \cdot 19H_2O$ and $C_2A \cdot 8H_2O$ may have only a short life or not be formed at all, or possibly a lower hydrate of dicalcium aluminate of formula $C_2A \cdot 3H_2O$ may be formed. Apart from these, the only compounds formed in the high-pressure steam-curing range are $C_3A \cdot 6H_2O$ and, above about 215 °C, the compound $C_4A_3 \cdot 3H_2O$. The position with regard to $C_4A \cdot 19H_2O$ and $C_2A \cdot 8H_2O$ is complicated by the slightly different structural arrangements possible in precipitation from supersaturated solution, but this does not appear to affect the overall picture.

Corresponding hydrated ferrites are limited, on present evidence, to metastable C_4F·aq. (there being no satisfactory evidence of a hexagonal C_2F·aq.) and "unstable" $C_3F \cdot 6H_2O$. In the latter case, experimental evidence and structural considerations suggest that a pure $C_3F \cdot 6H_2O$ structure is unstable and that the Al of $C_3A \cdot 6H_2O$ can only be replaced fully by Fe if room is made in the crystal lattice by replacing $2H_2O$ by SiO_2 ($4H^+$ by Si^{4+}). The experimental evidence seems at present not sufficiently decisive to say definitely whether similar spatial considerations apply in the case of C_4F·aq. Nor is there evidence which gives definitely the H_2O content of C_4F·aq. or indicates whether a possible hydrate $C_3F \cdot Ca(OH)_2 \cdot 18H_2O$ exists parallel to $C_3A \cdot Ca(OH)_2 \cdot 18H_2O$ (i.e., $C_4A \cdot 19H_2O$), dehydrating to $C_3F \cdot Ca(OH)_2 \cdot 12H_2O$.

Solid-solution series are formed both in hexagonal-plate and cubic structures in the systems $CaO–Al_2O_3–H_2O$ and $CaO–Fe_2O_3–H_2O$.

One form of solid solution is that exemplified between $C_4A\cdot 19H_2O$ and $C_2A\cdot 8H_2O$ in the system $CaO–Al_2O_3–H_2O$, where a limited solid solution is formed within the range $C_{2-2.4}A\cdot 8–10\cdot 2H_2O$.

Another form is that between C_4A·aq. and C_4F·aq. and between $C_3A\cdot 6H_2O$ and $C_3F\cdot 6H_2O$, where Al is replaced by Fe. Thus during hydration of cement compounds, when both aluminate and ferrite compounds are present together with sufficient lime, or both Al and Fe are present in the same compound, as in "C_4AF", hydration leads to a solid solution of the series C_4A·aq.–C_4F·aq., metastable with respect to the cubic solid solution series $C_3A\cdot 6H_2O–C_3F\cdot 6H_2O$, the latter however taking up silica from silicates present to a composition of the hydrogarnet type.

In the presence of sulfate, as in normal portland cements, sulfate will enter the structure of the hexagonal-plate lattice and produce either a solid solution of the hexagonal-plate type or the hexagonal-needle type depending on the relative amount of alumina, iron, and sulfate present. If such a solid solution reverts to the cubic structure, sulfate, but not iron, is liberated from the structure. Additionally, in the presence of chloride, Cl may also enter into the solid solution. It may be, however, that because of the relatively high solubility of alkali chlorides and $CaCl_2$, sulfate will be taken up preferentially into the structure.

This simplified picture appears to go as far as the present evidence and discussion permit. There is a need for further more exact experimental work to establish or refute the more conjectural aspects of the conclusions reached.

The importance of considering the problem in terms of the limited crystal lattice structures which appear to be possible may perhaps be stressed. There seems to be an obvious relationship between various compounds in the positions which they occupy in slight modifications of essentially the same lattice, and it seems clear that a further attack on structural aspects would give very valuable results. What is, for example, the exact structure of $C_2A\cdot 8H_2O$ in relation to $C_4A\cdot 19H_2O$, or of $CA\cdot 10H_2O$ in relation to both? What of the compound $C_2AS\cdot 8(?)H_2O$? This is apparently not resistant to attack by sulfates, whereas in the cubic lattice, replacement of $4H^+$ by Si^{4+} apparently confers sulfate resistance. It is hoped that what has been said will help to concentrate attention on these and other aspects of the problem, including the mutual interplay with calcium silicate hydrates also formed in cement hydration.

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Discussion

H. zur Strassen and C. H. Schmitt

On the Stability of C_3FH_6 and C_4FH_{14}

The authors [1, 2] have expressed the opinion that the C_3FH_6 phase would not exist in a pure state, but would only be formed in the presence of silica. If silica is not present, C_4FH_{14} would be formed instead. The experiments leading to this conclusion [1] are described here in a few words:

(1a) Freshly precipitated iron hydroxide is shaken with saturated lime solution and lime in excess, using polyethylene vessels. C_4FH_{14} is formed and still remains stable after a period of 39 weeks.

(1b) The same mixture in glass vessels yields hydrogarnet after 6 to 30 weeks, and contains 0.1 to 0.2 mole SiO_2 per mole Fe_2O_3.

(1c) The same mixture in polyethylene vessels with addition of highly reactive silica (aerosil) likewise yields hydrogarnet (silica-content: 0.23 to 0.28 mole SiO_2 per mole Fe_2O_3).

(2a) The hydration of C_2F with different excesses of lime yields C_4FH_{14} after a reaction time up to 26 weeks, eventually with additional $Ca(OH)_2$.

(2b) The same reaction in the presence of C_2S yields hydrogarnet with 0.17 to 0.20 mole SiO_2 per mole Fe_2O_3 and very small amounts of C_4FH_{14}.

The experiments mentioned in (2a) and (2b) were allowed to react up to a period of two years. With respect to (2b), the reaction product remains hydrogarnet. The mixtures under (2a), however, show partial decomposition of the original C_4FH_{14} to $Ca(OH)_2$, α-$Fe_2O_3 \cdot H_2O$ and a third substance not yet identified, with X-ray-lines at $d=5.40$ A and 4.29 A.

These results confirm the opinion that a stable C_3FH_6 does not exist in the system CaO-Fe_2O_3-H_2O. The C_4FH_{14} itself proves to be metastable and decomposes to iron hydroxide. Only the presence of small amounts of silica renders possible the formation of the very stable hydrogarnet phase.

Jones gives evidence that a C_3FH_6 free of silica could form from $C_3F \cdot CaCl_2 \cdot H_{10}$ by hydrolysis in NaOH-solution. This phase has not yet been prepared in a pure state and probably is completely unstable, as Jones himself emphasizes. According to our experiments the formation of a silica-containing hydrogarnet should be considered in all those cases in which an allegedly pure C_3FH_6 is said to be formed in the presence of calcium silicate hydrate.

Identification Chart of the Garnet-Hydrogarnet Solid Solution Series

Completely unobjectionable hydrogarnet phases can be obtained only if *dry* glasses of corresponding composition are allowed to react with water vapor, whereby a definite interval of temperature must be observed, dependent on the silica content of the glasses. The usual method of mixing the glasses with water and then putting them into the autoclave leads to initial reactions with a different tendency, which cannot be broken off, so that impure products are formed.

As a result of this, the identification chart is not completely exact and must be replaced by another. These investigations are not yet finished, so that the final identification chart cannot be presented at the moment.

On the Existence of the Compounds C_4ASH_{12} and $C_6AS_3H_{31}$

Flint and Wells [3] described the compounds $C_3A \cdot CS \cdot H_{12} (=C_4ASH_{12})$ and $C_3A \cdot (CS)_3 \cdot H_{31}$ $(=C_6AS_3H_{31})$. The first, isomorphous with $C_3A \cdot CaSO_4 \cdot H_{12}$, was said to be formed by mixing calcium silicate and calcium aluminate solutions. The second, isomorphous with $C_3A \cdot 3CaSO_4 \cdot H_{31}$, originated by transformation out of the first, the precipitate having been in contact with the solution for three years.

Dörr [4] was of the opinion that he had reproduced the compound C_4ASH_{12}, but later experiments [2] which had a reaction time of 1 and 2 years, respectively, showed only $Ca(OH)_2$, C_4AH_{13}, and calcium silicate hydrate. A repeated exhaustive control of the 2-yr samples showed in one case weak X-ray-lines ($d=9.7$ A, 5.6 A, 4.7 A), identical with the strongest lines of ettringite. The products, however, are free of sulfate and therefore they must be attributed to the $C_6AS_3H_{31}$ phase of Flint and Wells. In the other samples these lines were at least indicated.

The experiments are being continued, because the conditions of formation of the compound $C_6AS_3H_{31}$ are still obscure. It is remarkable that at this point hydrated silicate and aluminate phases coexist without formation of hydrogarnet [2]. Mohri [5, 6] also reported the compound $C_6AS_3H_{31}$.

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Discussion

C. H. Schmitt

With reference to the report submitted by Dr. Jones, there are submitted the following lines concerned with the substitution of aluminum by iron in gehlenite hydrate, C_2ASH_8. A detailed publication will be made elsewhere in the near future, as soon as investigations have been completed.

Gehlenite hydrate can be obtained in a pure form by treating a glass of gehlenite composition with half-saturated lime solution [1]. As starting materials glasses were used which had an increasing iron content ranging from C_2AS to $C_2A_{0.4}F_{0.6}S$ (table 1). Since the partial thermal decomposition of Fe_2O_3 during melting cannot be prevented, the finely ground glasses were subsequently carefully oxidized in an open electric furnace. The nonoccurrence of any crystallization was checked by X-ray diffraction. These glasses were shaken with half-saturated lime solution for 13 weeks; then the reaction products were washed with acetone and dried. The water content of the hydration products (table 1) did not increase during shaking over a longer period; i.e., the hydration process of the glasses thus could be considered as having come to an end. In all samples the X-ray test showed gehlenite hydrate as the newly formed hydrated phase (and very small amounts of calcium silicate hydrate, hydrogarnet and gibbsite).

Table 1. *Reaction of glasses $C_2A_{(1-x)}F_xS$ with half-saturated lime solution*

5.00 g glass+300 ml lime solution containing 63.6 mg CaO in 100 ml; reaction time 13 weeks.

(1) Analysis of the glasses				(2) Lime and water content after hydration		(3) Lattice constant A		(4) Refractive index
moles				*moles*				
C	A	F	S	C	H	*a* (±0.01)	*c* (±0.02)	
1.97	1.00	-------	1.00	2.07	7.97	9.96	12.56	1.512±0.003
1.99	0.90	0.10	1.00	2.09	8.01	10.00	12.56	------------
2.02	.80	.20	1.01	2.09	8.04	10.04	12.55	1.517±0.003
1.99	.70	.30	0.99	2.11	8.08	10.07	12.52	1.525±0.005
2.01	.60	.40	.99	2.13	7.76	10.08	12.54	1.525±0.005
2.00	.50	.50	1.00	2.11	6.85	10.08	12.55	1.525±0.005
2.00	.395	.605	1.00	2.08	5.30	--------	--------	------------

Table 2. *X-ray data of C_2ASH_8 (hydration product of the C_2AS-glass)*

I	*d*	*hkl*	*I*	*d*	*hkl*
s	12.58	001	m	2.367	303
m	6.28	002	vw	2.239	[d] 312
W	4.98	110	m	2.122	304
w	4.89	(a)	w	2.076	313
vw	4.39	(a)	w	2.047	[d] 106
w	4.28	200	m	1.8922	305
s	4.183	003	m-w	1.8602	206
w	3.534	202	vw	1.8363	(b)
vw	3.037	[b] (203)	vw	1.7637	(a)
vs	2.873	300	s	1.6623	330
vw	2.798	[b] (301)	m	1.6469	331
vw	2.718	(c)	m	1.6063	332
m	2.613	302	vw	1.5603	316
s	2.489	220	m	1.5440	333
w	2.438	(a)	m	1.4383	600
vw	2.404	(a)	w	1.3599	603
m	2.385	310			

[a] Possibly gibbsite.
[b] Possibly calcium silicate hydrate.
[c] Possibly hydrogarnet (C_3ASH_4).
[d] Possibly coincidence with gibbsite.

Up to an iron oxide content of 0.3 mole in the glasses, the hydrates formed were white or somewhat yellowish-white and contained 8 moles of H_2O after completed reaction, the lime content ranging from 2.07 to 2.11 moles per mole of R_2O_3. The hydration products of glasses containing 0.4 mole of iron oxide or more were of an increasingly brown color and no longer reached the water content of 8 moles.

From the X-ray diagrams of the hydrates, the conclusion must be drawn that the *a*-parameter of the hexagonal unit cell increases up to 0.3 mole of iron oxide in the glasses and remains constant at higher iron oxide contents (table 1). According to the results obtained hitherto, the *c*-parameter is not influenced by the entrance of iron.

Likewise, the refractive index of the hydrates increases up to an iron oxide content of 0.3 mole and remains constant at higher iron contents of the starting material.

All these results lead to the same conclusion that up to 0.3 mole or a value slightly exceeding this amount, aluminum in the gehlenite hydrate is replaceable by iron.

Comparing the dimensions of the unit cell of the gehlenite hydrate, $a=9.96\pm0.01$ A, $c=12.56\pm0.02$ A, with the values found by Fratini and Turriziani, $a=8.85$ A, $c=12.66$ A [2], it is obvious that the *a*-parameters are essentially different. The values given here have been calculated from the hk0- and 001-lines respectively according to the indices as listed in table 2.

References

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Discussion

H. zur Strassen

In Jones' paper the close relationship between C_2ASH_8 and C_4AH_{13} is mentioned; both should have the same hexagonal layer structure. Schmitt [1], however, has found for C_2ASH_8 another value of the *a*-axis than that found by Fratini and Turriziani [2].

The single-crystal electron-diffraction patterns of the two substances are compared in figure 1. In both cases the reciprocal lattice shows the same lattice distance and the same reflection arrangement; only the distribution of intensities differs (as to the distribution of intensities the lattice of C_2ASH_8 has only monoclinic symmetry). The great similarity of both diagrams confirms the assumption that gehlenite hydrate should belong to the group of the hexagonal layer structure typified by $C_3A \cdot Ca(OH)_2 \cdot aq$.

Buttler, Dent Glasser, and Taylor [3] have found by X-ray determination for β-C_4AH_{13} the value $a = 5.74$ A, which complies with the electron diffraction measurements. The a-axis of C_2ASH_8 as found by X-rays [1] is $a = 9.96 \text{ A} = \sqrt{3} \times 5.75$ A; a few reflections of the X-ray powder diagram which are not contained in the electron diffraction pattern require a unit cell of triple size.

References

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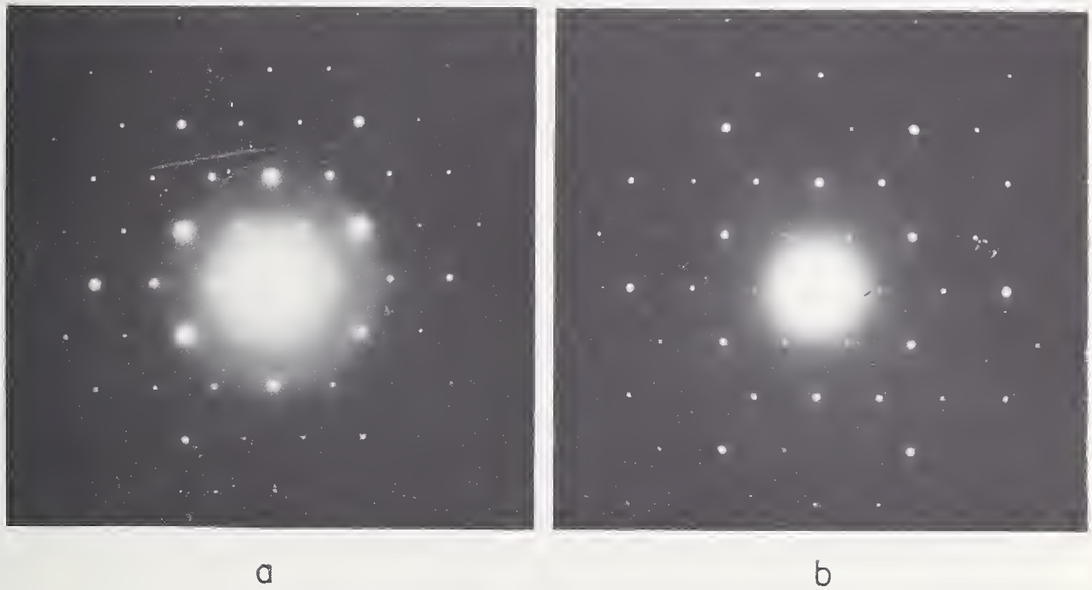

Figure 1. *Single-crystal electron diffraction patterns.*

(a) Gehlenite hydrate.
(b) β-C_4AH_{13}.

(Pictures by H. Grothe and G. Schimmel, Battelle Institute, Frankfurt a.M.)

Closure

M. H. Roberts

The contributions by zur Strassen and Schmitt to the discussion are of considerable interest and present new information.

The experiments on the stability of $C_3F \cdot 6H_2O$ and $C_4F \cdot 14H_2O$ show that while in the presence of silica a stable hydrogarnet phase is formed fairly readily, there appears to be no tendency for $C_4F \cdot 14H_2O$ in contact with saturated lime solution at room temperature to transform into $C_3F \cdot 6H_2O$ when silica is excluded. Nevertheless, it is still possible that the latter transformation may occur more readily at higher temperatures, as is the case for the conversion of $C_4A \cdot 19H_2O$ to $C_3A \cdot 6H_2O$. However, in one recent experiment at the Building Research Station it was observed that when a mix of $C_4F \cdot aq$. in saturated lime solution was shaken in a stainless steel tube for 2 weeks at 50 °C the $C_4F \cdot aq$. was unaffected. Since under similar conditions some conversion of $C_4A \cdot 19H_2O$ to $C_3A \cdot 6H_2O$ occurred in a few hours, there appears therefore to be a marked reluctance for $C_4F \cdot aq$. to convert to $C_3F \cdot 6H_2O$ in the absence of silica. This result does not accord well with the previous experiments described in the principal paper in which some conversion of $C_3F \cdot CaCl_2 \cdot aq$. to pure $C_3F \cdot 6H_2O$ was thought to have been obtained in NaOH solutions at 50° or 60 °C after only a few days. While it is possible that behavior in NaOH solutions is different from that in lime solutions, it must be noted, however, that there is now some doubt as to whether silica was completely excluded in the experiments using NaOH solutions. Recent analysis of the solid phase obtained by treating $C_3F \cdot CaCl_2 \cdot aq.$ in *N* NaOH solution at 60 °C for 5 months showed that 0.3 percent SiO_2 was present. This small amount of silica contamination may have arisen from the brief contact of the NaOH solution with a glass burette during the course of preparation of the mix. Furthermore, the chloroferrite preparations used may have contained traces of silica, because they were prepared by adding a mixed $CaCl_2$-$FeCl_3$ solution to a NaOH solution which again may have been contaminated with traces of silica. On present evidence, therefore, it seems doubtful whether a $C_3F \cdot 6H_2O$ preparation completely free from silica has yet been obtained, and it may well be, as concluded by zur Strassen and Schmitt, that the $C_3F \cdot 6H_2O$ structure is not stable without the presence of some silica.

With regard to the silicoaluminate compounds, the conclusion that the existence of $C_3A \cdot CaSiO_3 \cdot 12H_2O$ is doubtful is supported by Carlson [1] in his discussion of another paper in this Symposium. Similarly, the compound $C_3A \cdot 3CaSiO_3 \cdot 32H_2O$ does not yet appear to have been firmly established. Carlson and Berman [2] have indicated that it is unlikely that Mohri [3] obtained this compound, and furthermore showed that contamination with CO_2 may be a significant factor. This possibility requires further examination, and the results of further experiments on $C_3A \cdot 3CaSiO_3 \cdot 32H_2O$ will be awaited with considerable interest. The remaining silicoaluminate, $C_2AS \cdot 8H_2O$, appears now to be well established, and the new results showing limited substitution of up to about 0.3 mole of aluminum by iron in this compound are of interest in that they emphasize again that although solid solutions are formed there is not necessarily complete replacement of one ion by another. The assumption that $C_2AS \cdot 8H_2O$ belongs to the group of basic crystal lattice structures typified by such compounds as $C_3A \cdot Ca(OH)_2 \cdot aq.$, $C_3A \cdot CaCl_2 \cdot aq.$, $C_3A \cdot CaSO_4 \cdot aq.$, etc., is confirmed by zur Strassen's observation of a close similarity between the single crystal electron diffraction patterns of $C_2AS \cdot 8H_2O$ and $C_4A \cdot 13H_2O$. It seems that the value of the *a*-axis is almost the same for the compounds of this group, while the *c*-axis varies depending upon the space requirements of the anion and the water present. The limited single crystal X-ray and electron diffraction observations which have been made support the *a*-axis value of 5.75 A (or $\sqrt{3} \times 5.75 = 9.96$ A) rather than the value of about 8.8 A which has also been reported for some of these compounds. There is, however, a need for further work to establish these structures and the slight modifications brought about by changes in the states of hydration.

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Paper III–S1. Heat of Formation of Calcium Trisulfoaluminate at 25 °C*

H. A. Berman and E. S. Newman

Synopsis

Determinations were made of the heats of solution of $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31–33H_2O$ and of less completely hydrated samples of the same compound in 2*N* HCl. The preparations containing $2–8H_2O$ showed a continuous decrease in the heat of solution from −180 to −145 kilocalories per mole as the water content increased. A break occurred in the neighborhood of $8H_2O$, followed by a continuous decrease between 8 and $33H_2O$ from −145 to −74.9 kilocalories per mole at $31H_2O$ and −72.4 kilocalories at $32H_2O$. The rate of change of the heat of solution with increase in H_2O content in the $31–33H_2O$ region is 2.49 kilocalories per mole per mole H_2O. From these values and from the heats of solution of $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ and $CaSO_4{\cdot}2H_2O$ in the same acid solution, the heat of formation of the hydrated calcium trisulfoaluminate from these compounds was calculated to be −46.11 kilocalories per mole for a hydrate containing $31H_2O$ and −48.62 for one containing $32H_2O$. The heat of formation of the hydrated trisulfoaluminate from the elements was calculated to be −4122 kilocalories per mole for $31H_2O$ and −4193 for $32H_2O$. A possible tendency for CO_2 to enter the crystal structure of the hydrated calcium trisulfoaluminate in a manner similar to that of H_2O is discussed.

Résumé

On a fait des déterminations de la chaleur de dissolution en 2*N* HCl de $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31-33H_2O$ et d'échantillons de la même composition de moindre teneur en H_2O. Les préparations contenant $2-8H_2O$ ont montré une décroissement continue de la chaleur de dissolution de −180 à −145 kilocalories par mole lorsque la teneur en H_2O s'est augmentée. Il y eut une discontinuité environ de $8H_2O$, suivie d'une décroissement continue entre 8 et $33H_2O$ de −145 à −74.9 kilocalories par mole à $31H_2O$ et à −72.4 kilocalories à $32H_2O$. La vitesse de changement de la chaleur de dissolution contre l'augmentation de la teneur en H_2O dans la région $31-33H_2O$ est de 2.49 kilocalories par mole par mole H_2O. A partir de ces valeurs et des chaleurs de dissolution de $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ et de $CaSO_4{\cdot}2H_2O$ dans la même solution acide, on a calculé pour la chaleur de formation du trisulfoaluminate de chaux hydraté à partir de ces composés −46.11 kilocalories par mole pour un hydrate de $31H_2O$ et −48.62 pour un hydrate de $32H_2O$. On a calculé pour la chaleur de formation du trisulfoaluminate à partir des éléments −4122 kilocalories par mole pour un hydrate de $31H_2O$ et −4193 pour un hydrate de $32H_2O$. On envisage la possibilité que le CO_2 entre dans la structure du cristal du trisulfoaluminate de chaux hydraté d'une façon analogue à celle de l'eau.

Zusammenfassung

Die Lösungswärme von $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31-33H_2O$ und von weniger wasserhaltigen Proben derselben Komposition wurden in 2*N* HCl bestimmt. Die Lösungswärme der $2-8H_2O$ enthaltenden Präparate vermindete sich von −180 zu −145 Kilokalorien pro Mol (Kkal/Mol) mit zunehmendem Wassergehalt. Ein Knick in der Kurve tritt bei ca. $8H_2O$ auf; zwischen 8 und 33 H_2O, erfolgt ein kontinuierlicher Abfall von −145 Kkal/Mol, sodaß bei $31H_2O$ ein Wert von −74.9 Kkal/Mol und bei $32H_2O$ ein Wert von −72.4 Kkal/Mol erreicht wird. Die Abhängigkeit der Lösungswärme von der Wassergehaltszunahme zwischen 31 und $33H_2O$ ist 2.49 Kkal/Mol pro Mol H_2O. Von diesen Resultaten und den Lösungswärmen für $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ und $CaSO_4{\cdot}2H_2O$ in derselben Salzsäurelösung wurde die Formationswärme für das $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31-33H_2O$ aus diesen Verbindungen berechnet. Sie beträgt −46.11 Kkal/Mol für ein Hydrat mit $31H_2O$ und −48.62 für eins mit $32H_2O$. Die Formationswärme des Kalziumtrisulfoaluminathydrats aus den Elementen wurde berechnet und beträgt −4122 Kkal/Mol für $31H_2O$ und −4193 für $32H_2O$. Die Möglichkeit daß CO_2 eine ähnliche Tendenz hat, wie Wasser, in die Kristallstruktur des Kalziumtrisulfoaluminathydrats einzudringen, wird diskutiert.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the National Bureau of Standards, Washington.

Introduction

Calcium trisulfoaluminate, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31\text{–}33H_2O$ [1],[1] is formed by the aggressive action of sulfate waters on portland cement concrete and is a reaction product of the hydration of the slag-calcium sulfate cements used extensively in Europe [2] because of their resistance to such waters. Lerch's value of 149 calories per gram of SO_3 [3] for the heat of the reaction

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3(CaSO_4 \cdot 2H_2O) + 19H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O \qquad (1)$$

appears to be the only thermochemical data for the trisulfoaluminate in the literature. In the present work, the heat of formation of calcium trisulfoaluminate was calculated from measurements of its heat of solution in $HCl \cdot 26.61H_2O$ (2.00N HCl at 25 °C.) and similar values obtained by measurement or calculation for the reactants in the above equation. The heats of formation of the reactants were taken from Circular 500 [4] of NBS.

The water content of this compound is variously reported as $30H_2O$ [5], $31H_2O$ [1, 3, 6], $31.5H_2O$ [7], $32H_2O$ [8], and $31\text{–}33H_2O$ [9]. According to Lefol [5], the water between 8 and $30H_2O$ is loosely bound, and changes in water content are reversible, depending on ambient water vapor pressure. Electron microscope studies by Astreeva and Lopatnikova [6] show that part of the water of crystallization may be driven off without destroying the crystal structure but with the formation of intracrystalline voids. A study of this compound must consider the variability of water content. Calculations of the heat of formation have therefore been made for the hydrate at two compositions $31H_2O$ and $32H_2O$.

It is appropriate at this point to consider briefly the nomenclature of this compound and related compounds. The terms sulfoaluminate, chloroaluminate, carboaluminate, etc., are subject to question because they do not correctly represent the relationship of the various atoms involved. Although our knowledge of the crystal structure is incomplete, it seems clear that the "sulfoaluminates" might more correctly be called "aluminate sulfates". In particular, the "hydrated calcium trisulfoaluminate" might be more correctly called "hexacalcium aluminate trisulfate hydrate". The term "sulfoaluminate", however, has become firmly established through many years of usage and will be employed in this symposium paper in preference to the more cumbersome exact terminology.

Materials, Apparatus, and Procedure

Preparation of the Sulfoaluminate

Ten samples of the calcium trisulfoaluminate were prepared. Their properties and details of their preparation are listed in table 1. Two general methods were used to prepare them: (a) The reaction between calcium sulfate solution and a solution of calcium aluminate obtained by shaking a high-alumina cement[2] with water; (b) the reaction between solutions of calcium hydroxide and aluminum sulfate, sometimes in the presence of calcium sulfate solution. With the exception of the high-alumina cement, analytical reagents were used in all the preparations. In the case of samples *A* and *F*, precautions were taken to exclude atmospheric carbon dioxide during every step of the process. The distilled water used to dissolve the reagents was boiled to expel dissolved gases. The flask was closed, while cooling the boiled water, with a stopper containing an inlet tube equipped with a CO_2-absorption bulb. The solutions were prepared and the samples were precipitated, digested, filtered, and conditioned in closed systems protected from the laboratory air. "CO_2-free" air[3] was used to flush all containers and to transfer water, solutions, or slurries into the stoppered containers under pressure. For sample *B*, these precautions were taken only during the filtration and conditioning.

In general, the solutions shown in table 1 were added alternately in small quantities or simultaneously in approximately stoichiometric ratios. The reaction mixture was stirred magnetically during the addition of the reagents and with a current of "CO_2-free" air for several minutes afterwards. The precipitates formed were digested in the stoppered reaction flasks for various periods (from 8 days for sample *H* to 9 months for sample *B*), filtered on a Buchner funnel, and dried by several methods: (a) Washing with alcohol and ether, (b) conditioning over calcium chloride in an evacuated desiccator (sample *H*), (c) conditioning over saturated $MgCl_2 \cdot 6H_2O$ in a closed desiccator or in a desiccator through which a stream of "CO_2-free" air previously bubbled through saturated $MgCl_2 \cdot 6H_2O$ was passed (samples *A*, *B*, *F*). Samples *A*, *B*, and *F* were conditioned until their ignition loss at 1,000 °C. was constant, a process which required about 2 to 2½ months. Before and after removing a portion of the sample

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The high-alumina cement had been heated overnight in air at 950 °C to oxidize the sulfides present to sulfates.

[3] Compressed air passed through moisture- and CO_2-absorbents. The actual CO_2 content of this air may vary, depending on the rate of flow and the history of the absorbent. In one case, where the "CO_2-free" air was passed through the absorption tube of a CO_2-determination train overnight, the tube showed no gain in weight. When CO_2-determinations were run on sulfoaluminate samples, blank determinations prior to the runs showed gains of 0.0 to 1.0 mg in 1 hr., possibly from CO_2 in the water and acid used in the determination. When the water was not boiled in advance, but taken directly from the distilled-water supply, the blank determination occasionally showed a pickup of as much as 2.0 mg of CO_2.

TABLE 1. *Preparations of* $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 30\text{–}33H_2O$

Sample Designation	A		B		C	D	E	F	G	H	J	K
Method of preparatiou [a]	1		2		3	4	3	5	6	7	6	8
Heat of solution, $-\Delta H$, calories per gram	58. 1408 58. 2680 58. 4099 58. 3354 57. 8739 58. 7516 58. 2407		58. 704 59. 533 58. 549 57. 885 58. 655		59. 14 59. 39	61. 06 60. 84 61. 96 61. 67 60. 01	59. 62 59. 00 58. 55	58. 0685 57. 1606 56. 6756 57. 5242 57. 6190 57. 1509 56. 1170 57. 6998 57. 7546 58. 0854	58. 65 58. 37 59. 53	60. 45 62. 43 62. 41 62. 76 61. 53	57. 47 56. 32	49. 19 49. 04
Average	58. 289		58. 665		59. 26	61. 11	59. 06	57. 387	58. 85	61. 92	56. 90	49. 12
Standard deviation of average	. 120		. 262		0. 13	0. 34	0. 31	0. 197	0. 35	0. 42	0. 57	0. 07
Analysis, wt. percent CaO	26. 96	±0. 02	26. 70	±0. 02	27. 17	26. 63	27. 16	27. 28	26. 71	27. 06	26. 83	27. 54
Al_2O_3	8. 23	±0. 02	8. 09	±0. 017	8. 27	8. 09	8. 20	8. 63	8. 12	8. 54	7. 96	7. 26
SO_3	19. 11	±0. 08	18. 81	±0. 09	19. 38	19. 32	18. 97	19. 10	18. 66	19. 16	19. 60	21. 21
CO_2	0. 207	±0. 014	0. 24	±0. 014	1. 15	0. 29	0. 91	0. 46	1. 53	1. 49	0. 76	2. 12
H_2O	45. 44		45. 82		44. 12	45. 36	44. 78	44. 66	45. 88	43. 86	45. 18	41. 84
SiO_2	0. 00		0. 15	±0. 00	--------	--------	--------	0. 00	--------	--------	--------	--------
Mole ratios, CaO/Al_2O_3	5. 957	±0. 015	6. 000	±0. 014	5. 972	6. 152	6. 021	5. 747	5. 980	5. 760	6. 126	6. 896
SO_3/Al_2O_3	2. 958	±0. 014	2. 960	±0. 016	2. 984	3. 057	2. 945	2. 819	2. 927	2. 857	3. 135	3. 719
CO_2/Al_2O_3	0. 058	±0. 004	0. 069	±0. 004	0. 322	0. 083	0. 257	0. 123	0. 436	0. 404	0. 221	0. 676
H_2O/Al_2O_3	31. 255		32. 053		30. 185	31. 726	30. 900	29. 287	31. 972	29. 062	32. 114	32. 609
Mole ratios of compounds (to Al_2O_3):												
$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O$	0. 986	±0. 005	0. 987	±0. 005	0. 995	1. 000	0. 982	0. 940	0. 976	0. 952	0. 997	1. 000
where $n=$	31. 656		32. 425		30. 322	31. 600	31. 466	30. 965	32. 758	30. 376	31. 913	31. 171
$CaSO_4 \cdot 2H_2O$	--------		--------		--------	0. 057	--------	--------	--------	--------	0. 144	0. 719
$CaCO_3$	0. 041	±0. 032	0. 069	±0. 004	0. 004	0. 083	0. 131	0. 109	0. 126	0. 046	--------	0. 177
$Ca(OH)_2$	--------		0. 011	$\begin{cases}+0.035\\-0.011\end{cases}$	--------	0. 012	--------	--------	--------	--------	--------	--------
$Al_2O_3 \cdot 3H_2O$	0. 014	±0. 005	0. 013	±0. 005	0. 005	--------	--------	0. 060	--------	0. 048	0. 003	--------
CO_2	0. 017	$\begin{cases}+0.032\\-0.017\end{cases}$	--------		0. 318	--------	0. 126	0. 014	0. 310	0. 358	0. 221	0. 499
Weight percent purity	99. 4		99. 2		98. 7	98. 5	98. 5	98. 2	97. 9	97. 7	97. 3	88. 4
Heat of solution of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O$, $-\Delta H$:												
kcal. per mole	72.86_6		73.71_5		73.46_0	76.65_0	73.56_4	71.26_2	75.17_0	77.31_2	74.14_4	71.54_4
cal. per gram	58.34_3		58.37_4		59.97_2	61.42_2	59.06_3	57.63_2	59.24_5	63.06_7	59.14_7	57.68_8

[a] Method 1: Aluminum sulfate solution added to calcium hydroxide solution (alternate additions).
Method 2: Calcium aluminate solution added to calcium sulfate solution; calcium hydroxide solution added later.
Method 3: Aluminum sulfate—calcium sulfate solution added to calcium hydroxide solution.
Method 4: Calcium hydroxide and aluminum sulfate solutions added to calcium sulfate solution.
Method 5: Aluminum sulfate solution added to calcium hydroxide solution; calcium sulfate solution added to the mixture (alternate additions).
Method 6: Calcium aluminate solution added to gypsum-lime solution; calcium sulfate solution added later.
Method 7: Calcium hydroxide solution added to aluminum sulfate—calcium sulfate solution.
Method 8: Calcium aluminate solution added to gypsum-lime solution.

from the closed chamber for the purpose of determining ignition loss, the chamber was evacuated and refilled with "CO_2-free" air.

X-ray diffraction patterns of samples *A*, *B*, and *F* were obtained by the powder method on a Geiger-counter diffractometer with copper Kα radiation. The patterns are tabulated in table 2 and compared with data published by Fratini, Schippa, and Turriziani [8]. Since the preparations obtained showed more peaks than the published pattern, a series of possible *d*-spacings was calculated from the unit cell parameters proposed by these authors. The close correspondence between the observed and calculated *d*-spacings is a measure of the purity of the samples prepared and an indication of the impurities present in several instances where the correspondence was not as good. The X-ray data provide confirmation as well for the unit cell parameters calculated by these authors.

The oxide analysis in table 1 was obtained by duplicate or triplicate determinations for samples *A* and *B*, and the precision of the analysis and of the calculated mole ratios of the oxides (and of compounds calculated from the oxides) was determined. Duplicate or triplicate determinations of CO_2 content were made on all the samples. The standard deviation for each of the oxide analyses was obtained by pooling the variances of analyses for samples *A* and *B*. The designation and calculation of compounds present as impurities was based on the phase equilibrium studies of Jones [10] and of D'Ans and Eick [11] as discussed by Eitel [12], and on optical microscopic examination, chemical analysis, and X-ray diffraction patterns.

Preparation of the Gypsum

Fifty grams of plaster of Paris were dissolved in distilled water at room temperature, stirred 1 min, and quickly filtered. Crystallization of $CaSO_4 \cdot 2H_2O$ occurred in the filtrate about 15 min after the beginning of the filtration. The crystals were filtered, washed with alcohol and ether, and dried in the laboratory air. Chemical analysis gave the composition $CaSO_4 \cdot 2.018H_2O$.

Preparation of Hydrated Calcium Aluminate

Tricalcium aluminate hydrate, $3CaO \cdot Al_2O_3 \cdot 6H_2O$, was prepared by autoclaving $3CaO \cdot Al_2O_3$ at 150 °C for several days, according to the method of Thorvaldson, Brown, and Peaker [13]. The

TABLE 2. *X-Ray diffraction patterns of the* $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31–33H_2O$ *samples*

Calculated [a]		Observed *d*-spacings, Angstrom units		
hkl	*d*, Angstrom units	*A*	*B*	*F*
100	9.734	9.774	9.817	9.861
101	8.864	8.853	8.972	9.092
				9.036
110	5,620	5.623	5.67	5.647
112	4.978	4.979	5.01	4.995
200	4,867	[b] 4.849	[b] 4.897	[b] 4.897
				4.870
104	4.697	4.694	4.729	4.721
203	4.024	4.020	4.046	4.053
				4.035
114	3.880	3.880	3.899	3.895
210	3.679	3.679	3.696	3.693
				3.682
204	3.604	3.601		3.608
212	3.480	3.477	3.494	3.486
300	3.245	3.241	3.256	3.246
214	3.034	3.018	3.030	[c] 3.023
		3.015		
220	2.810	2.806	2.818	2.815
221	2.786		2.788	2.783
304	2.776	2.776		
310	2.700	2.696	2.706	2.706
				2.699
312	2.618	2.618	2.626	2.621
216	2.564	2.565	2.573	2.570
313	2.526		2.533	
224	2.489	2.486	2.497	
401	2.418		2.417	
314	2.411	2.410		2.412
208	2.348	2.351	2.359	2.352
320	2.233	2.232	2.238	2.233
404	2.216	2.208		2.212
322	2.186	2.184	2.191	2.194
				2.185
316	2.154	2.155	2.160	2.158
323	2.132	2.130		
410	2.124	2.124	2.127	2.126
412	2.084	2.082	2.087	
324	2.061	2.062	2.066	2.064
414	1.975	1.975	1.979	1.979
500	1.947	1.946	1.951	1.947
415	1.904	1.903	1.906	
330	1.873		1.878	
332	1.845	1.844	1.849	1.849
421	1.833	1.832	1.834	1.829
422	1.813	1.814	1.816	1.813
333	1.812	1.812		

[a] Calculated from the unit cell parameters published by Fratini, Schippa and Turriziani [8].
[b] May be a line of $Al_2O_3\cdot 3H_2O$.
[c] May be a line of calcite, $CaCO_3$.

hydrated aluminate was dried over potassium hydroxide. Chemical analysis gave the composition $3CaO\cdot Al_2O_3\cdot 5.859H_2O$ (plus 0.007 mole $CaCO_3$ per mole as impurity). The anhydrous aluminate had been prepared by repeated heating of lime and alumina with intervening moistening of the material to aid in dispersing the CaO, as described by the same authors.

Heat of Solution Measurements

The heats of solution of the compounds were determined in $HCl\cdot 26.61_4H_2O$ (2.00*N* HCl at 25 °C). A precision-type calorimeter, described by Newman [14] was used. Since it was inconvenient to prepare the sulfoaluminate in large quantities, 1-g samples of this compound were used with the normal quantity of acid for the calorimeter, 600 g. In accordance with equation 1, 0.4-g samples of gypsum and 0.3-g samples of calcium aluminate hydrate were used with the same quantity of acid. Larger amounts of these compounds were also employed to determine whether the greater precision of a larger sample would be usable, in view of the theoretical loss of some heat of dilution due to the formation of a more concentrated solution. Although equation 5 below, used in calculating the heat of the reaction, specifies that the gypsum be introduced into the solution already obtained by dissolving the calcium aluminate hydrate in the acid, the gypsum was instead added directly to the fresh acid. The effect of the presence of calcium aluminate on the heat of solution of gypsum is negligible, as shown by the experiments of Newman with anhydrite [14, 15]. A heat of solution of $-\Delta H = -12.75 \pm 0.34$[4] calories per gram was obtained for $CaSO_4$ previously ignited at 1,000 °C and dissolved in fresh acid. When the same material was dissolved in acid to which calcium aluminate had been added, the heat of solution was -12.69 ± 0.14. Since the ions present are the same for anhydrite and gypsum once they are in solution, the heat of solution of gypsum should be unaffected by the presence or absence of calcium aluminate in the acid solution, to the extent that the interaction can be measured.

The heat effect of adding the 19 moles of water appearing in equation 1 (or 20 moles when the sulfoaluminate contains 32 moles of H_2O) was estimated as the partial molal heat content of water in 2*N* HCl [4], neglecting the contribution of the small amounts of other solutes present.

To determine the effect of the water content of the calcium sulfoaluminate, portions of sample *H* were dried by various means and their heats of solution determined. The drying methods used were: (a) Heating at 60 °C, 110 °C, 145 °C, and 200 °C; (b) drying over calcium chloride or sodium hydroxide; and (c) vacuum pumping with a dry-ice-acetone trap.

Results and Discussion

Heats of Solution of the Preparations

The heats of solution obtained on the sulfoaluminate samples are shown in table 1, as well as the heats of solution and water contents of the pure $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot nH_2O$ calculated from the chemical composition of the sample itself. The samples are listed in descending order of purity.

The heats of solution and water contents obtained on the dried portions of sample *H* are shown in table 3, together with similarly calculated heats of solution and water content of the pure $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot nH_2O$.

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[4] The estimates of standard deviation quoted in this paper represent the standard deviation of the average, using $n-1$ degrees of freedom.

TABLE 3. *Preparations of* $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 0\text{–}20H_2O$

(Dried preparations of sample H)

Sample Designation	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-11
Method of drying: Heated at (°C)						([a])	60°	110°			
Conditioned over	$CaCl_2$	NaOH	Suction								
Treatment time	34 days	34 days	2 days	3 days	7 days	8 days	13 days	1 hr.	2 hr.	13 days	35 days
Heat of solution, $-\Delta H$, calories per gram	77.26	110.95	178.48	182.51	182.74	143.56	102.53	116.25	150.17	171.69	168.28
n = Molecules of H_2O per molecule $3CaO\cdot Al_2O_3\cdot 3CaSO_4$	25.756	17.737	7.880	7.655	7.693	7.436	19.066	16.825	11.170	7.794	7.715
Heat of solution of $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot nH_2O, -\Delta H$ kcal. per mole	90.21_7	113.58_8	151.27_5	153.95_9	154.27_9	120.45_0	107.39_1	117.12_3	136.11_6	145.23_3	142.10_5
cal. per gram	78.95_5	113.79_6	184.34_9	188.55_3	188.78_6	142.10_5	105.06_8	119.30_1	154.70_2	177.32_7	173.80_5

Sample Designation	H-12	H-13	H-14	H-15	H-16	H-17	H-18	H-19	H-20	H-21	H-22
Method of drying: Heated at (°C)	145°							200°			
Treatment time	45 min.	45 min.	1 hr.	1 hr.	1 hr.	20 hr.	1 hr.	1½ hr.	2 hr.	5 days	13 days
Heat of solution, $-\Delta H$, calories per gram	168.66	177.73	182.07	188.67	183.62	191.06	219.39	223.18	226.18	248.89	238.53
n = Molecules of H_2O per molecule $3CaO\cdot Al_2O_3\cdot 3CaSO_4$	7.605	7.445	5.329	6.105	6.938	6.140	4.246	3.846	3.805	2.068	2.561
Heat of solution of $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot nH_2O, -\Delta H$ kcal. per mole	141.78_6	148.92_1	145.77_5	153.55_8	152.19_3	155.62_9	171.28_0	172.63_7	174.79_5	184.59_9	179.01_6
cal. per gram	173.83_7	183.23_1	187.99_0	194.72_0	189.38_5	197.18_9	226.82_5	230.82_5	233.94_3	257.86_3	247.00_1

[a] Temperature unknown.

TABLE 4. *Calorimeter calibrations*

Calibration	1	2	3
Date	March 1956	November 1956	April 1959
Heat capacity of calorimeter, calories per ohm	5857.4 5861.8 5860.9 5855.9 5856.4 5861.9	5851.47 5846.27 5852.77 5859.16 5856.46 5847.47 5842.17	5838.23 5842.17 5840.69 5839.07 5840.63 5838.56 5842.13
Average	5859.05	5850.82	5840.21
Standard deviation of the average	1.01	2.25	0.61
Samples determined	C, D, E, G, H, J, K, and H-1 to H-22	B $CaSO_4\cdot 2H_2O$ $3CaO\cdot Al_2O_3\cdot 6H_2O$	A, F

TABLE 5. *Reactants*

	$C_3A.6H_2O$	$CaSO_4.2H_2O$
Heat of solution, $-\Delta H$ calories per gram	371.33 370.40 369.33 368.18 369.54 370.13 369.86 370.33 368.44	−32.84 −33.24 −32.93 −32.28 −32.91 −33.53
Average	369.73	−32.955
Standard deviation of average	0.33	0.17
Analysis, wt. percent CaO	44.52	----
Al_2O_3	26.93	----
CO_2	0.11	----
H_2O	27.88	21.08
$CaSO_4$	----	78.92
Mole ratios, CaO/Al_2O_3	3.007	----
CO_2/Al_2O_3	0.009	----
H_2O/Al_2O_3	5.859	----
$H_2O/CaSO_4$	----	2.018
Mole ratios of compounds (to Al_2O_3):		
$3CaO\cdot Al_2O_3\cdot 5.859H_2O$	1.000	----
$CaCO_3$	0.007	----
CO_2	.002	----
Heat of solution of the reactant, $-\Delta H$ kcal. per mole	$139.16_3\pm 0.12$	-5.685 ± 0.03
cal. per gram	$370.35_1\pm 0.33$	$-32.95_5\pm 0.17$

In figure 1, the heats of solution of both series of samples are plotted against the water contents. The inset in figure 1 is an enlargement of the 30 to 33 H_2O portion of the main curve.

The heat capacities obtained in the calorimeter calibrations are listed in table 4.

The heats of solution of the reactants, $3CaO\cdot Al_2O_3\cdot 5.859H_2O$ and $CaSO_4\cdot 2.018H_2O$, are shown in table 5.

Correction for Impurities

The calculated water contents and heats of solution were obtained on the assumption that that the impurities present were calcium hydroxide, calcite, gypsum ($CaSO_4\cdot 2H_2O$), and hydrated alumina ($Al_2O_3\cdot 3H_2O$). These assumptions are based on the equilibrium studies of Jones and of D'Ans and Eick [10, 11, 12] and the following additional observations.

The microscope showed small quantities of calcite in samples *A*, *B*, and *F*, roughly in proportion to the relative quantities calculated by chemical analysis. It was particularly noted that the visibility of the needles of calcium trisulfoaluminate under crossed Nicols was also roughly proportional to the $CaCO_3$ calculated from chemical analysis, and appeared to be caused by the entrapment of minute particles of calcite in the needle clusters or possibly by the growth of these clusters on the calcite grains. The strong calcite line at 3.035 A was observed in the X-ray patterns.

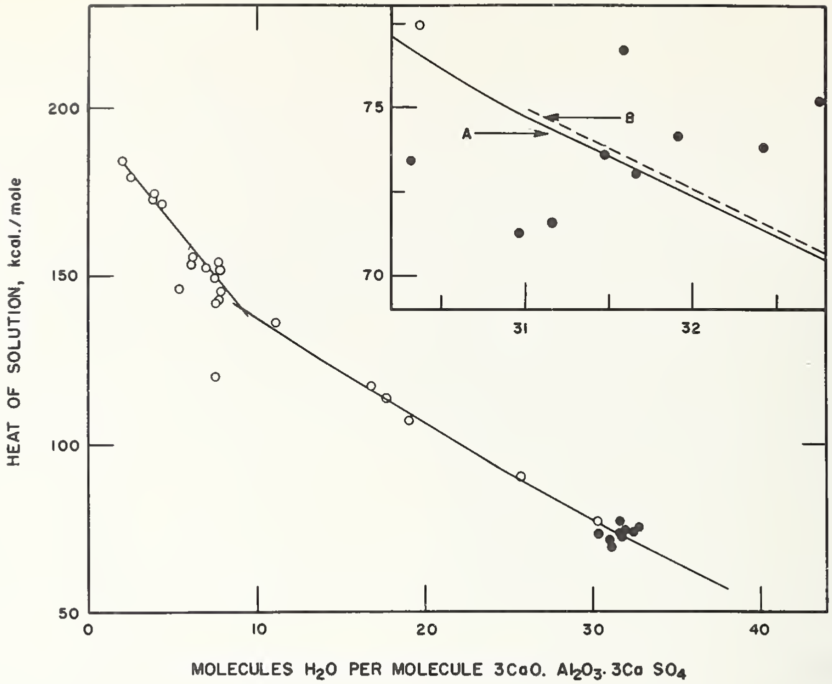

FIGURE 1. *Variation of the heat of solution of* $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O$ *with its water content,* n.

The inset is a representation of 30–33H_2O area on an expanded scale, with the same units as in the large figure.

● Closed circles represent all the preparations containing 30–33H_2O except sample H.

○ Open circles represent sample H and the dried samples obtained from sample H.

Although it could have been a possible sulfoaluminate line at 3.034 A, the deviation of this line in each pattern from 3.034 A was greater (or in the opposite direction from) the deviation of the rest of the observed pattern from the calculated lines. The presence of calcium monocarboaluminate, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$, had been suspected, but the main lines of this compound (reported by Turriziani and Schippa at 7.74 and 3.79 A [16] and by one of the authors of this paper at 7.57 and 3.78 A [17]) were not stronger than the pattern background and no plates or edge views of the monocarboaluminate were visible in the microscope. Mixed samples of the trisulfoaluminate and the monocarboaluminate were prepared in which no tendency to form solid solution was observed, although the possibility of solid solution to a small extent is not precluded.

Although $Al_2O_3 \cdot 3H_2O$ was not identified in the microscope except possibly as small, irregular, opaque particles, the X-ray line at 4.85 to 4.90 A in the various patterns was a poor fit with the rest of the sulfoaluminate pattern (as compared with the calculated pattern), and is considered to be a line of hydrated alumina [10]. In the heat-of-solution experiments, an opalescent undissolved residue was observed in those samples in which the analysis indicated free alumina, roughly proportional to the quantity calculated. The residue from one heat-of-solution determination of sample *F* was filtered and ignited, and found to be close to the weight expected from ignition of the quantity of $Al_2O_3 \cdot 3H_2O$ calculated as an impurity in the sample.

The X-ray line at about 8.85 to 9.09 A in the three patterns could be attributed to the presence of calcium monosulfoaluminate, $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$, which has a strong line at 8.99 A [8]. It has been attributed instead to the 101 plane of the trisulfoaluminate, calculated as 8.86 A from Fratini's unit cell parameters. The strong line of the monosulfoaluminate at 4.48 A is absent from the patterns and the presence of this compound is doubtful.

In the two instances where the CO_2 content of the sample was insufficient to account for all the excess CaO (samples *B* and *D*), the latter was calculated to $Ca(OH)_2$. When excess SO_3 and CaO was present (samples *D*, *J*, and *K*), $CaSO_4 \cdot 2H_2O$ was assumed to be present. Although no X-ray or optical evidence was found for these two compounds (their major X-ray lines conflict with those of the sulfoaluminate), both assumptions are in accordance with phase equilibrium data.

Carbon dioxide in excess of the quantity required to form $CaCO_3$ was taken as free CO_2. This assumption is discussed later in connection with speculation on the possible constitution of the sulfoaluminate hydrate.

The small quantity of SiO_2 in sample *B* (0.03 mole per mole Al_2O_3) is probably due to the long period of digestion of the precipitate and alkaline mother liquor in a glass container (9 mo). Some of the CaO in this sample, which has been attributed to $CaCO_3$ and $Ca(OH)_2$, may be present as a calcium silicate. Inasmuch as there are many possible compositions for calcium silicate hydrates, the correction in this case would be uncertain. A calculation based on the simple composition $CaO{\cdot}SiO_2{\cdot}H_2O$ shows that the change in the corrected heat of solution would be small, only 0.09 calories per gram or 0.13 kilocalories per mole of sulfoaluminate.

It should be noted that the calculated standard deviation for the molar content of minor impurities is obtained from the standard deviation of the content of major oxides. For this reason, the calculated quantity of a minor constituent is on occasion less than its standard deviation.

The calculation of the composition of a sample and of the heat of solution of the pure sulfoaluminate present in a sample is shown in the appendix, with sample *A* as the example.

Heat of Solution of the Trisulfoaluminate

It is evident from table 1 and figures 1 and 2 that there is considerable scatter both in the heat of solution and in the water content of the various preparations, even after correction for the impurities. This scatter is evident in individual determinations on each sample as well. The following sources of scatter may be summarized:

(a) Variations in chemical composition and water content within each sample. This source was evident in the chemical analysis, particularly in SO_3 determinations.

(b) Variations in chemical composition between samples. The correction for impurities may be incomplete, particularly for interaction between impurities and for the effect of CO_2 in those samples which contained an appreciable quantity. Figure 2, in which the corrected heat of solution in calories per gram has been plotted against the weight percent purity, shows that even after correction there is a residual scatter which seems to decrease as 100 percent purity is approached.

(c) The small heat of solution of the compound, which produces a rise of only 0.1 °C in the calorimeter. Although the temperatures can be read to the nearest 0.00004 °C, the accumulation of experimental errors in the calculation of corrected temperature rise is capable of producing uncertainties of 0.5 percent for the 0.1 °C rise.

(d) A residual variation, even among samples low in impurities and especially low in CO_2, as in samples *A*, *B*, *D*, and *F*, which is difficult to explain.

Figure 1 indicates that, for one sample (*H*), the heat of solution decreases in a continuous manner with increase in the H_2O content in the 2 to $8H_2O$ range. There appears to be a discontinuity at about $8H_2O$ and then a continuous decrease in the 9 to $33H_2O$ range. The 7 to $9H_2O$ region is where most investigators postulate the appearance of a definite hydrate, the structure of which differs from that of the 30 to $33H_2O$ compound. Forsén's hydrate [7] is at $7.5H_2O$, obtained by drying over P_2O_5. Lefol's [5] is at 6.5 to $8H_2O$, depending on ambient water vapor pressure. With the electron microscope Astreeva and Lopatnikova [6] have observed the delayed change in structure with removal of water, but do not state the water content at which it occurs. Drying experiments made in this laboratory resulted in a drop in water content to about $20H_2O$ for 60 °C, $8H_2O$ for 110 °C, $6H_2O$ for 145 °C, 2 to $3.5H_2O$ for 200 °C, in general agreement with Lefol's data. The X-ray diffraction pattern for a sample containing $23.0H_2O$ was almost identical to the pattern for the $32H_2O$ sample except for an increase in the intensity of the line in the vicinity of 3.49 A. Patterns for samples at 11.3 and $8.3H_2O$ were different, however. The intense 9.8 A and 5.6 A lines had disappeared and new lines appeared at 7.7 A and 6.1 A. For samples containing 6.6 and $5.3H_2O$, the largest *d*-spacing dropped still farther to $7.4H_2O$. These results agree well with Lefol's concept of a definite hydrate at 6.5 to $8H_2O$ and also with his suggestion of an intermediate hydrate between 8 and $30H_2O$. Samples ignited to $0H_2O$ showed their most intense line at 3.5 A, probably indicating $CaSO_4$ (anhydrite), and included no lines above 5 A.

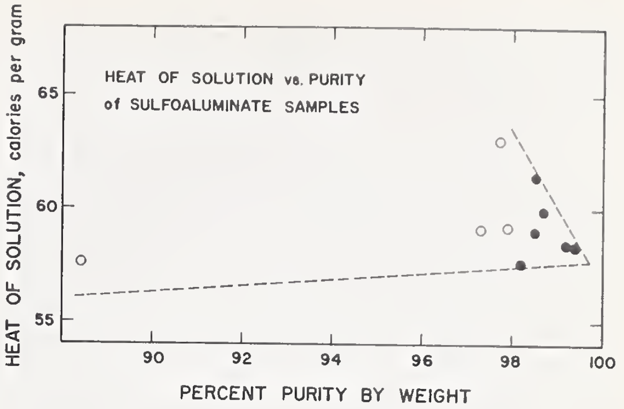

Figure 2. *Relationship between heat of solution of the preparations and purity.*

● Closed circles represent samples included in the average.
○ Open circles represent samples not included in the average.

The inset in figure 1, which is an expansion of the main part of the figure in the 30 to $33H_2O$ region, shows no readily apparent trend for the heat of solution versus nH_2O in that range. The scatter among the preparations, however, is probably responsible for this condition. From the main portion of the figure, the slope of the curve for sample *H* in the 31 to $33H_2O$ range is −2.49 kilocalories per mole per mole H_2O. Line *A* in the inset represents this slope and the position of the curve for sample *H* transferred to the expanded figure. It is reasonable to suppose that the slope for each preparation is the same as for sample *H*, but that the curve is displaced vertically in each case. For this reason, the average heat of solution and the average H_2O content of the preparations have been calculated, and from this pair of values a curve of heat of solution versus nH_2O has been drawn with the same slope as for sample *H*.

To eliminate a major source of error, only the results for the purest preparations have been included in the average. As already stated, there is still a residual dependence of the heat of solution on purity. The uncertainty of the CO_2 correction (see the calculation in the appendix) also made it desirable to include all the samples with low CO_2 content in the average. Two pairs of averages were calculated, one set for the four preparations low in CO_2 (samples *A*, *B*, *D*, and *F*), and one set which includes two additional samples of equally high purity by weight (samples *C* and *E*). The averages for the first set are 73.62±1.13 kilocalories per mole and 31.66 moles H_2O; for the second set 73.59±0.72 and 31.41. (For all ten samples, the averages are 73.86±0.62 and 31.46.) The value $-\Delta H=73.60$ kilocalories per mole at 31.54 moles H_2O was assigned to the sulfoaluminate, with a slope of -2.49 kilocalories per mole per mole change in H_2O content in the 31 to $33H_2O$ range. Line *B* in the inset of figure 1 represents this slope and average for the heat of solution versus nH_2O.

The heat of solution of $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$ is then $-\Delta H=74.94$ kilocalories per mole, and the figure for $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$ is 72.45 kilocalories per mole.

Heat of Formation of the Product From the Reactants

The heat of the reaction

$$3CaO\cdot Al_2O_3\cdot 5.859H_2O+3(CaSO_4\cdot 2.018H_2O) +19.087H_2O\rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O \quad (2)$$

or

$$3CaO\cdot Al_2O_3\cdot 5.859H_2O+3(CaSO_4\cdot 2.018H_2O) +20.087H_2O\rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O \quad (3)$$

is calculated from the heats of solution of the reactants and product as follows:

For equation (2):

$$3CaO\cdot Al_2O_3\cdot 5.859H_2O+1438.666(HCl\cdot 26.614H_2O) \rightarrow 3CaCl_2+2AlCl_3+1426.666(HCl\cdot 26.846H_2O) \quad -\Delta H=+139.163 \text{ kilocalories} \quad (4)$$

$$3(CaSO_4\cdot 2.018H_2O)+1426.666(HCl\cdot 26.846H_2O) \rightarrow 3CaSO_4+1426.666(HCl\cdot 26.850412H_2O) \quad -\Delta H=-17.054 \text{ kilocalories} \quad (5)$$

$$3CaCl_2+2AlCl_3+3CaSO_4 +1426.666(HCl\cdot 26.863791H_2O) \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O +1438.666(HCl\cdot 26.614H_2O) \quad -\Delta H=-74.94 \text{ kilocalories} \quad (6)$$

$$1426.666(HCl\cdot 26.850412H_2O)+19.087H_2O \rightarrow 1426.666(HCl\cdot 26.863791H_2O) \quad -\Delta H=+0.303 \text{ kilocalorie} \quad (7)$$

The heat of formation is the sum of the heat effects of eqs (4), (5), (6), and (7), or $-\Delta H=47.472$ kilocalories per mole $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$.

By a similar calculation, the heat of formation in eq (3) is $-\Delta H=49.978$ kilocalories per mole $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$.

Correction for the Water Content of the $3CaO\cdot Al_2O_3\cdot 5.859H_2O$ and the $CaSO_4\cdot 2.018H_2O$

These corrections are found by adding to the heat of reaction for eqs (2) or (3) the heat of the following reactions:

$$3CaO\cdot Al_2O_3\cdot 6H_2O\rightarrow 3CaO\cdot Al_2O_3\cdot 5.859H_2O +0.141H_2O \quad (8)$$

$$3(CaSO_4\cdot 2H_2O)+0.054H_2O\rightarrow 3(CaSO_4\cdot 2.018H_2O). \quad (9)$$

These are very small corrections, approaching the precision of the measurements. The error in the heat of eq (8) will be small if the heat of the reaction is assumed to be 0.141/6.00 times the heat of hydration of anhydrous $3CaO\cdot Al_2O_3$ to the hexahydrate.

Thorvaldson, Brown, and Peaker [13] have reported the heat of this hydration to be $-\Delta H=214$ calories per gram (or 57.8 kilocalories per mole) of $3CaO\cdot Al_2O_3$ at 20 °C. In the absence of data indicating a difference in the heat capacities of the hydrate and anhydrous $3CaO\cdot Al_2O_3$, the effect of transforming this value from 20 to 25 °C and from 20° calories to thermochemical calories may be considered negligible. The calculated correction is therefore $-57.8\times 0.141/6.00$ or -1.36 kilocalories per mole $3CaO\cdot Al_2O_3$.

Assuming the analysis of the gypsum to be accurate, the correction for gypsum may be calculated from its heat of solution in water. The correction for eq (9) calculated on this basis is negligible, only -0.0009 kilocalorie.

If these corrections are applied, the heat of formation of $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$ from $3CaO\cdot Al_2O_3\cdot 6H_2O$, $CaSO_4\cdot 2H_2O$, and additional H_2O (eq 1) is $-\Delta H=47.472-1.36$ or 46.11 kilocalories per mole. For $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$, the corrected value is 48.62 kilocalories per mole.

Heat of Formation

The heat of formation of the calcium sulfoaluminate is the sum of the heat effect of eq (1) and the heats of formation of the reactants in that equation [4], and is calculated as follows:

$\Delta H_f^\circ\ 3CaO\cdot Al_2O_3\cdot 6H_2O = -1329.$[5] kilocalories
$\Delta H_f^\circ\ 3(CaSO_4\cdot 2H_2O) = -1449.18$ kilocalories
$\Delta H_f^\circ\ 19H_2O = -1298.03$ kilocalories
$\Delta H\ 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$ from these reactants $= -46.11$ kilocalories

$\Delta H_f^\circ\ 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O = -4122.$ kilocalories per mole.

By a similar calculation, the heat of formation of $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$ is $\Delta H_f^\circ = -4193$ kilocalories per mole. The calculated uncertainty of each of these results, based on a standard deviation for the heat of solution of 0.72 kilocalorie per mole for the sulfoaluminate, 0.12 for the $3CaO\cdot Al_2O_3\cdot 5.859H_2O$, and 0.09 for the $CaSO_4\cdot 2.018H_2O$, is 0.74 kilocalorie per mole. This value does not include the uncertainty in the heat of formation of the reactants, which is certainly of the order of 1 kilocalorie per mole for the hydrated calcium aluminate, nor the uncertainties due to the chemical analyses.

Role of Carbon Dioxide

Several of the preparations contained more CO_2 by chemical analysis than that equivalent to the CaO available to form $CaCO_3$, unless a lower percentage of $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot nH_2O$ and large quantities of hydrated alumina and gypsum were assumed to be present. The oxide ratios, however, were in all cases close enough to the stoichiometric ratios for calcium trisulfoaluminate to make assumption of free CO_2 more reasonable. Microscopic examination generally indicated the preponderance of the sulfoaluminate needles.

The presence of more CO_2 in complex calcium compounds than can be accounted for as $CaCO_3$ is not unusual. Gaze and Robertson report the same observation in calcium silicate hydrate (tobermorite) [18] and express the opinion that CO_2 may enter the inter-layer spacings in the crystal structure. The variation in the water content of the trisulfoaluminate without change in structure as reported by different authors [5, 6, 7] and observed in this work shows that this structure can accommodate additional molecules. It is possible that CO_2 may play a role similar to that of H_2O. The related compound, $3CaO\cdot Al_2O_3\cdot CaCO_3\cdot 11H_2O$, shows some tendency for the sum of H_2O and free CO_2 to be constant, although such a tendency was not observed in these sulfoaluminate preparations.

If it is assumed that the free CO_2 found in the preparations is part of the molecule rather than an impurity, there is no change in the calculated heat of solution in terms of kilocalories per mole. There is a change, however, in the heat of solution in terms of calories per gram and in the relative purity of the preparations. The effect of purity on heat of solution in this instance is shown in figure 3. The heats of solution tend to congregate about the limiting lines of the diagram, instead of spreading more or less uniformly between them as in figure 2. If the six purest preparations in figure 3 (samples *C*,

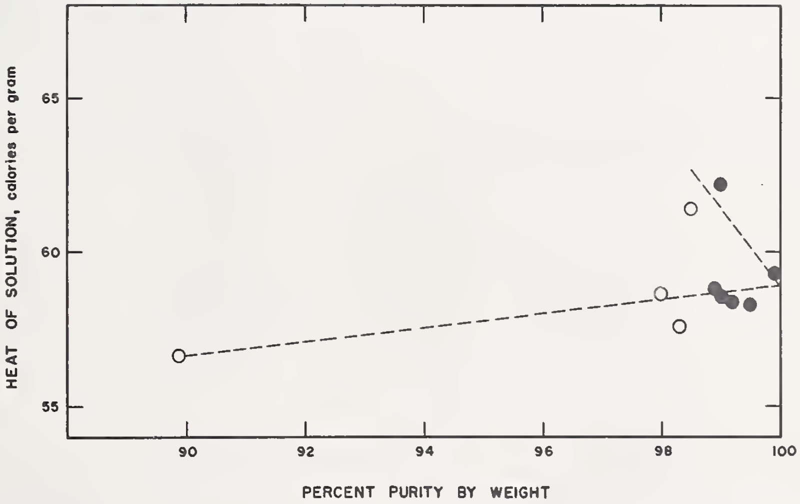

FIGURE 3. *The same plot as in figure 2, but with residual CO_2 included in the sulfoaluminate molecule.*

The samples, and their corresponding purities based on this calculation, are:

C—99.9%
A—99.5
B—99.2
G—99.0 (58.60 cal/g)
H—99.0 (62.23 cal/g)

E—98.9%
D—98.5
F—98.3
J—98.0
K—89.9

● Closed circles represent samples included in the average for this calculation.
○ Open circles represent samples not included in the average.

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[5] In accordance with established practice, exothermic heats of formation are negative. For convenience of tabulation, exothermic heats of solution and reaction were considered positive in the earlier portion of this paper.

A, B, G, H, and *E,* in descending order of purity) are used to calculate the average heat of solution, the result is 74.35 kilocalories per mole and 31.69 molecules of combined H_2O and CO_2. It is not certain whether these results or the arrangement of figure 3 are significant, but it appears that more investigation concerning the role of CO_2 in the complex calcium aluminate salts is desirable. Regardless of the effect of CO_2, however, the heat of solution of 73.60 kilocalories per mole for the 31.54 H_2O hydrate calculated above, as well as the heats of formation obtained from this value, should be considered more representative of the pure compound because it was obtained largely from compounds low in CO_2 content.

Appendix

Calculation of the Impurities, H_2O Content, and Heat of Solution of a Preparation of Calcium Trisulfoaluminate

Sample A

From the mole ratios of the oxides (table 1), the mole ratio of $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot nH_2O$ to Al_2O_3 is taken (in this case) as ⅓ the mole ratio SO_3/Al_2O_3, or 0.986, of which the equivalent CaO is 5.916 and the equivalent Al_2O_3 is 0.986. The excess CaO $(5.957 - 5.916=0.041)$ is calculated to 0.041 mole $CaCO_3$, which accounts for 0.041 mole CO_2. The remaining CO_2 (0.017) is taken as free CO_2. The remaining Al_2O_3 (0.014) is assigned to $Al_2O_3\cdot 3H_2O$. The H_2O in the $Al_2O_3\cdot 3H_2O$ (0.042 mole) is subtracted from the total H_2O to obtain 31.213 moles H_2O per mole Al_2O_3 or $31.213/0.986=n=31.656$ moles H_2O per mole $3CaO\cdot Al_2O_3\cdot 3CaSO_4$.

The heat of solution of each impurity is multiplied by its weight per mole Al_2O_3, the total subtracted from the product of the heat of solution of the sample and the total weight of the sample per mole Al_2O_3. This result divided by the mole ratio of sulfoaluminate to Al_2O_3 is the heat of solution of the sulfoaluminate present in calories per mole; if this quotient is further divided by the formula weight of the sulfoaluminate, the heat of solution is obtained in calories per gram. Thus, for sample *A:*

0.986 mole $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31.656H_2O$ $\times 1248.93=1231.445$ grams
0.041 mole $CaCO_3$ $\times$ $100.09=$ 4.104 grams
0.014 mole $Al_2O_3\cdot 3H_2O$ $\times$ $156.01=$ 2.184 grams
0.017 mole CO_2 $\times$ $44.01=$ 0.748 gram

Total weight of sample per mole Al_2O_3 $=1238.481$ grams
Total heat of solution per mole Al_2O_3 $=$ 58.289 cal/g$\times$1238.481 $=72{,}189.8$ calories
Heat of solution of $CaCO_3=4.104\text{g}\times$ 83.72 cal/g $=$ 343.6 calories
Heat of solution of $Al_2O_3\cdot 3H_2O$ and of CO_2 $=$ 0.0 calorie

Net heat of solution of sulfoaluminate per mole Al_2O_3 $=71{,}846.2$ calories
Net heat of solution per mole sulfoaluminate

$$=\frac{71{,}846.2}{0.986}=72{,}866 \text{ calories}$$

Heat of solution of the sulfoaluminate per gram

$$=\frac{71{,}846.2}{1231.445}=58.343 \text{ calories}$$

The heat of solution of the $Al_2O_3 \cdot 3H_2O$ was taken as zero because it did not go into solution. The physical and chemical state of the CO_2 is uncertain and no heat of solution is therefore included, but its weight is taken into account. If it escapes into the air, its heat contribution is minor; but if it dissolves, the contribution is about 57 calories per gram, a correction which, in the case of sample *A*, amounts to only 0.04 kilocalorie per mole and is within the precision limits of the heat-of-solution determination. The heat of solution of $Ca(OH)_2$ was taken from the work of Wells and Taylor [19], corrected for the fact that their figures were in calories per gram CaO. The value used for the heat of solution of $CaCO_3$ is the result of a recent redetermination of this quantity in this laboratory, to be reported more fully in a pending publication [20].

The authors acknowledge with thanks the help of Howard E. Swanson and coworkers, who made the X-ray diffraction measurements, and R. M. Senior, who performed much of the early calorimetric work and prepared the dehydrated samples.

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Paper III-S2. The Composition of Ettringite in Set Portland Cement*

H. G. Midgley and D. Rosaman

Synopsis

X-ray powder diffraction patterns and differential thermograms of synthetic calcium sulfo- and hydroxyaluminate hydrates of known chemical composition were recorded and compared with the X-ray spacings and peak temperatures of the "ettringite" phase in set portland cement.

Using the calibration curves for X-ray spacing and normalized peak temperature obtained from the synthetic compounds, the composition of the "ettringite" phase in setting portland cements has been determined.

For three cements it was found that the phase first precipitated was very near to the pure calcium sulfoaluminate hydrate composition, but as the cements were stored for longer periods the composition changed, the solid solution containing more of the calcium hydroxyaluminate hydrate.

Résumé

L'exposé présente des diagrammes de diffraction des rayons X à travers de la poudre et des thermogrammes différentiels d'hydrates synthétiques de sulfo- et hydroxy-aluminate de calcium de composition chimique connue. Ils sont ensuite comparés aux espacements des rayons X et aux températures des crochets des courbes pour la phase "ettringite" dans le ciment Portland pris.

La composition de la phase "ettringite" dans des ciments Portlands en train de prendre est déterminée par des courbes d'étalonnage pour l'espacement des rayons X et la température normalisée du crochet obtenue à partir des composés synthétiques.

On trouva que pour trois ciments la phase précipitée d'abord était très proche de la composition du sulfo-aluminate de calcium hydraté pur. Mais à mesure que les ciments étaient conservés pendant de plus longues périodes, la composition changeait et la solution solide contenait une plus forte proportion d'hydrate d'hydroxy-aluminate de calcium.

Zusammenfassung

Röntgendiagramme von Pulvern und Differentialthermogramme der synthetischen Kalzium-Sulfo- und Hydroxyaluminathydrate bekannter chemischer Zusammensetzung wurden aufgezeichnet und mit den Röntgenbeugungslinien und den Spitztemperaturen für die sogenannte Ettringitphase im abgebundenen Portlandzement verglichen.

Bei Anwendung der Eichkurven für die Röntgenbeugungslinien und der normalisierten Spitztemperaturen der synthetischen Verbindungen war man in der Lage, die Zusammensetzung der sogenannten Ettringitphase im abbindenden Portlandzement zu bestimmen.

In drei Zementen wurde gefunden, daß die zuerst präzipitierende Phase beinahe die Zusammensetzung des reinen Hydrats des Kalziumsulfoaluminats hat, daß aber, wenn die Zemente für längere Zeiten abgelagert wurden, die Zusammensetzung sich verändern würde, sodaß die feste Lösung mehr Hydrat des Kalziumhydroxylaluminat enthält.

Introduction

The mineral ettringite occurs in set portland cement as a result of the reaction between the hydrating calcium aluminates and the calcium sulfate. It was first observed by Candlot, and since it is formed in large quantities during the destructive attack of sulfate solutions on cement mortars and concretes it has been called the "cement bacillus." The usually accepted formula for ettringite is $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, although Kalousek [1][1] has suggested that there is a solid solution between $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot aq.$ and $3CaO \cdot Al_2O_3 \cdot 3Ca(OH)_2 \cdot aq.$ and a solid solution between the "low sulfate" sulfo-aluminate $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot aq.$ and $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot aq \cdot$ Of these compounds $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot aq.$, $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot aq.$, and $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot aq \cdot$ are well established. $3CaO \cdot Al_2O_3 \cdot 3Ca(OH)_2 \cdot aq.$ was first described by Flint and Wells, [2] who did not give any X-ray powder data but described it as having a pattern indistinguishable from that given by $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot aq.$

It had been noticed by the present authors that the X-ray pattern given by the ettringite phase in set portland cement mortars and concretes had *d* values a little lower than those for the pure calcium sulfoaluminate hydrate, and also the temperature of the differential-thermal-analysis peak was higher than for the pure compound.

This paper is a report on the investigations undertaken to find an explanation for these differences.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Building Research Station, Department of Scientific and Industrial Research, Watford, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

Methods

The two methods used in this investigation were X-ray powder diffraction and differential thermal analysis (DTA). The X-ray analyses were carried out with cylindrical Debye-Scherrer cameras, diameter 10 cm. or 11.4 cm.; the radiation used was Cobalt K alpha filtered with iron foil. The long spacing at about 9.7 A was found to be of most use.

The differential thermal analyses were carried out with ceramic crucibles, chromel-alumel thermocouples, alpha alumina as the inert substance, and a heating rate of 10±1 °C/min.

Thermograms for some of the compounds likely to be met with in this investigation are given in figure 1. The problem of specifying the temperature of the peak for each of the substances was solved in the following manner. Samples of the pure compounds were diluted with alpha-alumina, a known weight was placed in the DTA crucible and the analysis was carried out. From the thermograms it was discovered that for any one substance the following relationship between the peak area and the peak temperature existed; $T=a+b \ln A$, where T is peak temperature in °C, a and b are two arbitrary constants, and A is the area of the peak. This means that peak temperatures may be compared in relation to some arbitrary area; for this investigation 1,000 sq mm was used, and the corresponding temperature is called the normalized peak temperature. The results for the compounds met with in this investigation are given in figure 2, from which it may be seen that an unknown substance present in a mixture at an unknown concentration may be identified by finding on which of the curves it lies.

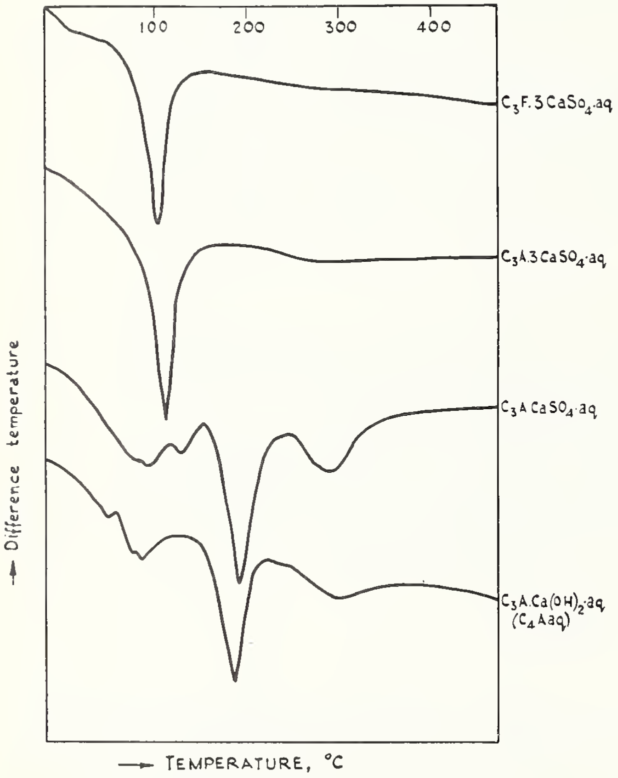

FIGURE 1. *Differential thermograms of pure calcium aluminate salt hydrates*

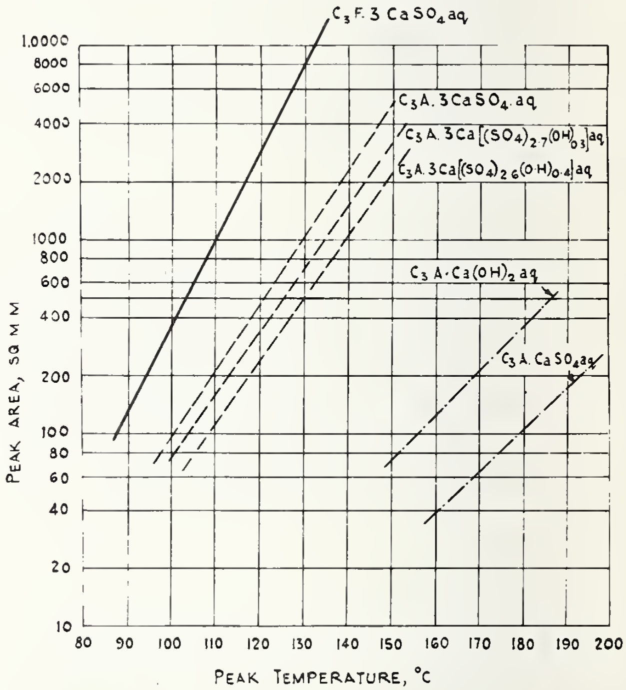

FIGURE 2. *Peak area and peak temperature for calcium sulfo- and hydroxyaluminate hydrates*

Portland Cements

TABLE 1. *Normalized peak temperature and d value of long spacing of ettringite phase in set portland cement cured at 18 °C in water*

Age	1 day	7 days	14 days	28 days	3 mo.	6 mo.
Normalized peak T °C	136	144	149	152	156	156
d A	9.75	9.75	9.73	9.67	9.65	9.63

A series of DTA and X-ray examinations of a set portland cement of different ages was carried out. From a series of DTA's of different dilutions, the set of curves given in figure 3 was obtained.

The normalized peak temperatures of ettringite for a series of set portland cements stored at 18 °C in water are given in table 1.

The normalized peak temperature of ettringite is shown to increase with age of storage. This change in peak temperature could be caused by two factors: by a change in the grain size of the ettringite crystals, or by a change in the composition of the ettringite phase. X-ray powder-diffraction analyses of the same cements gave the *d* values for the longest spacing as in table 1. This result would seem to support the view that there is a change in composition of the ettringite solid solution. It has not been possible to separate the ettringite phase from the cement, so analysis was impossible. An attempt was therefore made to discover the identity of the solid solution responsible for the change in the X-ray pattern. The compounds investigated included $C_3F{\cdot}3CaSO_4{\cdot}aq.$, $C_3A{\cdot}CaSO_4{\cdot}aq.$, and $C_4A{\cdot}aq.$ The normalized peak temperature (from figure 2) and the *d* values are given in table 2.

Table 2

Compound	Normalized peak temperature	*d*
	°*C*	*A*
$C_3F{\cdot}3CaSO_4{\cdot}32H_2O$	111	9.78
$C_3A{\cdot}CaSO_4{\cdot}12H_2O$	224	8.95
$\beta C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$	200	7.94

None of these compounds fitted the data given by the ettringite solid solutions in set portland cement.

Another possible compound is $C_6A{\cdot}aq.$ (or $C_3A{\cdot}3Ca(OH)_2{\cdot}aq.$) which may be regarded as ettringite having all its sulfate ions replaced by hydroxyl ions. This compound was first described by Flint and Wells [2] who said that its X-ray pattern was almost indistinguishable from that of ettringite, although they gave no detailed X-ray or DTA data.

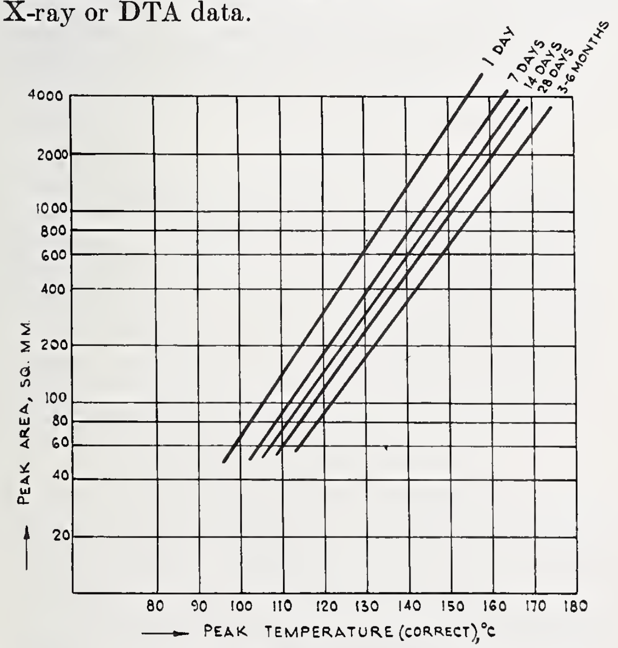

Figure 3. *Plot of peak area vs. peak temperature of ettringite in cement No. 555*

All attempts by the present authors to prepare this compound were unsuccessful.

Attempts were also made to prepare members of the solid solution $C_3A{\cdot}3CaSO_4{\cdot}aq.$-$C_3A{\cdot}3Ca(OH)_2{\cdot}aq.$ by preparing a lime-sugar solution containing 16.6 g CaO/l, adding 1.45 g and 0.38 g of gypsum respectively to two separate 450-ml portions and then adding 450 ml of calcium aluminate solution to each. The calcium aluminate solution was prepared by shaking 10 g of "Secar 250" white high-alumina cement with 1 liter of air-free distilled water for 24 hrs at 25 °C. The filtered solution gave the following analysis; 1.026 g CaO/l and 1.815 g Al_2O_3/l. After shaking the reactants in polyethylene bottles for 7 days, the white precipitate was filtered off and chemically analyzed. Differential thermograms and X-ray powder-diffraction patterns of each solid were recorded after the solids had been stored over saturated ammonium sulfate (R.H. 81 percent) for one week. The two compounds E and F produced the following data: (table 3).

Table 3

Component	Molar ratios		
	E	F	Ettringite (theoretical)
CaO	5.50	5.96	6.0
Al_2O_3	1.00	1.00	1.0
SO_3	2.58	2.72	3.0
X-ray diffraction, *d*A			
	9.70	9.75	9.75
Normalized peak temperature, °C			
	140	135	130

These results indicate that there is a solid solution, at least part of the way, between $C_3A{\cdot}3CaSO_4{\cdot}aq.$ and $C_3A{\cdot}3Ca(OH)_2{\cdot}aq.$

A relationship between the normalized peak temperatures and composition of these pure compounds can be obtained, figure 4. From this relationship the formula of a solid solution of unknown composition may be inferred from the differential thermogram. To check the validity of this assumption, the composition of six "ettringites" in a setting portland cements were obtained in this manner; the values of the long spacing on the X-ray diffraction pattern were also obtained. The results of change in X-ray *d* value and composition are given in figure 5 and are in reasonable agreement, indicating that the composition given by DTA cannot be very far out.

This method of obtaining the compositions of the "ettringite" phase in setting portland cement has been carried out on three cement types; a) normal 545, b) rapid hardening 549, and c) sulfate resisting 555. The results of this composition determination in relation to the age of the set cement are given in figure 6.

All samples show the same trend; the ettringite first produced is nearest to the pure sulfate end member, but with increasing time of hydration the ettringite phase becomes more substituted by hydroxy end member.

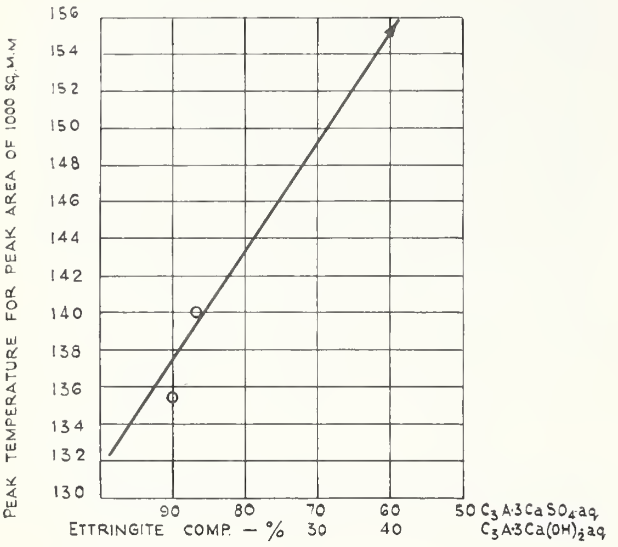

FIGURE 4. *Relationship between normalized peak temperature of endotherm and composition of ettringite solid solution.*

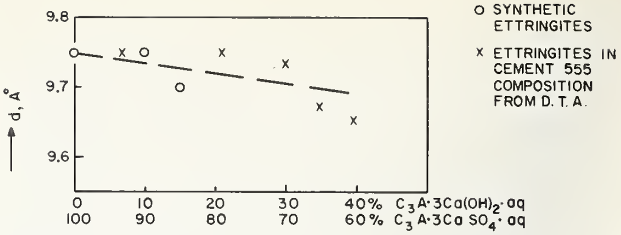

FIGURE 5. *Relation of d value for longest spacing of ettringite solid solutions to composition.*

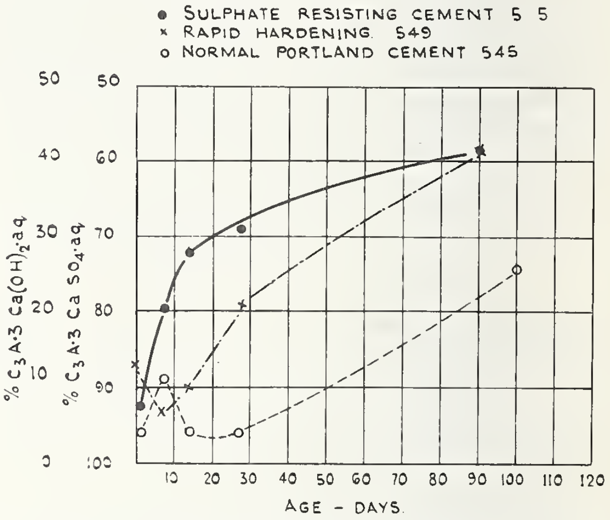

FIGURE 6. *Change in composition of ettringite composition with age of set portland cements.*

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Paper III–S3. The Temperature Coefficient of the Rate of Hydration of β-Dicalcium Silicate*

John H. Taplin

Synopsis

A synthetic preparation of β-C_2S was hydrated at 25 and 43 °C. Possible rate-determining processes are discussed by using the particle-size distribution and assuming spheres. It is found that, except for the initial part of the reaction, a rate-determining process involving the transport of material through the hydration products is more consistent with the observed kinetics than is a process at the β-C_2S surface. The apparent activation energy is 18 kcal/mole.

Résumé

On a procédé à l'hydration à 25 et 43 °C d'une préparation synthétique de β-C_2S. Discussion est faite des méthodes possibles pour déterminer la vitesse, au moyen de la distribution par dimensions des particules et en supposant qu'elles soient sphériques. Il en résulte que, exception faite pour la partie initiale de la réaction, une méthode de détermination de la vitesse impliquant le transport de matériaux à travers les produits d'hydration est plus logique par rapport à la cinétique observée que ne l'est une méthode à la surface de β-C_2S. L'activation apparente de l'énergie est de 18 kcal/mole.

Zusammenfassung

Ein synthetisch hergestelltes β-C_2S wurde bei 25 und bei 43 °C hydratisiert. Die Prozesse, die möglicherweise die Geschwindigkeit bestimmen, werden an Hand von Teilchengrößenbestimmungen besprochen, wobei es angenommen wird, daß die Teilchen kugelförmig sind. Es wurde gefunden, daß, mit Ausnahme des Reaktionsbeginnes, ein geschwindigkeits-bestimmender Prozeß, bei welchem ein Materialtransport durch die Hydratisierungsprodukte angenommen ist, den beobachteten kinetischen Verhältnissen besser entspricht, als ein Vorgang an der Oberfläche des β-C_2S. Die scheinbare Aktivierungsenergie ist 18 Kal/Mol.

Introduction

Brunauer and Greenberg [1][1] have discussed the temperature coefficient of the rate of hydration of C_3S and β-C_2S. The apparent activation energies of about 2 kcal/mole which they quote are much less than those obtained by us. This paper describes an experiment with a preparation of β-C_2S, which illustrates the evidence for higher temperature coefficients.

Experimental

Materials

The β-C_2S was prepared by repeated firing to 1400 °C of a stoichiometric mixture of calcium carbonate and precipitated silica, together with 0.5 percent of boric oxide. The preparation gave a negative result when tested for free lime by White's reagent. At least 95 percent of the preparation had a refractive index above 1.698.

The sand was an 18-to-25 B.S.S. mesh, washed-quartz sand from Leighton Buzzard, England.

Particle-Size Distribution

The β-C_2S was ground in a ball mill and then subjected to air elutriation and the coarse material removed. The remainder was used to make the specimens. The particle-size distribution of this material was determined microscopically using Feret's diameter [4] as the criteria of classification.

The particle-size distribution was determined in two stages. Particles less than 0.5 μ were neglected. In the first stage particles were classified into groups which had a range of 1.0 μ, starting from 0.5 μ. In this manner it was established that 1.1 percent of the material by weight had a diameter less than 2.5 μ. In the second stage particles were classified into groups with a range of 2.0 μ starting from 2.5 μ. The results of the two counts were combined, with the following result:

Mean diameter (μ)	1.5	3.5	5.5	7.5	9.5	11.5	13.5	15.5	17.5
Weight percent	1.1	8.3	17.8	20.9	12.7	13.2	8.5	13.0	4.6

The major uncertainty in this size distribution resides with the large particles. By scanning additional fields it was estimated that the 17.5 μ fraction was, if anything, overestimated.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Cement and Refractories Section, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia.

[1] Figures in brackets indicate the literature references at the end of this paper.

Specimens

All specimens were right rectangular prisms having dimensions 4×½×½ in., formed from 1:1 mortars of β-C_2S and sand. The specimens with a water/C_2S ratio of 0.27 were produced by tamping [2], and those with a water/C_2S ratio of 0.474 by casting in a steel mold.

The specimens were cured in individual stoppered tubes to which excess curing water was added as soon as the specimens started to harden. The specimens reached their curing temperature within an hour of mixing.

Strength

The compressive strength was measured by a method which has been described [3]. These strengths are quoted in units of force because the area stressed is uncertain although it is constant.

Hydration

The extent of the hydration reaction was estimated as follows. The larger fragments from the strength test were dried under vacuum and placed in a test tube. The mouth of the tube was drawn out to form a short capillary tube in order to minimize the rate of reabsorption of moisture on cooling. The tube and contents were heated to 120 °C for 22 hr and, after cooling and weighing, to 650 °C for several hours. The weight loss per gram of C_2S was corrected for the weight loss of the unhydrated C_2S (0.0059) and taken as a measure of the amount of C_2S hydrated. This measure is designated h/C. (It should not be confused with the similar but different measure, H/C, described in reference [3]).

Rate-Determining Processes

It is instructive to consider some of the possible rate-determining processes. The paste hydrations of C_3S and β-C_2S are heterogeneous reactions characterized by solid reactants which are particulate and by reaction products which form a cohesive network and occupy a greater volume than the clinker minerals. Those products which are inside or outside the original boundaries of the clinker mineral particles have been designated inner and outer products respectively [3]. The following three types of process may control the rate at some stage of the reaction: (a) the rate of transport of some substance through the inner products, (b) the rate of transport of some substance through the outer products, and (c) the rate of a reaction at the clinker-mineral surface. In each case it will be assumed that the concentrations in solution remain constant.

Resistance to Flow Through the Hydration Products

It is convenient to treat (a) and (b) type processes together for they are, perhaps, better regarded as extreme examples of a single type of process in which the rate is controlled by the rate of transport of clinker material outwards or of water inwards. In general, the specific resistance of the inner products will differ from that of the outer products, either because they are formed at different concentrations of the substance whose flow is rate-determining, or because only the inner products are formed on the clinker-mineral surface, which might influence their structure.

A mathematical treatment for an isolated spherical particle is indicated below.

r=the radius of the spherical particle.
F=the fraction of the particle reacted.
t=the curing time.
i=the specific resistance of the inner products.
o=the specific resistance of the outer products.
c=the concentration or pressure difference which drives the transport process.
η=the resistance.
ν=the ratio of the volume of the outer products to that of the inner products.

At the appropriate stages of the analysis the equations for type (a) and (b) processes will be obtained by introducing the conditions $i \gg o$ and $i \ll o$ respectively.

From the geometry of a sphere

$$\text{thickness of inner products} = r[1-(1-F)^{1/3}]$$

$$\text{thickness of outer products} = r[(1+\nu F)^{1/3}-1]$$

For a small amount of further reaction dF

increase in thickness of inner products $= r\,dF/3(1-F)^{2/3}$

increase in thickness of outer products $= \nu r\,dF/3(1+\nu F)^{2/3}$

the new layer of inner products has an area $4\pi r^2(1-F)^{2/3}$

the new layer of outer products has an area $4\pi r^2(1+\nu F)^{2/3}$.

The increase in resistance of the inner products due to the extra reaction dF is

$$d\eta_i = ir\,dF/3(1-F)^{2/3}\cdot 4\pi r^2(1-F)^{2/3}.$$

After simplifying and integrating from O to F

$$\eta_i = i[1-(1-F)^{1/3}]/4\pi r(1-F)^{1/3}$$

and similarly for the outer products

$$\eta_o = o[(1+\nu F)^{1/3}-1]/4\pi r(1+\nu F)^{1/3}.$$

The total resistance $\eta = \eta_i + \eta_o$.

The rate of reaction per unit original volume of particle is

$$dF/dt = 3c/\eta 4\pi r^3.$$

Now, the condition for process (a) amounts to $\eta \approx \eta_i$ so that for the rate controlled by the resistance of the inner products

$$dF/dt = 3c(1-F)^{1/3}/ir^2\,[1-(1-F)^{1/3}] \qquad (1)$$

and similarly for the rate controlled by the resistance of the outer products

$$dF/dt = 3c(1+\nu F)^{1/3}/or^2[(1+\nu F)^{1/3}-1]. \qquad (3)$$

Rearranging the full expression for dF/dt

$$(\eta_i+\eta_o)dF = 3cdt/4\pi r^3$$

and after integrating (assuming $F=0$ when $t=0$)

$$i[1-(1-F)^{2/3}-2F/3]+(o/\nu)[1+2\nu F/3 - (1+\nu F)^{2/3}] = 2\,c\,t/r^2.$$

After again applying our conditions for processes (a) and (b) for the rate controlled by the resistance of the inner products

$$1-(1-F)^{2/3}-2F/3 = 2ct/ir^2 \qquad (2)$$

and for the rate controlled by the resistance of the outer products

$$1+2\nu F/3-(1+\nu F)^{2/3} = 2\nu ct/or^2. \qquad (4)$$

If the particle is not isolated so that the outer products merge with the outer products of other particles, then the situation is more complicated. However, the resistance of the inner products is not affected, and provided the particles are not packed too closely the kinetics will not be very different from eq (4). For uniform spheres in cubical packing (octahedral coordination) it can be shown that, for $\nu=1$, the following relation holds approximately in place of eq (4)

$$F^2 \propto t/r^2.$$

This relation corresponds to behavior intermediate between eqs (2) and (4) and is in fact the relation applicable to a plane surface.

A Process at the Clinker Mineral Surface

If the rate depends on some process at the surface of the clinker mineral, so that the rate is proportional to the surface area, then the reaction will penetrate into particles at a constant rate.

For a sphere, if the penetration rate is K

$$dF/dt = 3K(1-F)^{2/3}/r \qquad (5)$$

and

$$1-(1-F)^{2/3} = Kt/r. \qquad (6)$$

Because eqs (1) and (3) predict an infinite rate at $F=0$ we see that a surface reaction will be slower at the very beginning of the reaction and, because of the different dependence of the rate on the radius, it will remain as the slower process for a greater fraction of the reaction if the particles are smaller.

Results and Discussion

Figure 1 is a plot of compressive strength against h/C for the water/C_2S ratio of 0.27. It is assumed that essentially the same reaction occurs at 25 and 43 °C, because the hydration products develop the same strength.

Figure 2 shows the hypothetical reaction relations for the three rate-determining processes discussed above; i.e., the rate is limited by a process at the C_2S interface, by the flow of material through the inner products, or by the flow of material through the outer products. The curves are obtained by summing the contribution of each size fraction at a particular time. It is assumed that the particles are spheres with the experimental particle-size distribution. In applying eq(4) it is assumed that $V=1$.

The curve for the rate limited by a process at the interface will plot as a straight line in the form log (1–F) against penetration distance (and consequently against time). Figure 3 is a plot of this kind. A straight line is obtained for the data at a water/C_2S ratio of 0.474 if h/C at complete hydration is assumed to be 0.20. This result can be interpreted as a penetration rate of $6\times10^{-4}\ \mu$ per hr at 25 °C. In order to obtain straight lines for the data at a water/C_2S ratio of 0.27, it is necessary to assume h/C at complete hydration is 0.17. However this rate-determining process cannot explain the influence of water/C_2S ratio.

The points in figure 2 corresponding to the rate limited by the flow of material through the outer products are close to the relationship, F^2 proportional to time. The hydration data are tested against this relationship in figure 4. A better fit is obtained by assuming an induction period of 250 hr at 25 °C. This assumption is reasonable in view of the very obvious induction periods obtained with other preparations of β-C_2S [1, 5]. Thus it appears likely that the flow of material through the hydration products does determine the rate, except at the beginning.

The apparent activation energy calculated from figure 3 or figure 4 is 18 kcal/mole. This is much greater than the 2 kcal/mole quoted by Brunauer and Greenberg [1] but more consistent with the value of 10 kcal/mole obtained by us [5] for portland cement paste. It may be significant that a value of about 10 kcal/mole is obtained by extrapolating the permeability activation energy data of Powers [6] to the porosity of cement gel (0.28).

Activation energies of above 10 kcal/mole have been obtained in this laboratory for two more preparations of β-C_2S. Two preparations of C_3S (alite composition) behaved in different ways. The temperature coefficient for the first preparation was initially very large but decreased as the reaction proceeded, eventually becoming negative. The second preparation gave a more constant temperature coefficient corresponding to an activation energy of about 10 kcal/mole.

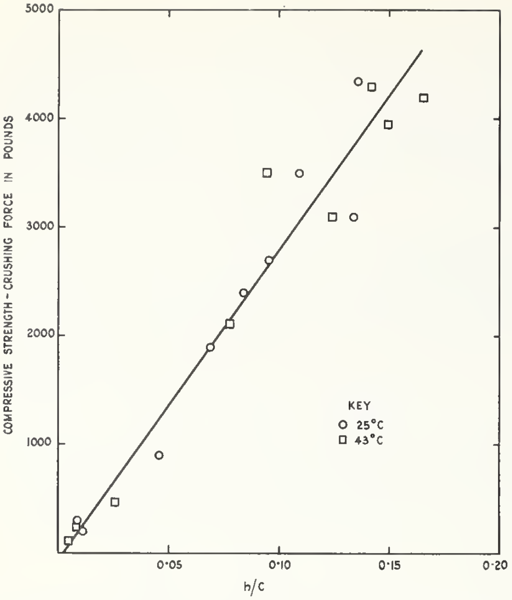

Figure 1. *Data for a water/*C_2S *ratio of 0.27 showing that the relationship between compressive strength and hydration is not affected by curing temperature.*

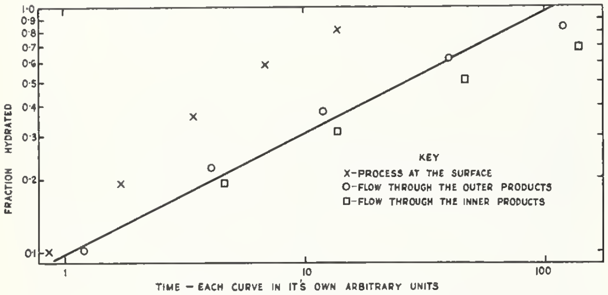

Figure 2. *A plot of log fraction reacted against log curing time.*

The fraction reacted is calculated for various hypothetical rate-controlling processes assuming spherical particles with the experimental size distribution. The straight line represents the relation: square of fraction reacted proportional to time.

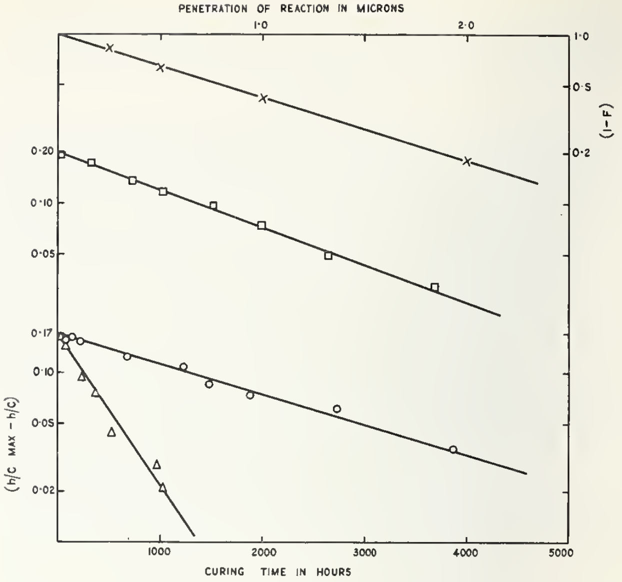

Figure 3. *Plots to test the empirical relation: log fraction not reacted, proportional to penetration distance, proportional to time.*

X=Fraction not reacted, calculated for the rate controlled by a process at the surface, assuming spherical particles with the observed size distribution.

□ Log $(0.20 - h/C)$ versus curing time for water/C_2S = 0.474 and 25 °C
○ Log $(0.17 - h/C)$ versus curing time for water/C_2S = 0.27 and 25 °C
△ Log $(0.17 - h/C)$ versus curing time for water/C_2S = 0.27 and 25 °C

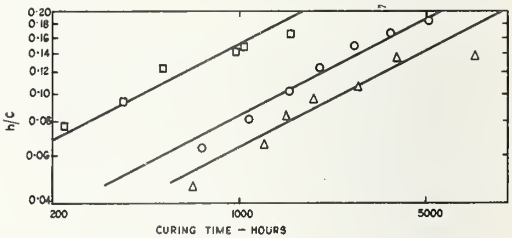

Figure 4. *The experimental data tested against the relation: square of the fraction reacted proportional to time, by plotting log* h/C *versus log time.*

△ Water/C_2S ratio of 0.474, 25 °C
○ Water/C_2S ratio of 0.27, 25 °C
□ Water/C_2S ratio of 0.27, 43 °C

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Paper III–S4. Hydraulic Properties and Hydration of Glasses of the System $CaO\text{-}Al_2O_3\text{-}SiO_2$*

F. W. Locher

Synopsis

In the ternary system $CaO\text{-}Al_2O_3\text{-}SiO_2$ some 45 glasses were melted with CaO contents between 36 and 52 percent, Al_2O_3 contents between 9 and 56 percent, and SiO_2 contents between 3 and 55 percent. Some of these glasses contained in addition 5 percent of MgO. The glasses, which had been ground to a uniform specific surface of 4000 cm^2/g, were activated with portland cement clinker (blast-furnace cement), with anhydrite (slag-sulfate cement) and with calcium hydroxide (lime-slag cement), and tested in the form of small mortar bars.

The hydraulic strengths rise with an increasing Al_2O_3 content, reach a maximum, fall sharply with a further increase in the Al_2O_3 content, and then rise again with a still higher Al_2O_3 content to a second maximum. Beyond this second maximum follows a second minimum and, in fields with less than 10 percent of SiO_2, the maximum alumina cement hardening.

The X-ray diffraction determinations of the hydrate phases showed that in glasses with medium Al_2O_3 contents gehlenite hydrate, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$, occurs as a strength-forming hydrate phase. The three maxima of hydraulic strength occurring in the ternary system $CaO\text{-}Al_2O_3\text{-}SiO_2$ are caused, therefore, by the formation of calcium silicate hydrate in the field of high SiO_2 and lower Al_2O_3 contents, of calcium aluminate hydrate in the field with low SiO_2 and high Al_2O_3 contents, and of calcium silicoaluminate hydrate (gehlenite hydrate) in the field of medium SiO_2 and Al_2O_3 contents.

In the hardened cements gehlenite hydrate is not stable but is transformed while absorbing CaO into a hydrogarnet whose composition approximately conforms to the formula $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$. The MgO content promotes this transformation.

In the hardened glasses with Al_2O_3 contents of less than 18 percent the X-ray pattern revealed only very little gehlenite hydrate in addition to slight amounts of calcium aluminate hydrate. As the lime content of the glasses is not adequate to form aluminate hydrates rich in lime it must be assumed that, irrespective of the kind of activation, the Al_2O_3 content of the glasses poorer in alumina is also bound in the gehlenite hydrate and that the errors in the determinations by the X-ray diffraction method must be attributed to the poor lattice arrangement of the gehlenite hydrate. The assumption of the formation of gehlenite hydrate in the hardening glasses and technical slags tallies with the practical behavior of the slag-bearing cements towards sulfate solutions. It could be demonstrated that gehlenite hydrate is resistant to sodium sulfate and calcium sulfate solutions, but that it disintegrates in lime-rich sulfate solutions while forming ettringite. Gehlenite hydrate is also nonresistant to magnesium sulfate solutions.

According to the results of the investigations, the effect of the activators is to contribute to the formation of a liquid phase of favorable composition out of which the dissolved constituents of the slag can be precipitated again in the form of strength-forming hydrates of various kinds. Due to the precipitation of the hydrate phases, the solvent effect of the liquid phase is retained.

Résumé

Environ 45 verres du système ternaire $CaO\text{-}Al_2O_3\text{-}SiO_2$ furent fondus, les teneurs en CaO variant de 36% à 52%, les teneurs en Al_2O_3 variant de 9% à 56%, et les teneurs en SiO_2 variant de 3% à 55%. Certains de ces verres contenaient de plus 5% de MgO. Les verres, qui avaient été pulverisés en une surface specifique uniforme de 4000 cm_2/g, furent activés avec du clinker de ciment Portland (ciment de haut-fourneau), avec de l'anhydrite (ciment de laitier sulfaté) et avec de l'hydroxide de calcium (ciment de laitier à la chaux).

La résistance hydraulique s'élève avec une augmentation de la teneur en Al_2O_3, atteint un maximum, tombe brusquement avec une augmentation supplémentaire de la teneur en Al_2O_3, et puis s'élève de nouveau à un second maximum avec une teneur encore plus forte en Al_2O_3. Au delà de ce second maximum fait suite un second minimum et, quand on a moins de 10% de SiO_2, le durcissement maximum du ciment alumineux.

Les déterminations des phases d'hydrate par diffraction des rayons X indiquèrent que dans les verres avec une teneur moyenne en Al_2O_3 un hydrate de gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$, se produit sous forme de phase d'hydrate générative de résistance. Les trois maxima de résistance hydraulique qui se produisent dans le système ternaire $CaO\text{-}Al_2O_3\text{-}SiO_2$ sont donc causés par la formation d'hydrate de silicate de calcium quand on a une forte teneur en SiO_2 et une faible teneur en Al_2O_3, d'hydrate d'aluminate de calcium avec une faible teneur en SiO_2 et une forte teneur en Al_2O_3, et d'hydrate de silico-aluminate de calcium (hydrate de gehlénite) avec des teneurs moyennes en SiO_2 et en Al_2O_3.

Dans les ciments durcis, l'hydrate de gehlénite n'est pas stable mais se transforme, tandis qu'il absorbe CaO, en un hydrogrenat dont la composition répond approximativement à la formule $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$. La teneur en MgO contribue à cette transformation.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Forschungsinstitut der Zementindustrie, Düsseldorf, Germany.

Dans les verres durcis à teneur en Al_2O_3 inférieure à 18% la diagramme aux rayons X ne révélait que très peu d'hydrate gehlénite en plus d'une légère quantité d'hydrate d'aluminate de calcium. Comme la teneur en chaux des verres n'est pas suffisante pour former des hydrates d'aluminate riches en chaux, il faut supposer que, indépendamment du genre d'activation, la teneur en Al_2O_3 des verres les plus pauvres en alumine est également trouvé dans l'hydrate de gehlénite et que les erreurs de détermination par la méthode de diffraction des rayons X doivent être attribuées a l'arrangement imparfait du réseau de l'hydrate de gehlénite. La supposition de la formation de l'hydrate de gehlénite dans les verres et laitiers techniques en train de durcir concorde avec le comportement pratique des ciments de laitier dans des solutions de sulfate. On pourrait démontrer que l'hydrate de gehlénite est résistant aux solutions de sulfate de sodium et de sulfate de calcium, mais qu'il se désintègre dans les solutions de sulfate riches en chaux, formant alors de l'ettringite. L'hydrate de gehlénite n'est pas résistant non plus aux solutions de sulfate de magnésium.

Suivant les résultats des expériences, l'effet des activateurs est de contribuer à la formation d'une phase liquide de composition favorable hors de laquelle les constituents dissous du laitier peuvent être précipités de nouveau sous forme d'hydrates de différentes sortes et générateurs de résistance. A cause de la précipitation des phases d'hydrate, l'effet dissolvant de la phase liquide est maintenu.

Zusammenfassung

Im Dreistoffsystem CaO-Al_2O_3-SiO_2 wurden etwa 45 Gläser erschmolzen mit CaO-Gehalten zwischen 36 und 52%, Al_2O_3-Gehalten zwischen 9 und 56% und SiO_2-Gehalten zwischen 3 und 55%. Einige dieser Gläser enthielten zusätzlich 5% MgO. Außerdem wurden 4 technische Hochofenschlacken in die Versuche einbezogen. Die auf eine einheitliche spez. Oberfläche von 4000 cm^2/g gemahlenen Gläser und Schlacken wurden angeregt mit Portlandzementklinker (Hochofenzement), mit Anhydrit (Sulfathüttenzement) und mit Calciumhydroxyd (Kalkschlackenzement). Die hydraulischen Festigkeiten steigen an mit zunehmendem Al_2O_3-Gehalt, erreichen ein Maximum, fallen mit weiter steigendem Al_2O_3-Gehalt schroff ab, um bei noch höheren Al_2O_3-Gehalten zu einem zweiten Maximum anzusteigen. Jenseits dieses zweiten Maximums folgt ein zweites Minimum und in Bereichen mit weniger als 10% SiO_2 das Maximum der Tonerdezementerhärtung.

Röntgenographische Bestimmungen der Hydratphasen zeigten, daß in Gläsern mit mittleren Al_2O_3-Gehalten Gehlenithydrat, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$, als festigkeitsbildende Hydratphase entsteht. Die drei im Dreistoffsystem CaO–Al_2O_3–SiO_2 auftretenden Maxima der hydraulischen Festigkeit werden also hervorgerufen durch die Bildung von Calciumsilikathydrat im Bereich hoher SiO_2- und geringerer Al_2O_3-Gehalte, von Calciumaluminathydrat im Gebiet mit geringen SiO_2- und hohen Al_2O_3-Gehalten und von Calciumsilicoaluminathydrat (Gehlenithydrat) im Bereich mittlerer SiO_2- und Al_2O_3-Gehalte.

In den erhärteten Zementen ist Gehlenithydrat nicht beständig, sondern wandelt sich unter Aufnahme von CaO in einen Hydrogranat um, dessen Zusammensetzung ungefähr der Formel $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$ entspricht. Der MgO-Gehalt fördert diese Umwandlung.

In erhärteten Gläsern mit Al_2O_3-Gehalten unter 18% war röntgenographisch nur sehr wenig Gehlenithydrat neben geringen Mengen Calciumaluminathydrat nachzuweisen. Da zur Bildung kalkreicher Aluminathydrate der Kalkgehalt der Gläser nicht ausreicht, muß angenommen werden daß auch der Al_2O_3-Gehalt der tonerdeärmeren Gläser unabhängig von der Art der Anregung im Gehlenithydrat gebunden wird und daß die Fehler der röntgenographischen Bestimmung auf die schlechte Gitterordnung des Gehlenithydrats zurückzuführen sind. Die Annahme der Gehlenithydratbildung in den erhärtenden Gläsern und technischen Schlacken steht im Einklang mit dem praktischen Verhalten schlackenhaltiger Zemente gegenüber Sulfatlösungen. Es konnte gezeigt werden, daß Gehlenithydrat gegenüber Natriumsulfat- und Calciumsulfatlösungen beständig ist, daß es sich jedoch in kalkreichen Sulfatlösungen unter Ettringitbildung zersetzt. In Magnesiumsulfatlösungen ist Gehlenithydrat ebenfalls instabil.

Nach den Untersuchungsergebnissen wirken die Anregerstoffe in der Weise, daß sie zur Bildung einer günstig zusammengesetzten flüssigen Phasen beitragen, aus der die gelösten Bestandteile der Schlacken möglichst schnell in Form von erhärtungsfähigen Hydraten verschiedener Art wieder ausgeschieden werden können. Durch das Ausfällen der Hydratphasen bleibt die lösende Wirkung der flüssigen Phase erhalten.

Introduction

Simply composed glasses of the ternary system CaO-Al_2O_3-SiO_2 have often been used to find a connection between the chemical composition of blast-furnace slags and their hydraulic properties. Mention may here be made of the works of F. Keil and F. Gille [1], T. Tanaka, I. Sakai, and J. Yamane [2] and S. Solacolu [3][1]. As these investigations had been exclusively concerned with the hardenability of the glasses, it was now intended to establish the reactions which produce the hydraulic properties.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Preparation of the Glasses

The glasses were melted in the manner indicated by W. Dyckerhoff [4] with an acetylene-oxygen flame from mixtures of reagent-grade basic substances, and the drops of the melt were quenched in water. The glass sand thus obtained was dried and ground to a specific surface of 4,000 cm²/g.

Figure 1 shows the chemical composition of these 33 glasses in their position in the ternary system CaO-Al_2O_3-SiO_2. The melts are arranged in four series according to their CaO content, i.e., Series 10 with a CaO content of 52.5 percent, Series 10a with 50 percent of CaO, Series 20 with 44 percent of CaO, and Series 30 with 36 percent of CaO. Between these series lie a number of other glasses which were used only for the strength investigations. To investigate the influence of the magnesia content of the glass on the hydraulic properties, fifteen additional glasses, designated M in figure 1, were melted with an MgO content of 5 percent, the constituents CaO, Al_2O_3 and SiO_2 being proportionately reduced.

Activation of the Glasses

The ground glasses were activated in three different ways:

1. with 18 percent of portland cement clinker and 5 percent of gypsum (blast-furnace-slag cement),
2. with 15 percent of anhydrite and 2 percent of portland cement clinker (slag-sulfate cement),
3. with 10 percent of $Ca(OH)_2$ (lime-slag cement).

Hydraulic Properties

The properties were tested by the small-scale testing method described by F. Keil and F. Gille [5] on small mortar bars (1×1×6 cm). The findings of these investigations have already been published [6].

Figure 2 shows the results of the strength tests of the glasses activated with clinker, in the form of lines of similar compressive strength. It is seen that between the area of the silicatic hardening of blast-furnace cement with SiO_2 contents of about 30 percent and the area of the aluminatic hardening of glasses poor in silica, there lies a third area of high strength with SiO_2 contents of about 20 percent and Al_2O_3 contents of about 37 percent.

Figure 3 represents the strength behavior of all the glasses with 44 percent of CaO, i.e., without MgO, at the top, and with an MgO content of 5 percent below. In the top part of the figure the curve clearly shows the three high-strength areas and the very poor hardenability of glasses 23, 23b and 24a with about 27 to 34 percent of Al_2O_3. It can also be recognized that these glasses show considerably higher strengths where activation is accomplished with $Ca(OH)_2$ than with clinker

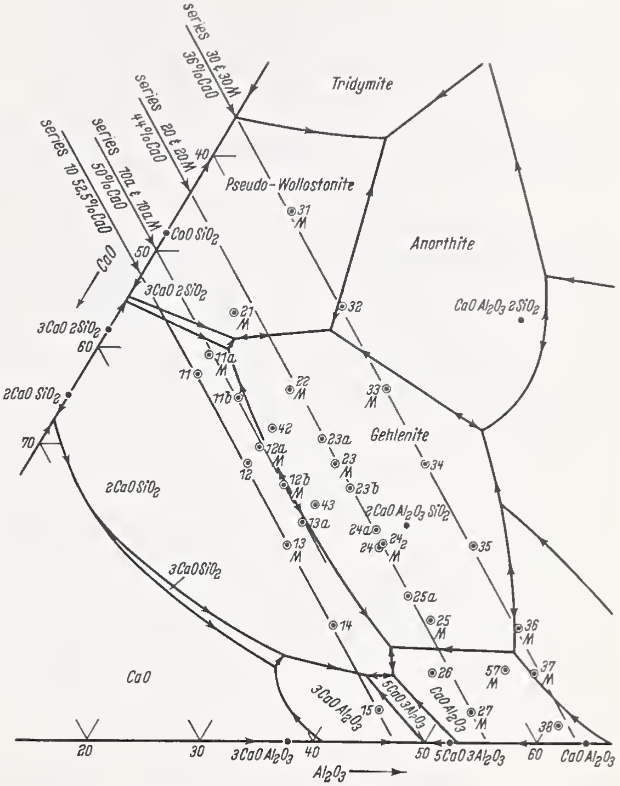

FIGURE 1. *Chemical compositions of the synthetic glasses presented in the ternary system CaO-Al_2O_3-SiO_2.*

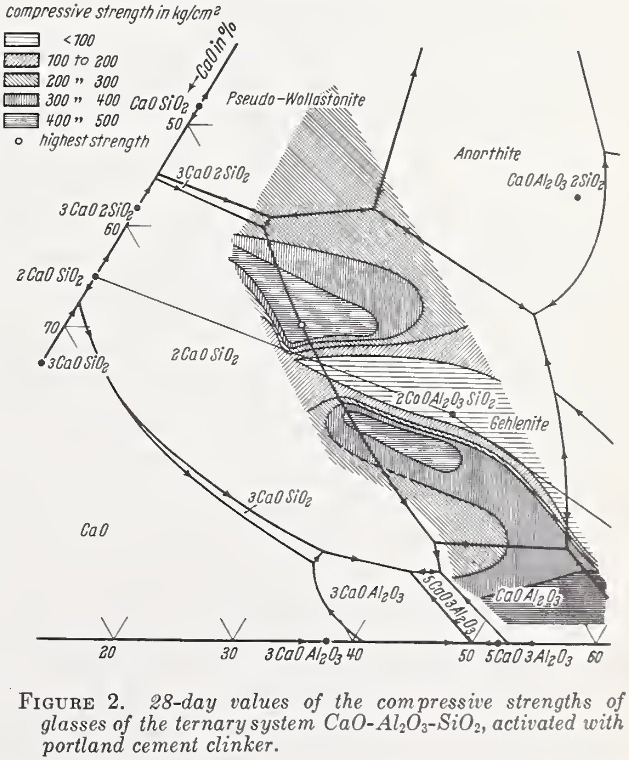

FIGURE 2. *28-day values of the compressive strengths of glasses of the ternary system CaO-Al_2O_3-SiO_2, activated with portland cement clinker.*

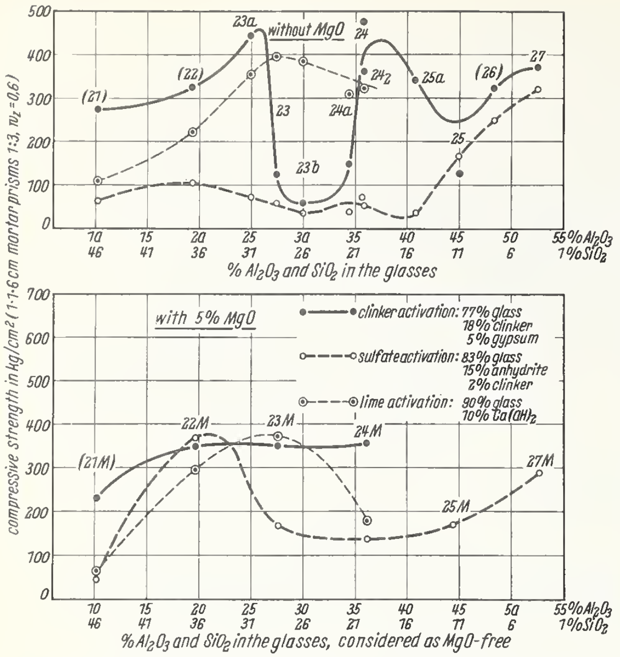

FIGURE 3. *Compressive strengths of the glasses with 44 percent of CaO after 28 days' curing in water, with clinker, sulfate, and $Ca(OH)_2$ activation.*

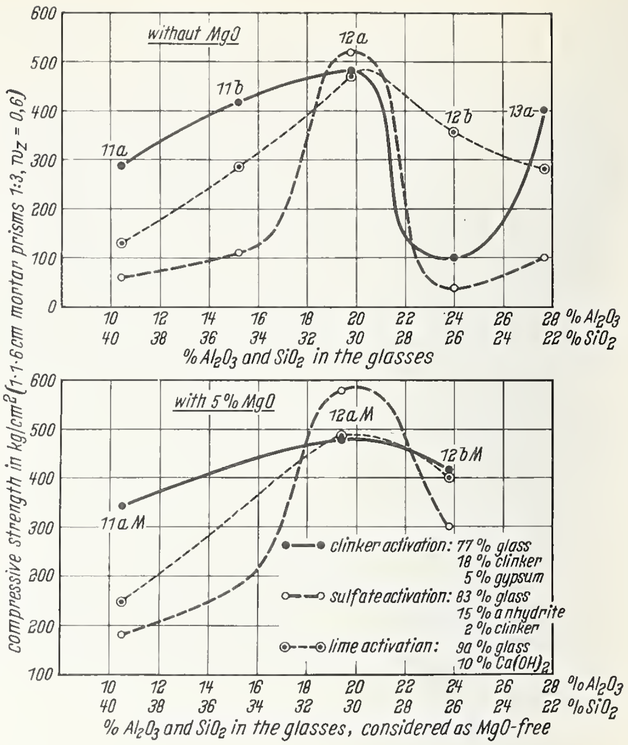

FIGURE 4. *Compressive strengths of the glasses with 50 percent of CaO after 28 days' curing in water, with clinker, sulfate, and $Ca(OH)_2$ activation.*

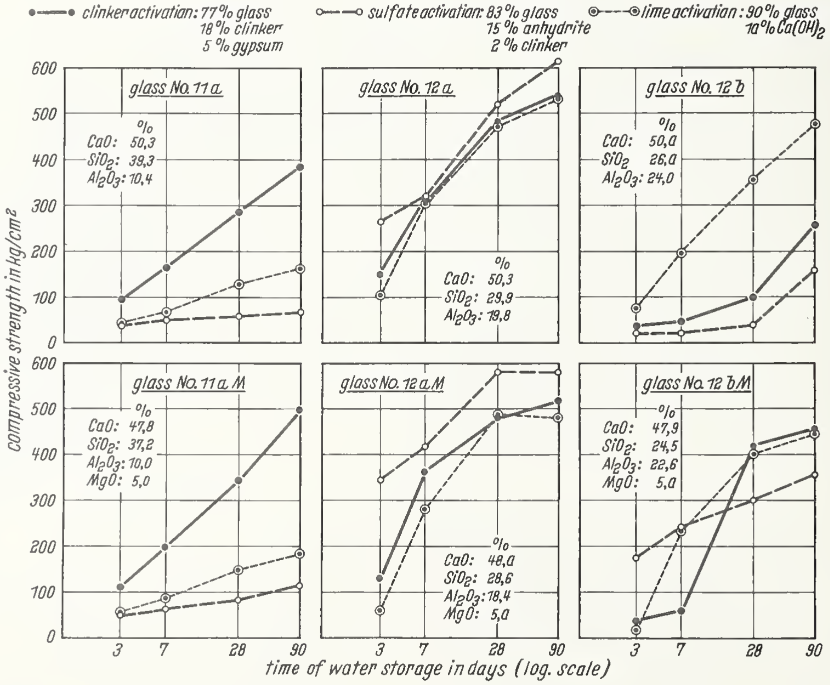

FIGURE 5. *Development of the compressive strength of glasses with 50 percent of CaO with clinker, sulfate, and $Ca(OH)_2$ activation.*

activation. Similarly favorable effects in this area are obtained with an MgO content of 5 percent. With sulfate activation these glasses, comparatively poor in lime, i.e., with 44 percent of CaO, achieve only low strengths. An MgO content of 5 percent improves the hydraulic properties, particularly in glass 22M.

Figure 4 indicates the strengths of the glasses with 50 percent of CaO. One recognizes the very high strengths of glass 12a with 20 percent of Al_2O_3 and 30 percent of SiO_2 and the low strengths of glass 12b with 24 percent of Al_2O_3 and 26 percent of SiO_2. As in the case of the glasses with poor hardenability, 23, 23b, and 24a with 44 percent of CaO, the hydraulic properties are also improved in glass 12b when it is activated with $Ca(OH)_2$, or when the glass contains 5 percent of MgO. In the lime-rich glasses with 50 percent of CaO, sulfate activation also produces very high strengths.

It is seen from the strength development (fig. 5) that glass 12b from the field of low strengths also possesses hydraulic properties, but that it hardens only very slowly when activated with clinker, while activation with $Ca(OH)_2$ results in rapid hardening and produces very high strengths. Furthermore, the figure reveals that the strength development of this glass is greatly accelerated by an MgO content of 5 percent.

The results of the present investigations indicated a "most favorable" glass composition for all kinds of activation of 50 percent of CaO, 31 percent of SiO_2, and 19 percent of Al_2O_3. Similar results have already been published by T. Tanaka, I. Sakai, and J. Yamane [2].

Possible Explanations of the Hardening Behavior

The strength investigations revealed that in certain areas of the chemical composition there are abrupt changes in the hydraulic properties of the glasses. In order to clarify the causes of this behavior, the investigation started from the following conceptions of hydraulic hardening: The capacity of certain compounds to harden hydraulically presupposes that these compounds react with water or with hydrous solutions and form strength-giving hydrates. Here it is essential that the anhydrous compounds dissolve and that the hydrates separate again out of this solution.

Assuming such a reaction there are the following two possibilities of explaining the afore-mentioned abrupt changes of the hydraulic properties. Either the dissolution behavior of the glass changes erratically or erratic changes will be established in the formation of the hydrate phases. These two possibilities were investigated.

Behavior of the Glasses in Basic Ammonium Citrate Solution

To investigate the dissolution behavior, a number of glasses with particularly good and with very poor hydraulic properties were agitated in a ten-percent basic ammonium citrate solution according to the method described by F. Keil and F. Gille [7]. At fixed intervals they were filtered, and CaO, Al_2O_3 and SiO_2 were determined in the filtrate. The residue was suspended in a fresh solution and agitated again. The investigations showed that the solubility of the glasses changes continuously and not erratically if SiO_2 is replaced by Al_2O_3. Consequently, there is no connection between the behavior of the glasses in ammonium citrate solutions and their hydraulic properties.

Formation of the Hydrate Phases

Investigations

It followed, therefore, that the explanation for the hydraulic behavior of the glasses was to be found in the formation of the hydrate phases. For this reason it was necessary to determine the hydrate phases in hardened neat mixtures of glass and activators by the X-ray diffraction method. The neat mixtures hardened both in pastes ($W/C=0.4$) and also suspended in calcium hydroxide solutions, and these suspensions contained 10 g of the glass-activator mixture in 150 ml $Ca(OH)_2$ solution. The phases present in the hydrated mixtures were first qualitatively determined. No calcium silicate hydrate could be found. Only the X-ray lines of ettringite were revealed, which was formed from the gypsum added in clinker activation, and the lines of tetracalcium aluminate hydrate, gehlenite hydrate, hydrogarnet, and calcium hydroxide. Ettringite and gehlenite hydrate were then determined quantitatively by the X-ray diffraction method, with fluorspar as an internal standard. In the same way the portion of the activators which had not yet taken part in the reactions was also determined.

Results of the X-ray Diffraction Investigations

The patterns of the X-ray determinations showed that with activation with clinker and calcium hydroxide first of all tetracalcium aluminate hydrate occurs, and that it is formed in greater amounts when activation is with calcium hydroxide than with clinker activation. It apparently occurs predominantly in the glasses rich in lime and poor in alumina.

Gehlenite hydrate ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}nH_2O$) forms primarily in the alumina-rich glasses whose chemical composition approaches that of gehlenite. The quantitative determinations showed that in the glasses containing MgO, considerably less gehlenite hydrate was formed than in the MgO-free glasses.

Hydrogarnet could be ascertained mainly in the glasses which also contained a large amount of gehlenite. The hydrogarnets which occurred in the hydration of these iron-free glasses are phases from the solid-solution series

$$3CaO \cdot Al_2O_3 \cdot 6H_2O \text{———} 3CaO \cdot Al_2O_3 \cdot 3SiO_2$$

$$Ca_3Al_2(H_{12}O_{12}) \text{———} Ca_3Al_2(Si_3O_{12}).$$

In such solid-solution series, the interatomic distances in the crystal lattice change continuously with the chemical composition, and these can be measured by the X-ray diffraction method. The connection between the lattice spaces and the SiO_2 content of hydrogarnet was determined by H. zur Strassen [8]. For the hydrogarnet occurring here, a chemical composition was determined corresponding to the formula: $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$. A comparison with the formula of gehlenite hydrate, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$ shows that the two formulas only differ in the CaO content, if the water content is disregarded. It might be assumed, therefore, that the hydrogarnet was formed from the gehlenite hydrate while absorbing CaO, that is to say, that in the presence of CaO gehlenite hydrate is not stable. A similar result was obtained by the investigations of H. zur Strassen [8] who showed that when shaken in saturated calcium hydroxide solution gehlenite hydrate disappears and hydrogarnet occurs.

The Silicoaluminatic Hardening

In order to be able to assess the content of hydrogarnet, various mixtures were prepared from gehlenite hydrate and a hydrogarnet which contained 1 mole SiO_2 per formula unit. Figure 6 shows the hydrogarnet lines in the mixtures in comparison with the same lines in the hardened test specimens. It is seen that the glasses 24 and 24M, activated with calcium hydroxide, contain about 60 and 80 percent respectively of hydrogarnet after 90 days hydration. The X-ray diffraction determination of the gehlenite hydrate content for these two glasses gives values of 21 and 5 percent (glass 24M); that is to say, both samples consist of more than 80 percent of gehlenite hydrate or a hydrogarnet which was a secondary formation from gehlenite hydrate. As these two phases contain all the available SiO_2, the hydraulic strength cannot be attributed in this case to the formation of calcium silicate hydrate. In these glasses, therefore, gehlenite hydrate is the strength-forming phase.

This result of the investigation leads to the following conclusion: The results of the strength investigations, as presented in figure 2, reveal three fields of high compressive strength. We know that in the glasses that contain a large amount of silica and little alumina the hydraulic hardening is due to the formation of the calcium silicate hydrate. It is also known that in the field of alumina cement the hardening is due to the formation of calcium aluminate hydrates poor in lime.

The present investigations now show that the high strengths obtained by the glasses with medium contents of silica and alumina were caused by gehlenite hydrate. Between the areas of the "silicatic" and the "aluminatic" hardening, therefore, lies the field of the "silicoaluminatic" hardening. Gehlenite hydrate is not stable in the presence of calcium hydroxide, but changes into hydrogarnet while absorbing lime. It may be assumed that the strength of the hardened cement is reduced by this transformation. This change probably accounts for the decrease in strength which can be observed particularly clearly for glass 24M, i.e., for the glass in which an extremely high content of hydrogarnet was determined.

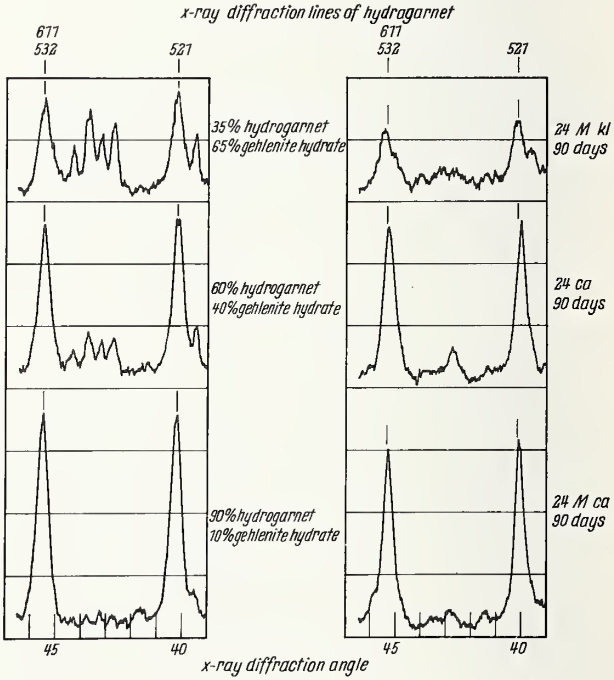

FIGURE 6. *Hydrogarnet lines in the X-ray diagrams of a number of hydrated samples and in mixtures of gehlenite hydrate and hydrogarnet of the composition $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$.*

Sample 24Mca with 5 percent of MgO contains less gehlenite hydrate and more hydrogarnet than the MgO-free sample 24ca with an otherwise similar chemical composition.

The Aluminate Phase in the Hardened Glasses Poorer in Alumina

In the paste hardening of the glasses poorer in alumina, gehlenite hydrate occurs only in very small amounts, up to about 3 percent. With clinker activation it could be found only after 28 days, while with anhydrite activation it was not found at all. If the mixtures of glass and activators was hydrated in suspension, that is to say, with a high excess of water, gehlenite hydrate was formed in every case, also with sulfate activation. For this reason it is assumed that in the hydration of the glasses poorer in alumina the major portion of the alumina is also bound in the gehlenite hydrate, though the latter crystallizes so badly that it can only be established in small amounts in the X-ray pattern.

This assumption is supported by the following finding: The content of free calcium hydroxide, which was determined in the hardened glasses and slags after curing in water for 3, 7, 28, and 90 days, changes only slightly with progressive hydration. Thus the diagrams in figure 7, for instance, show that in the hardened glasses 12a with the maximum strengths and 12b with very poor hydraulic properties the content of free calcium hydroxide remains approximately the same, while the content of nonevaporable water (water that escapes above 110 °C) increases, that is to say, hydration progresses. Figure 7 shows furthermore that with lime activation the content of free calcium hydroxide varies only slightly around 10 percent. As 10 percent of calcium hydroxide was added to the anhydrous glass, there has been no decrease in the content of free calcium hydroxide.

These investigations show that in the hardening of the glasses the lime of the activator is not used to form the hydrate phases. In all hydrate phases, therefore, only so much lime can be bound as was available in the glass alone. Glass 12a, which yielded the maximum strengths, contains 1.8 mole CaO per mole of SiO_2. In the calcium silicate hydrate phase which is formed with the hydration of these silica-rich glasses, the molecular ratio CaO/SiO_2 is very probably about 1.5. Only a very small amount of lime, therefore, would be available for the binding of the alumina. It might be assumed, therefore, that part of the silica is bound not only to lime but, together with alumina and lime, forms gehlenite hydrate. These considerations are valid both for activation with clinker and also for lime and anhydrite activation.

It may be reckoned that part of the alumina is taken up into the calcium silicate hydrate phase, in the form of mixed-layer crystal structures of calcium silicate and gehlenite hydrate layers. Similar mixed-layer crystal structures are possessed by numerous clay minerals. The absence of X-ray lines of aluminate hydrate phases might be explained in this way.

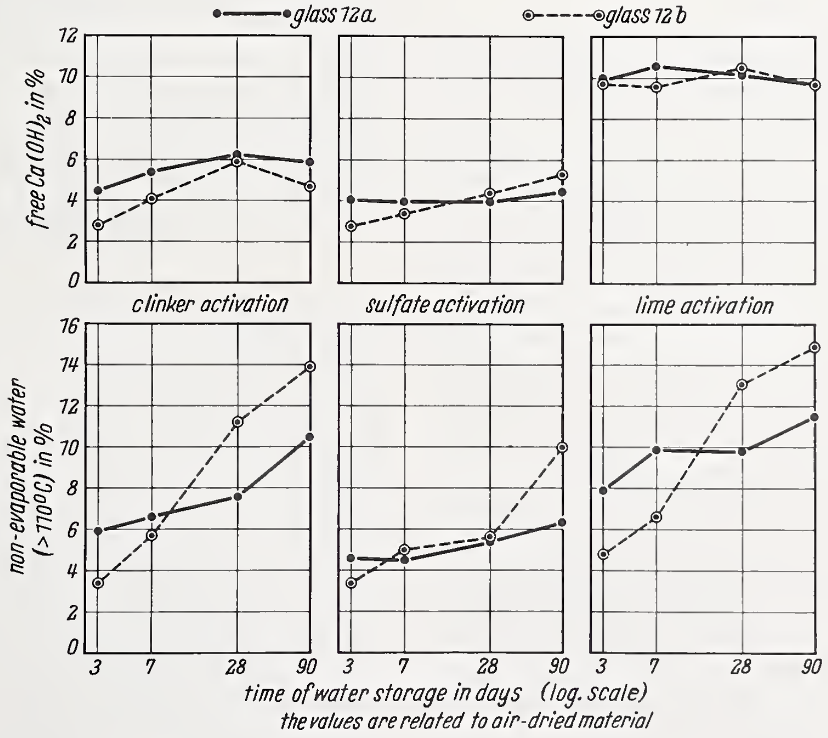

FIGURE 7. *Content of free $Ca(OH)_2$ and of non-evaporable water in the hardened glasses 12a and 12b with clinker, anhydrite, and lime activation.*

The Behavior of Gehlenite Hydrate in Sulfate-Bearing Solutions

According to investigations carried out by G. Malquori and V. Cirilli [9, 10], gehlenite hydrate is not stable in lime-saturated gypsum solutions and forms ettringite. This finding was confirmed by H. zur Strassen [8]. If it is assumed that gehlenite hydrate occurs in major amounts not only in the hydration of the glasses used here but also in the hardening of slag-bearing cements, these cements must be expected to have only a very low resistance to sulfate. However, as the practical behavior reveals just the opposite, it might be concluded that no gehlenite hydrate is formed in these cements. As G. Malquori and V. Cirilli investigated the behavior of gehlenite hydrate only in a lime-saturated gypsum solution, similar experiments were made with a saturated gypsum solution, a solution saturated with calcium hydroxide and gypsum, a 0.15-molar Na_2SO_4 solution, and a 0.15-molar $MgSO_4$ solution, 3g of gehlenite hydrate being agitated for 4 weeks in 1 liter of solution.

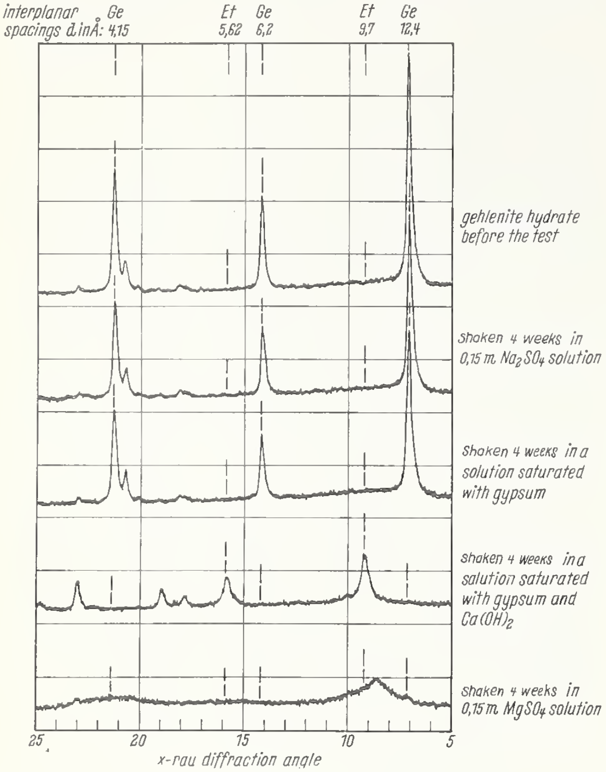

FIGURE 8. *Sections from the X-ray diagrams of an untreated gehlenite hydrate sample and of gehlenite hydrate samples which were agitated for 4 weeks in* Na_2SO_4 *solution, saturated gypsum solution, lime-saturated gypsum solution, and* $MgSO_4$ *solution.*

The X-ray pattern of the investigation (fig. 8) revealed that the gehlenite hydrate was transformed into ettringite in the solution saturated with gypsum and calcium hydroxide and disintegrated in the $MgSO_4$ solution, but that it was stable in the gypsum solution and in the Na_2SO_4 solution. Applying this information to practical conditions, one would arrive at the following conclusions: If gehlenite hydrate is the sole aluminate phase in the hardened blast-furnace cements, these cements are stable in sulfate solutions if the solutions are poor in lime and free from $MgSO_4$ and if the hardened cement contains little free calcium hydroxide. Furthermore, it follows that the resistance of the blast-furnace cement to sulfate is influenced very largely by the amount of the clinker content and only to a secondary degree by the Al_2O_3 content of the slag.

The Progress of Reaction in the Hardening of the Glasses

Activation of the Glasses

The high strengths in three different fields of the ternary system $CaO\text{-}Al_2O_3\text{-}SiO_2$ were attributed to the formation of calcium silicate hydrate, gehlenite hydrate, and calcium aluminate hydrate. In these fields the afore-mentioned phases were primarily formed during hydration. The probable explanation is that in the field between the "silicatic" and the "silicoaluminatic" hardening, neither the calcium silicate hydrate nor the gehlenite hydrate can form rapidly and that the glass therefore hydrates slowly.

The effect of the activators can be similarly explained. Glasses and slags alone do not hydrate and harden, or if at all, only slowly, that is to say, they do produce a solution, in which, however, strength-forming hydrate phases cannot form quickly enough. By the addition of an activator the chemical composition of the solution is so changed that the substances dissolved out of the slag can rapidly form strength-producing hydrate phases.

The Progress of Hardening of Slag-Containing Binding Agents

The following pattern emerges for the progress of the hardening: The reactions of cement hardening proceed in a system that contains a large amount of cement and very little water. The water, in which parts of the cement are dissolved, coats all the particles of the system, that is to say, also the yet unhydrated particles of the cement, with a very thin liquid film, the so-called intergranular film. Hydration reactions of the yet unhydrated cement and the formation of the hydrate phases proceed in the intergranular film, that is to say, in the immediate vicinity of the original cement grains. The solution which forms the liquid film is not saturated in respect to the anhydrous cement but is supersaturated in respect to the hydrate phases. The more rapidly the hydrate phases are precipitated, and the lower, therefore, the concentration of the substances to be dissolved, the more rapid is the dissolution of the anhydrous cement. If no hydrate phases are precipitated, the concentration increases in the solution phase, and hydration of the anhydrous cement ceases. The activators of latent hydraulic binders have therefore only the task of adjusting the concentration conditions in the solution in such a manner that the dissolved substances can be precipitated again as quickly as possible in the form of strength-forming hydrates.

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Discussion

H.-G. Smolczyk

The excellent paper of Dr. Locher has been of great interest for the Forschüngsinstitut für Hochofenschlacke at Rheinhausen, for it is a valuable development towards basic problems of the hydration of portland blast furnace slag cements. But it must be taken into account that our technical blast furnace slags cannot entirely be compared with the high-alumina melts of chemically pure components mentioned by Dr. Locher.

I must refer to this, for otherwise one might get a wrong impression of the behavior of blast furnace slag cements. Thus, at the annual German cement meeting at Salzburg (1960), Dr. zur Strassen stated—and he was fully agreed with by Professor Schwiete—that blast furnace slag cements of various types did not show any X-ray diffraction pattern of hydrogarnets even after having been cured in water for years. (We have never observed any hydrogarnet peaks either, after water curing under normal conditions.) These observations are in accordance with Dr. Locher's statement that there had been only very weak peaks of gehlenite hydrate in hydrated technical blast furnace slags. Furthermore I want to state that we have tested X-ray diagrams of at least 100 blast furnace slag cements at different stages of hydration, and in only one or two specimens with very high alumina content have we found a very weak peak of gehlenite hydrate at a very early stage of hydration. This peak, however, disappeared after 28 days of water curing.

Another difference for the chemically pure glass melts is the decrease of the $Ca(OH)_2$ content in good blast furnace slag cements. After 7 days of water curing the $Ca(OH)_2$ content in the low-clinkered type of these cements would be reduced to a very small amount. The $Ca(OH)_2$ content of special blast furnace slag cements, as well as that of supersulfated cements would be brought down almost to zero.

This phenomenon is one of the causes for the well-known resistance of these cements to various aggressive fluids. As for a concrete using these cements as matrix, there will certainly not be any disintegration in contact with an $MgSO_4$ solution either.

Closure

F. W. Locher

The results of H.-G. Smolczyk show that, as a rule, no gehlenite hydrate can be established in hydrated blast furnace slags and slag cements, and our own findings tally with these results. It must then be explained, however, in what hydrated phases the alumina is present in hardened slag-sulfate cements. Our own X-ray diffraction investigations showed that only a small portion of the alumina forms aluminates rich in lime. The lime content of low-clinker blast furnace cements is not sufficient to bind all the alumina of the slag in this form. It may be expected, therefore, that aluminate hydrate phases poorer in lime are formed. When mixtures of glass or slag with various activators were shaken in diluted and saturated calcium hydroxide solutions, gehlenite hydrate occurred in every case and it was therefore assumed that gehlenite hydrate was also formed in the paste during hydration of these mixtures. The non-occurrence of X-ray interferences might be attributed to the fact that the gehlenite hydrate in the paste is as ill-crystallized as the calcium silicate hydrate.

H.-G. Smolczyk established that the calcium hydroxide content decreases in the course of hardening and that practically no calcium hydroxide is contained in the hardened special blast furnace cements and slag-sulfate cements. The results of our own investigations do not agree with this finding. As in the hydration of the pure glasses, in the hydration of four technical blast furnace slags of various compositions a definite content of calcium hydroxide occurred which showed little change with progressive hardening. This behavior did not depend on the kind of activation. With an activation with anhydrite also, a calcium hydroxide content of about 4 to 5 percent was observed in the cement.

Paper III–S5. The Precipitation of $CaO \cdot Al_2O_3 \cdot 10H_2O$ From Supersaturated Calcium Aluminate Solutions at 21 °C*

A. Percival, F. G. Buttler, and H. F. W. Taylor

Synopsis

Deposition from clear, supersaturated solutions, made by shaking anhydrous calcium aluminates with water has been studied at 21 °C. Alkali-free solutions containing initially more than 0.85 g CaO, 1.46 g Al_2O_3/l yield C_2AH_8, CAH_{10}, and AH_3; after sufficiently long times, only CAH_{10} and AH_3 are found. With weaker solutions, down to 0.48 g CaO, 0.81 g Al_2O_3/l, the usual products are C_2AH_8 and AH_3; CAH_{10} appears irreproducibly. With still weaker solutions, only AH_3 is found. The effect of using NaOH instead of water to prepare the supersaturated solution has been studied. One thousandth molar NaOH solution behaves no differently from water; M/100 NaOH alters the concentrations but not the general course of precipitation; M/10 NaOH yields solutions, very weak in CaO, which did not precipitate within 28 days.

The results obtained using water or M/1000 NaOH support the metastable solubility curve for CAH_{10} previously reported by Percival and Taylor and not the modified curve proposed by Jones and Roberts. Reasons are also advanced for preferring the 5 °C curve for CAH_{10} determined by Buttler and Taylor to that proposed by Jones.

Résumé

On a etudié les precipités formés dans des solutions claires et sursaturées, préparées d'aluminates de calcium anhydre agités dans l'eau à 21 °C. Les solutons sans alcali et contenant originellement plus de 0.85 g de CaO, 1.46 g de Al_2O_3/l donnent C_2AH_8, CAH_{10}, et AH_3; après des périodes suffisamment longues on ne trouve que CAH_{10} et AH_3. Avec des solutions plus faibles descendant jusqu'à 0.48 g de CaO, 0.81 g de Al_2O_3/l, C_2AH_8 et AH_3 sont habituellement produits; CAH_{10} apparaît quelquefois. Avec des solutions encore plus faibles, on ne trouve que AH_3. L'effet de l'utilisation de NaOH au lieu d'eau dans la préparation des solutions sursaturées est étudié. M/1000 NaOH se comporte de façon semblable à l'eau; M/100 NaOH modifie les concentrations mais pas le cours général de précipitation; M/10 NaOH donne des solutions, très faibles en CaO, qui ne précipitaient pas pendant 28 jours.

Les résultats obtenus, si l'on utilise ou l'eau ou M/1000 NaOH, supportent la courbe métastable de solubilité présentée précédemment par Percival et Taylor et non pas la courbe modifiée proposée par Jones et Roberts. Les raisons pour préférer la courbe 5 °C pour CAH_{10} déterminée par Buttler et Taylor à celle proposée par Jones sont également présentées.

Zusammenfassung

Die Ausfällung der klaren, übersättigten Lösungen, die durch das Schütteln des wasserfreien Kalziumaluminats mit Wasser erhalten wurden, wurde bei 27 °C studiert. Alkalifreie Lösungen, die ursprünglich mehr als 0.85 g CaO und 1.46 g Al_2O_3/l enthalten, liefern C_2AH_8, CAH_{10} und AH_3; nach einer genügend langen Zeit werden nur noch CAH_{10} und AH_3 beobachtet. Wenn die Lösungun verdünnter sind, bis zu 0.48 g CaO und 0.81 g Al_2O_3/l, wird meistens C_2AH_8 und AH_3 erhalten; CAH_{10} entsteht manchmal, aber es ist nicht reproduzierbar. Bei weiterer verdünnter Lösungen wird nur AH_3 beobachtet. Es wurde auch untersucht, wie sich die Benutzung von NaOH an Stelle des Wassers für die Bereitung der übersättigten Lösung auswirkt. M/1000 NaOH zeigt dieselben Wirkungen wie Wasser; M/100 NaOH verändert die Konzentrationen, aber hat keinen Einfluß auf den Gang der Niederschlagsprozesse; M/10 NaOH liefert Lösungen, die wenig CaO enthalten und die während 28 Tagen keinen Niederschlag ausfallen lassen.

Die mit Wasser oder M/1000 NaOH erhaltenen Ergebnisse zeigen, daß die metastabile Löslichkeitskurve, die Percival und Taylor früher für CAH_{10} beschrieben haben, richtig ist, und nicht die abgeänderte Kurve, die von Jones und Roberts in Vorschlag gebracht wurde. Gründe werden auch angegeben, warum die 5°-Kurve für CAH_{10}, die von Buttler und Taylor bestimmt wurde, der Kurve, die Jones vorgeschlagen hat, vorzuziehen ist.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Department of Chemistry, University of Aberdeen, Scotland.

Introduction

It is generally agreed that the hydration of either CA or aluminous cement in pastes at 21 °C gives CAH_{10} as a major product. In contrast, most of the investigators who have studied deposition from clear, supersaturated solutions at or near this temperature have not reported formation of CAH_{10}. Jones and Roberts [1][1], however, recently obtained CAH_{10} from such solutions at 20 °C. They also obtained it, though irreproducibly, at 25 °C, and in some unthermostatted experiments at 19 to 23 °C.

The present work was done to find whether CAH_{10} is reproducibly obtainable from clear, supersaturated solutions at 21 °C, and if so to define the conditions of its formation. The influence of alkali was also studied. The results provide further evidence about the position of the metastable solubility curve for CAH_{10}.

Experimental

Precipitation From Alkali-Free Solutions

The solutions were made by shaking weighed amounts (20 to 100 g) of "Secar 250" (a white high-alumina cement made from commercial calcined alumina, and consisting of CA, CA_2 and corundum) with boiled distilled water (1 liter) in a large, stoppered polythene bottle for 1 to 4 hours. The resulting suspensions were filtered in CO_2-free air immediately after shaking, and the filtrates transfered to 500-ml polythene bottles. These were immediately closed with polyvinylchloride gasketed screw stoppers, and placed in a 21 °C thermostat. Portions of the clear filtrates were analyzed for CaO and Al_2O_3. By varying the shaking time and the amount of cement used, a range of supersaturated solutions of differing concentrations was obtained. It was extended to concentrations below 0.4 g CaO/l by diluting the filtrates with water.

After varying times, bottles containing initially clear solutions of different concentrations were removed from the thermostat. The precipitated solids were filtered off under CO_2-free conditions, dried over saturated $CaCl_2$ solution, and X-ray powder photographs taken. The filtrates were analyzed for CaO and Al_2O_3. The $CaO:Al_2O_3$ ratios in the solids were calculated from the changes in the solution compositions.

The principal phases deposited were C_2AH_8, CAH_{10}, and hydrous alumina which gave diffuse X-ray patterns approximating in varying degrees that of gibbsite. In a few cases, small amounts of C_4AH_{13} or of $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ were also detected. Some precipitates in which only AH_3 was detected by X-rays had calculated C/A ratios as high as 0.4. These high ratios can probably be attributed mainly to adsorption of Ca ions or their incorporation into the poorly crystallized structure; traces of $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ may also have been present.

Experiments Using NaOH Solutions

The above procedure was followed, but the "Secar 250" was shaken with dilute solutions of NaOH instead of with water. When M/1000 or M/100 NaOH was used, precipitates were formed, and the experimental procedure was completed as with water. With M/10 NaOH, no precipitation occurred, at least in periods of up to 3 weeks.

Results

The results are given here in abbreviated form; full tables of data may be obtained on request to the authors.

Alkali-Free Solutions

Figure 1 shows the initial concentrations, times in the thermostat to approach equilibrium, and phases detected in the precipitates using X-rays. It also gives an indication of the molar C/A ratios of the precipitates. Only one variable is needed to express the initial concentration, because all the initial solutions had the same molar C/A ratio (1.07±0.01).

Figure 2 shows the paths followed by the solution compositions in some typical cases, with the experimental points for most of the runs of over 120 days duration. Variation of CaO and Al_2O_3 concentrations with time is shown in more detail in figure 3 for the runs where high initial concentrations were used.

The phases detected by X-rays varied with both initial solution composition and time. Three ranges of initial solution composition can be distinguished:

Range 1—At high initial concentrations (above about 0.85 g CaO, 1.46 g Al_2O_3/l) and short times, CAH_{10}, C_2AH_8, and AH_3 are usually all observed. The C_2AH_8 lines gradually become weaker in the X-ray pattern, and after a few months usually only CAH_{10} and AH_3 can be detected. The decrease in the proportion of C_2AH_8 is also shown by a fall in the C/A ratio of the precipitate. The variation in solution composition with time (fig. 3) was substantially the same for all the initial concentrations within this range. The concentrations drop within

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[1] Figures in brackets indicate the literature references at the end of this paper.

1 day to about 0.45 g CaO, 0.60 g Al_2O_3/l. The concentration of CaO falls to a minimum at 5 to 14 days and afterwards rises again; that of Al_2O_3 continues to decrease for at least six months. After eight months the concentration of Al_2O_3 has become almost constant at about 0.15 g/l, but that of CaO is still increasing slowly. This rise in CaO concentration provides incidental confirmation that no appreciable CO_2 contamination is occurring; its significance is discussed later. Closely similar data were obtained by Wells and Carlson [2] and by Jones and Roberts [1] some of whose results are included in figure 3. Wells and Carlson considered the final concentrations to be 0.46 g CaO, 0.16 g Al_2O_3/l, but the present results suggest that the final CaO concentration may be above 0.46 g/l.

Range 2—At moderate initial solution compositions (down to about 0.48 g CaO, 0.81 g Al_2O_3/l) the usual combination of phases found by X-rays is C_2AH_8 and AH_3 (fig. 1). Particularly at the lower initial solution concentrations in this range, AH_3 was the dominant phase in the X-ray pattern; the lines of C_2AH_8 and of CAH_{10}, when it occurred, were relatively weak. Sometimes CAH_{10} was observed, and it was present in two out of the three runs of over 150 days duration, but its occurrence in this range was irreproducible, at any rate in quantities detectable with X-rays. Some of the supersaturated solutions gave it readily, while others of similar concentration did not, although they had been prepared by a seemingly identical method. As in the previous range, the C/A ratio of the precipitate falls with time, though less markedly. The paths followed by the solution compositions (fig. 2) were similar to those noted for Range 1, but the CaO concentrations tended to be less as the initial concentration decreased. There were no significant differences as regards solution compositions between the runs in which CAH_{10} was detected in the precipitate and those in which it was not.

Range 3—At low initial solution concentrations (below about 0.48 g CaO, 0.81 g Al_2O_3/l), X-ray

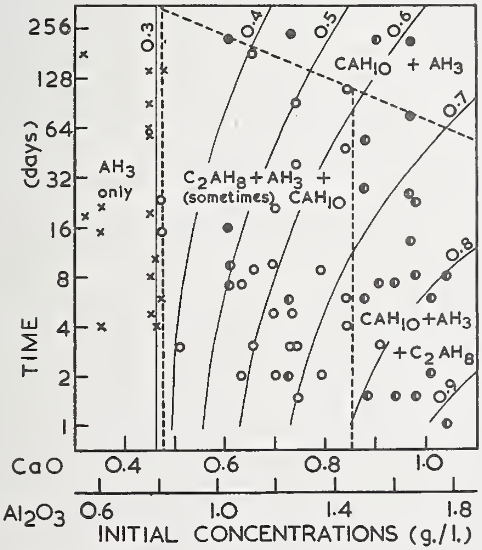

FIGURE 1. *Initial solution compositions, times, and principal solid phases detected by X-rays in alkali-free runs.*

Principal solid phases:
O, C_2AH_8, AH_3. ◑, $C_2AH_8+CAH_{10}+AH_3$. ●, $CAH_{10}+AH_3$. ×, AH_3. Thin full lines give a general indication of molar C/A ratios of precipitates. Broken lines define fields in which different combinations of solid phases usually occur.

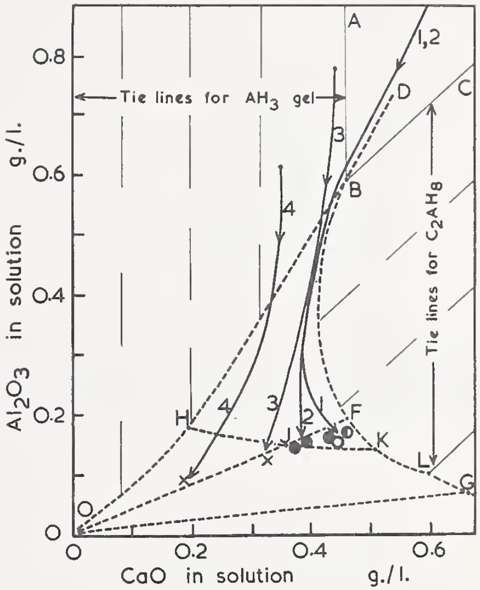

FIGURE 2. *Typical paths (full lines) followed by solution compositions in alkali-free runs.*

[Curves 1–4 are for initial CaO concentrations of 0.88–1.04, 0.61, 0.45, and 0.32–0.35 g/l respectively. Heavy broken lines represent stable or metastable solubility curves (*DBFKL*–C_2AH_8, *LG*–C_4AH_{19}, *HJK*–CAH_{10}, *OHB*–AH_3 gel, *OJH*–microcrystalline AH_3, *OG*–gibbsite). Experimental points are given only for long term runs, and have the same significance as in figure 1.]

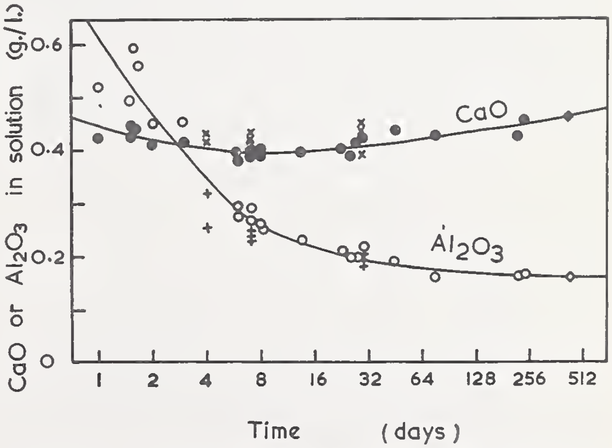

FIGURE 3. *Variation with time in the concentrations of* CaO *and* Al_2O_3 *for all alkali-free runs with initial* CaO *concentrations* ≥ 0.88 g/l ($Al_2O_3 \geq 1.53$ g/l).

[●, CaO; ○, Al_2O_3 (this investigation, 21 °C.) ×, CaO; +, Al_2O_3 (Jones and Roberts, 20 °C). ◆, CaO; ◇ Al_2O_3 (Wells and Carlson, 21 °C). The curves are drawn through the points at 21 °C.]

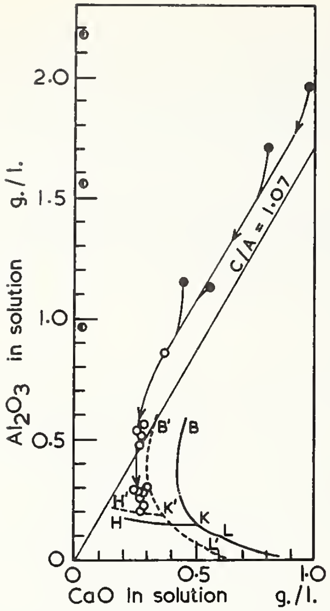

FIGURE 4. *Results of runs using M/10 or M/100* NaOH.

◑, ●, initial solution composition using M/10 and M/100 NaOH respectively. ○, final solution compositions using M/100 NaOH. Heavy full lines represent metastable solubility curves in absence of alkali for C_2AH_8 (*BKL*) and CAH_{10} (*HK*). Broken lines represent positions of these curves in M/100 NaOH.

examination of the precipitates showed only AH_3, apart from traces of $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ in some cases. The results agreed closely with those obtained in a similar study by Wells and Carlson [2] and will therefore not be reported or discussed in detail.

Solutions Containing Alkali

Eighteen runs were made using M/1000 NaOH; the initial CaO concentrations were 0.539—1.09 g/l, and the times were 0.5—143 days. The results did not differ significantly from those obtained using water. The results with M/10 and M/100 NaOH are shown briefly in figure 4. The solutions made with M/10 NaOH did not precipitate. Those made with M/100 NaOH precipitated, and 12 runs were made with times of 1 to 92 days. The two more concentrated solutions ($CaO \geq 0.8$ g/l, $Al_2O_3 \geq 1.7$ g/l) gave C_2AH_8, CAH_{10}, and AH_3 at all ages studied. With the two weaker ones ($CaO \leq 0.55$ g/l, $Al_2O_3 \leq 1.15$ g/l) only C_2AH_8 and AH_3 were detected. The approximate rates of precipitation, and the course followed by the solution compositions, were similar to those found with water or M/1000 NaOH, but the CaO concentrations were consistently lower.

Discussion

Precipitation of CAH_{10} From Alkali-Free Solutions

The results show that CAH_{10} is precipitated at 21 °C from supersaturated solutions to which no additional lime has been added, provided the concentration immediately after filtration is high enough. This observation is consistent with the known behavior of CA on paste hydration at 21 °C, where CAH_{10} is formed as the main product, though usually with some C_2AH_8 and AH_3. In a partly hydrated paste, the concentrations of CaO and Al_2O_3 in solution are presumably kept high by the presence of unreacted CA.

Range 1—Initial precipitation from solutions in this range is probably always of AH_3 and C_2AH_8. This conclusion can be correlated with the fact that the initial solution compositions lie in the field *ABC* (fig. 2) between the tie lines of these two phases. During the first 1 to 2 days, the solution composition therefore reaches the unstable triple point at *B*. In the present work, periods under 1 day were not studied, but Wells and Carlson's results suggest that AH_3 alone is precipitated at first; afterwards, AH_3 and C_2AH_8 are precipitated together, and the solution compositions move down the upper part *DB* of the C_2AH_8 metastable solubility curve towards the triple point.

The next stage in the precipitation may begin even before the first is complete and continues for some 6 to 12 months. It appears to involve three separate processes. Firstly, the C_2AH_8 is unstable and reacts with the solution, abstracting alumina to give CAH_{10}. Secondly, the crystallinity of the AH_3 gradually improves so that its effective solubility curve changes from ' *OB* ("AH_3 gel") to *OF* ("microcrystalline AH_3") (fig. 2). These are, of course, only two stages in a continuous sequence which continues beyond *OF* in the direction of fully crystalline gibbsite (curve *OG*). Thirdly, the CAH_{10} is probably also poorly crystalline at first (Buttler and Taylor, [3]), and its effective solubility curve may be supposed to fall gradually towards the limiting curve *HJK* for CAH_{10} of maximum crystallinity. The solution composition moves towards a triple point *J* between solution, CAH_{10}, and microcrystalline AH_3 (fig. 2). Its path can perhaps be regarded as the locus of the unstable triple point which occurs at the intersection of a constantly changing series of unstable solubility curves for AH_3 with a similar series of curves for CAH_{10}.

Towards the end of this stage of precipitation, the CaO concentration, which has passed through a minimum at 5 to 14 days, begins to increase. This is because the CAH_{10} has almost attained its maximum crystallinity, but that of the AH_3 is continuing to increase. CAH_{10} therefore begins to redissolve as the solution composition is now tending to move to the right along, or just above, the curve *JK*. Eventually, at the triple point *K*, C_2AH_8 may be expected to reprecipitate, but several years would probably be needed for this CaO concentration to be reached.

Range 2.—The behavior of the solutions in this range presents a difficulty in that CAH_{10} was detected in only a few of the solids, whereas the trends in solution and solid compositions closely resembled those found for Range 1. The most likely explanation is perhaps that CAH_{10} was formed in amounts sufficient to influence the solution compositions, but usually insufficient for detection by X-rays. The minimum proportion of CAH_{10} that can be so detected in the presence of larger amounts of AH_3 and C_2AH_8 is not known, but may be quite high, especially when the CAH_{10} is poorly crystallized. On this hypothesis, the sequence of reactions is essentially the same as for Range 1, but the formation of CAH_{10} at the expense of C_2AH_8 occurs less reproducibly. The rate at which this process occurs seems to depend on a number of factors that are not properly understood. The high concentrations in solution initially present in Range 1 seem to trigger off the process in some way. Some observations by Jones and Roberts [1] suggest that seeding with preformed CAH_{10} may also be effective. Lastly, the present results show that two clear, filtered solutions in Range 2 may have approximately the same concentrations and yet differ markedly in the ease or speed with which they yield CAH_{10}. This suggests that the properties of a supersaturated calcium aluminate solution are not uniquely determined by its composition. It is tempting to speculate on the possibility of differing degrees of condensation or molecular weight in the aluminate anion, but there are no satisfactory data on this subject.

Range 3.—The initial solution compositions lie in a region of AH_3 tie lines, at CaO concentrations too low for the precipitation of C_2AH_8 (fig. 2). Precipitation is therefore essentially of AH_3, the crystallinity of which gradually improves with time. The paths followed by the solution compositions cross the CAH_{10} curve *HJK*. After 6 to 12 months the solution compositions reach the curve *OF* for microcrystalline AH_3 which was established by Wells and Carlson.

The Influence of Alkali on the Precipitation of CAH_{10} at 21 °C

The present results show that NaOH in M/1000 concentration has negligible effect on the composition or behavior of the supersaturated solutions. One hundredth-molar NaOH solution lowers the CaO concentration for a given Al_2O_3 concentration, though not to an extent equivalent to the amount of NaOH added. Detectable amounts of CAH_{10} are formed if the initial solution is concentrated enough, as with water or M/1000 NaOH. Tenth-molar NaOH appears to inhibit the formation of hydrated calcium aluminates entirely. There do not appear to be any precise data regarding the alkali concentrations in setting pastes of commercial aluminous cements. The fact that these yield CAH_{10} under much the same conditions as does pure CA (Wells and Carlson, [2]; Schneider, [4]) suggests that the alkali concentrations probably do not exceed M/100.

The results using M/100 NaOH suggest tentative placings of the metastable solubility curves for C_2AH_8 and CAH_{10} in this medium at *B′K′L′* and *H′K′* respectively (fig. 4).

Metastable Solubility Curve for CAH_{10} at 21 °C

The present results cause us to alter our view (Percival and Taylor, [5]) that the CAH_{10} metastable solubility curve cannot be reached from supersaturation at 21 °C. The failure to reach this curve from supersaturation in the experiments reported earlier can be explained mainly by the fact that most of the initial solutions used were too dilute; in a few cases they were sufficiently concentrated, but carbonation was afterwards found to have occurred in the longer-term experiments, destroying the CAH_{10} that had been formed.

Jones [6] has suggested that the CAH_{10} curve does not follow the line *HK* proposed by Percival and Taylor [5], and used in the foregoing discussion, but the hypothetical line *PYQ* (fig. 5). He bases this view mainly on an analogy with the positions of similarly revised curves for CAH_{10} at 1° and at 5 °C, which in turn were derived from reinterpretations of the results of Carlson [7] and of Buttler and Taylor [3] respectively. It will therefore be necessary to consider the data for lower temperatures. First, however, the direct evidence at 21 °C for and against each of the two CAH_{10} curves will be considered.

Percival and Taylor obtained their curve from undersaturation. In lime solutions of medium concentration, the CAH_{10} dissolved congruently, giving solution compositions at a number of points along *HK*. With water or dilute lime solutions some AH_3 was formed, giving solution compositions at a metastable triple point *H;* with stronger lime solutions there was some formation of C_2AH_8, or C_4AH_{19}, or both, and the solution compositions were at or near the triple point *K* (fig. 5). The present results show that the lime-rich end of

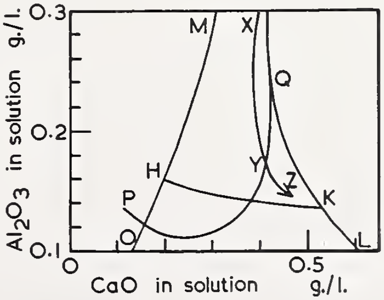

FIGURE 5. *Metastable solubility curves in the alkali-free system at 21 °C.*

QKL, C_2AH_8. *OHM*, AH_3 gel. *HK*, CAH_{10} according to Percival and Taylor. *PYQ*, CAH_{10} according to Jones. *XYZ*: path followed by solution compositions for supersaturated solutions in range 1.

the curve, near *K*, can also be reached, or closely approached, from supersaturation. Jones' curve *PYQ*, in contrast, explains neither the results obtained from undersaturation nor those obtained from supersaturation. He refers to experiments by Jones and Roberts [1] at 20 °C in which CAH_{10} was precipitated. These experiments were closely similar to some of those starting from Range 1 in the present investigation, and their durations were 1 to 28 days. The 28-day experiments gave solution compositions near the point *Y*, in close agreement with the present results and with those of Wells and Carlson [figs. 3 and 5]. This point happens to lie on the CAH_{10} curve proposed by Jones, but with longer times the solution compositions move off this curve towards that proposed by Percival and Taylor. The agreement with Jones' proposed curve therefore appears fortuitous.

Metastable Solubility Curve for CAH_{10} at 5 °C

Figures 9 and 10 of Jones' paper show selected experimental points obtained by Buttler and Taylor [3], with the curve *HC* for CAH_{10} deduced by them from these data (fig. 10) and the somewhat different curve *ZT* (fig. 9) which Jones considered to explain the data more satisfactorily. His main grounds for this were as follows:

(1) All of Buttler and Taylor's runs yielding CAH_{10} from supersaturation gave final solution compositions approximately on, or else above *ZT*. None fell decisively between *ZT* and *HC*.

(2) The C/A ratios for the solid phases existing in contact with solutions whose compositions lay on the hexagonal plate curve are shown in Jones' figure 8. He argues that the sharp drop from 3 to approximately 1 at point *T* indicates that this is the triple point for CAH_{10} and C_2AH_8 with solution, and that the absence of any sharp drop at about 0.53 g CaO/l shows that there is not a triple point in the position suggested by Buttler and Taylor.

(3) Jones rejects the results of runs from undersaturation, such as C11 and C12 (his fig. 10) on the ground that equilibrium was not reached.

It must be admitted that the results at 5 °C are harder to interpret than are those at 21 °C. Carlson's curve for CAH_{10} at 1 °C [7] differs from Buttler and Taylor's at 5 °C by more than seems likely to be explained by the difference in temperature. Also, Carlson's results indicate the existence of a triple point CAH_{10}-C_2AH_8-solution, whereas Buttler and Taylor's demand instead a triple point CAH_{10}-C_4AH_{19}-solution. Further experimental work at low temperatures is needed to settle these points. Nevertheless, we consider that Buttler and Taylor's curve for CAH_{10} at 5 °C. fits the evidence at least as well as Jones' for the following reasons:

(1) The data do not support Jones' assertion that the runs from supersaturation reach equilibrium more readily than those from undersaturation. In figure 6, CaO and Al_2O_3 concentrations are plotted against time for three key groups of runs by Buttler and Taylor. Group 1, from undersaturation, includes points C11 and C12 which are on their curve but not on Jones' curve (his fig. 10). The results suggest that equilibrium is being reached. Group 2, from supersaturation, includes point 9C on Jones' figure 9, which is also close to Buttler and Taylor's curve; the results suggest a near approach to equilibrium. Group 3, also from supersaturation, includes point 21C on Jones' figure 9. This point lies on Jones' curve, but the results suggest that equilibrium has not been reached. An appreciable further decrease in Al_2O_3 concentration could be expected to occur.

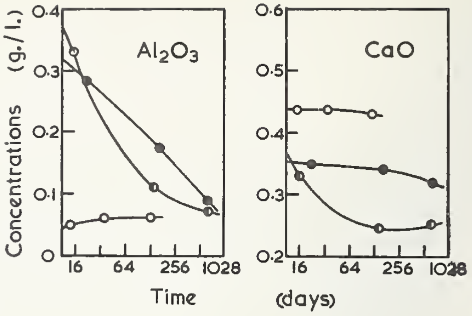

FIGURE 6. *Variation with time in* CaO *and* Al_2O_3 *concentrations for some typical groups of runs made by Buttler and Taylor (3).*

○, CAH_{10} treated with lime solution containing initially 0.440 g CaO/l. ◑, deposition from supersaturated solution containing initially 0.475 g CaO, 0.593 g Al_2O_3/l. ●, deposition from supersaturated solution containing initially 0.676 g CaO, 0.566 g Al_2O_3/l.

(2) The data given in Jones' figure 8 can equally well be explained if the formation of CAH_{10} from supersaturated solutions at 5 °C follows a similar mechanism to that proposed here for its formation at 21 °C. The sharp change in the C/A ratios of the solids at point *T* can be attributed to the fact that the paths followed by the solution compositions in those runs where CAH_{10} is formed at the expense of C_2AH_8 or C_4AH_{19} diverge from the C_2AH_8 curve at or near this point. No sharp change in the observed C/A ratios of the solids would be expected to occur at the triple point C_4AH_{19}-CAH_{10}-solution, on the C_4AH_{19} curve, because the runs from which this curve was obtained were all ones in which CAH_{10} was not involved.

This work was carried out as part of a program of research on the system CaO-Al_2O_3-H_2O supported by the Lafarge Aluminous Cement Company Ltd., whose generous assistance is gratefully acknowledged.

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Paper III–S6. Steam Curing of Cement and Cement-Quartz Pastes*

A. Aitken and H. F. W. Taylor

Synopsis

Pastes of neat cement, and of finely divided quartz mixed with cement in weight ratios of 0.23–3.0, were cured at temperatures mostly between 75 and 200 °C. The phases existing in the products were investigated mainly by X-ray diffraction. Neat cements give poorly crystallized tobermorite minerals, $Ca(OH)_2$, tricalcium silicate hydrate, C_2S α-hydrate, and, at low temperatures only, hydrated aluminate or sulfoaluminate phases. Cement-quartz mixtures give poorly crystallized tobermorite minerals, $Ca(OH)_2$, tobermorite, xonotlite, C_2S α-hydrate, scawtite (presumably resulting from carbonation), and possibly a hydrogarnet. The conditions of temperature, time, and composition needed to give each of these phases are defined.

Résumé

Des pâtes de ciment pur, et de quartz finement divisé mélangé avec le ciment dans des rapports de poids de 0.23–3.0, ont été conservées à des températures variant pour la plupart entre 75 et 300 °C. Les phases existant dans les produits ont été examinées principalement par diffraction des rayons X. Les ciments purs donnent des minéraux tobermorites médiocrement cristallisés, $Ca(OH)_2$, hydrate de silicate tricalcique, C_2S α-hydrate, et, aux températures basses seulement, des phases d'aluminate hydraté ou de sulfoaluminate. Les mélanges ciment-quartz donnent des minéraux médiocrement cristallisés, $Ca(OH)_2$, tobermorite, xonotlite, C_2S α-hydrate, scawtite (qui résulte probablement de la carbonatation), et peut-être un hydrogrenat. Les conditions de température, de temps, et de composition nécessaires à l'obtention de chacune de ces phases sont définies.

Zusammenfassung

Purzementpasten und feingemahlener Quarz der mit Zement in Gewichtsverhältnissen 0.23–3.0 vermischt wurde, wurden bei Temperaturen zwischen 75 und 200 °C aushärten gelassen. Die in den Produkten existierenden Phasen wurden meistens mit Röntgenstrahlen untersucht. Purzemente liefern Tobermoritmineralien, die nicht zu gut kristallisieren, $Ca(OH)_2$, hydratisiertes Trikalziumsilikat, das α-Hydrat des C_2S, und bei niedrigen Temperaturen werden auch hydratisierte Aluminate oder Sulfoaluminatphasen beobachtet. Zement-Quarzmischungen liefern Tobermoritmineralien, die schlecht kristallisieren, $Ca(OH)_2$, Tobermorit, Xonotlit, das α-Hydrat des C_2S, Scawtit (welcher vermutlich durch Kohlensäureaufnahme entstanden ist), und vielleicht auch einen Hydrogranat. Die Temperatur-, Zeit- und Zusammensetzungsbedingungen, unter denen eine jede solche Phase entstehen kann, werden beschrieben.

Introduction and Experimental Methods

Previous work on the phases detectable in autoclaved cement and cement-quartz pastes is reviewed elsewhere in this symposium. This contribution describes some new results.

Materials Used

Cement—To reduce complications caused by the presence of iron- and alkali-bearing phases, a white cement low in alkali was used. Table 1 gives its analysis and potential phase composition: the latter was calculated assuming the small amount of iron to occur as C_4AF. X-ray powder photographs showed C_3S, β-C_2S, and C_3A. To obtain a more detailed qualitative idea of the phase composition, some of the cement was

TABLE 1. *Analysis and potential phase composition of the cement (Snowcrete; A.P.C.M. Ltd., England)*

Analysis	%	Potential phase composition	%
SiO_2	22.16	C_3S	48.5
Al_2O_3	4.62	β-C_2S	26.9
Fe_2O_3	0.41	C_3A	11.6
FeO	.02	C_4AF [a]	1.3
MgO	.20	$Ca(OH)_2$	6.3
MnO	.03	MgO	0.2
CaO	67.44	$CaSO_4 \cdot 2H_2O$	2.5
Na_2O+K_2O	0.34	$CaSO_4 \cdot \frac{1}{2}H_2O$	2.1
Insol. res	.27	Na_2O K_2O MnO FeO Insol.	0.7
SO_3	2.34		
S^{2-}	Nil.		
Ignition loss	2.17		
	100.00		
Free CaO	4.76		
$Al_2O_3:Fe_2O_3$	11.27		

[a] Of doubtful occurrence: see text.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Department of Chemistry, University of Aberdeen, Scotland.

divided by successive specific gravity fractionations with methylene iodide-benzene mixtures into 25 fractions. The denser fractions consisted of C_3S and β-C_2S. They were dark, and therefore probably contained most of the iron, but no ferrite phase was detected optically or by X-rays. The middle fractions contained C_3S and C_3A. The least dense fractions contained C_3S, C_3A, $Ca(OH)_2$, gypsum, and hemihydrate. These results confirm that C_3S, β-C_2S, and C_3A are the main phases. The apparent absence of a ferrite phase suggests that the iron may occur in the silicates, though its presence there is not certain. The assignment of the free CaO and the SO_3 in table 1 is based on the observation that $Ca(OH)_2$, gypsum, and hemihydrate were all present. An attempt was made at quantitative X-ray determination of the phases, but the results were unconvincing, and it was decided that further experience with the method was needed before it could be considered reliable.

Silica—Three samples of fine quartz were used, two of them the same as, and all of them similar to, those used in the work on lime-quartz pastes (Aitken and Taylor, [1][1]). All passed completely through a 300-mesh sieve. One sample possibly reacted a little more slowly than the others, but no important differences between the samples were found.

Experimental Methods

The cement and quartz were intimately mixed in the required proportions, and the mixture transferred to a small silver test tube. Carbon dioxide-free distilled water was added to give a water: cement weight ratio of 0.4, and the paste mixed as quickly as possible to reduce contamination by atmospheric CO_2. The silver tube was placed immediately in either a stainless steel bomb, or a glass test tube which was then sealed off. In either case, the outer vessel contained also enough water to saturate the atmosphere at the temperature subsequently used. The vessel was placed in an oven regulated to ±1 °C for the desired time. The heating and cooling processes were probably each complete in less than 30 min. The products were equilibrated over saturated $CaCl_2$ before examination. All were examined with X-rays, using 11.46-cm-diam powder cameras with filtered copper radiation. Thermal weight-loss curves were obtained for some specimens, using a Stanton recording thermobalance. The conclusions regarding the phases present were based mainly on the X-ray results, supplemented in some cases by those obtained using the thermobalance.

Results and Discussion

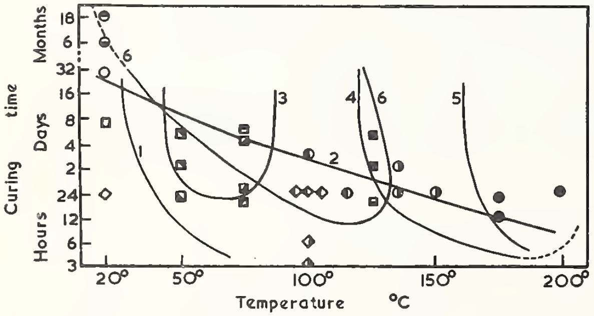

FIGURE 1. *Phases detected in neat cement pastes.*

Curve 1: Upper limit of detection of separate hydrated aluminate or sulfoaluminate phases. Curve 2: Substantially complete reaction of C_3S. Curve 3: Possible low-temperature field of formation of $C_3SH_{1\frac{1}{2}}$. Curve 4: Lower limit of formation of C_2S α-hydrate. Curve 5: Lower limit of high-temperature range of formation of $C_3SH_{1\frac{1}{2}}$ Curve 6: Region of maximum formation of CSH gel. Key to experimental points:

◇, ettringite
⬖, CSH gel } $+C_3S$, β-C_2S, C_3A, & $Ca(OH)_2$
⬗, —

○, ettringite, C_4AH_{13} [a]
◒, C_4AH_{13} [a]
⊖, C_4AH_{13} [a], CSH gel
◐, CSH gel } $+\beta$-C_2S, $Ca(OH)_2$, & (?) C_3S
◑, C_2S α-hydrate
●, C_2S α-hydrate, $C_3SH_{1\frac{1}{2}}$

□, C_4AH_{13} [a], ettringite
◩, (?) ettringite
◪, (?) ettringite (?) $C_3SH_{1\frac{1}{2}}$
◩, (?) $C_3SH_{1\frac{1}{2}}$
◪, CSH gel, $C_3SH_{1\frac{1}{2}}$ } $+C_3S$, β-C_2S, & $Ca(OH)_2$
⊟, CSH gel, (?) $C_3SH_{1\frac{1}{2}}$
⊟, CSH gel
■, CSH gel, C_2S α-hydrate

[a] C_4AH_{13} or related phases such as low-sulfate calcium sulfoaluminate.

Neat Cement Pastes

The results are shown in figure 1; the main conclusions are as follows:

(1) Separate aluminate or sulfoaluminate phases (ettringite and C_4AH_{13} or low-sulfate calcium sulfoaluminate) are formed with certainty only at 18 °C, though there were doubtful indications of ettringite at 50 °C. The results do not confirm Kalousek's conclusion [2] that hydrated aluminate or sulfoaluminate phases are formed transiently at 50–100 °C, though X-ray methods are possibly less sensitive than differential thermal analysis for detection of these compounds. No evidence of C_3AH_6 was found in any of the neat cement pastes.

(2) Disappearance of unreacted cement compounds is naturally more rapid with rising temperature; no C_3S nor C_3A could be detected after about 3 days at 100 °C (fig. 1, curve 2). The ratio of β-C_2S to C_3S appeared from inspection of the X-ray patterns to increase steadily with time at all temperatures studied, suggesting that the hypothesis of equal fractional hydration rates is not obeyed. There is evidence that C_3A reacts less quickly than is sometimes supposed; lines were found that seemed to be attributable to it for up to 1 day at 100° or 105 °C.

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[1] Figures in brackets indicate the literature references at the end of this paper.

(3) The immediate products of hydration of the C_3S and β-C_2S are probably $Ca(OH)_2$ and a lime-rich tobermorite-like gel. This probably does not differ greatly from that formed at room temperature, and its Ca:Si ratio is probably in the region 1.5–2.0. It will be called CSH gel. Curve 6 defines the conditions under which formation of this gel appeared from the X-ray evidence to be at a maximum.

(4) C_2S α-hydrate forms at 125 °C and above, to at least 200 °C, the highest temperature studied. The probable boundary of its field of formation is given by curve 4.

(5) Tricalcium silicate hydrate forms definitely above about 165 °C (curve 5). There were indications of its formation also at 50 and 75 °C (curve 3); this conclusion is based on the appearance of an X-ray spacing of 8.7 A, which is one of the strongest for this phase.

(6) Calcium hydroxide was always present. It might be supposed that less of this phase would form above 165 °C, because of the formation of tricalcium silicate hydrate. If there was less, it was not apparent from the X-ray photographs; probably not enough tricalcium silicate hydrate was formed.

Comparison with the results of earlier investigators—These results are broadly similar to those obtained by Buckle and Taylor [3] for C_3S pastes. The temperature ranges over which tricalcium silicate hydrate is formed are somewhat different in the two cases; the low-temperature range is more constricted with cement, and even its existence is not quite certain. The high-temperature range extends to slightly lower temperatures with cement. No evidence was obtained of the formation of hillebrandite at 80–120 °C, as reported by Kalousek, nor of inversion of β- to give γ-C_2S, as found by Funk [4, 5] on hydrothermal curing of pastes of β-C_2S containing certain stabilizers. The formation of C_2S α-hydrate at 175–185 °C confirms the results of Kalousek [2] and Sanders and Smothers [6], neither of whom, however, reported the formation of tricalcium silicate hydrate. The non-appearance of C_3AH_6 confirms the findings of earlier workers.

Cement-Quartz Pastes: General Survey of the Reactions

The main results are given in figures 2 to 7 and table 2. As well as the phases there indicated, quartz was always found, though sometimes only in traces. Some general conclusions are as follows:

Minimum temperature of reaction between cement and quartz—Runs made at 18 and 75 °C with cement-quartz mixtures gave no indication that the behavior of the cement was significantly influenced by the presence of the quartz (table 2). At or above 85 °C this is no longer true. The first sign of reaction is that less $Ca(OH)_2$, or none at all, is detected (fig. 2). New phases, formation of which could be attributed directly to the presence of the quartz, were first detected at 115 °C, when tobermorite was found after one day in a paste of high quartz:cement ratio (fig. 3).

Phases formed in autoclaved cement-quartz pastes—The hydrated phases found in pastes cured at 85 to 200 °C were CSH gel, $Ca(OH)_2$, tobermorite, C_2S α-hydrate, xonotlite, CSH(A) or scawtite, and possibly a phase of the hydrogarnet type. Tricalcium silicate hydrate was not found except in one case.

TABLE 2. *Phases detected in cement-quartz pastes for curing times other than 25 hours*

Temp. °C	Time	Ratio quartz: cement [a]	Crystalline phases detected [b]				
			C_3S	β-C_2S	T	CSH(A)	Others
18	36 days	1.00	+	+			CH, E, C_4
75	5 days	1.00	+	+			CH, C_3A, TSH
125	18 hrs	1.00	?	?	+		α, HG(?)
155	5 days	0.45	?	?	+	+	HG(?), α
155	4 hr	1.00	+	+			C_3A, HG(?)
155	5 days	1.00			+	+	Xon(?)
165	4 hr	1.00	?	?	+		
175	4 hr	3.00	?	?			CSH gel
175	12 hr	3.00			+		
185	4 hr	1.00	+	+	+	+	

[a] By weight.

[b] T=tobermorite, CH=$Ca(OH)_2$, E=ettringite or related phase, C_4=C_4AH_{13} or related phase, TSH=tricalcium silicate hydrate, α=C_2S α-hydrate, HG=hydrogarnet, Xon=xonotlite.

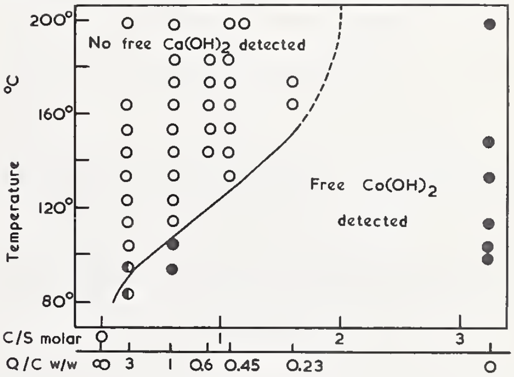

FIGURE 2. *Occurrence of free* $Ca(OH)_2$ *in cement and cement-quartz pastes cured for 25 hours.*

●, Free $Ca(OH)_2$ detected. ◐, Free $Ca(OH)_2$ doubtful or in traces. ○, No free $Ca(OH)_2$ detected.

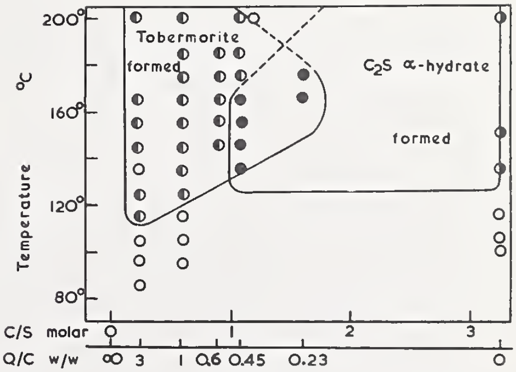

FIGURE 3. *Occurrence of tobermorite and of* C_2S *α-hydrate in cement and cement-quartz pastes cured for 25 hours.*

○, Neither phase detected. ◐, Tobermorite detected. ◑, C_2S α-hydrate detected. ●, Both phases detected.

The influence of quartz on the rate of reaction of the cement—Figure 4 shows the effect of quartz on the temperature needed to obtain complete reaction of the cement within 25 hours. The results are only approximate, but there appears to be a definite trend towards more rapid reaction as the proportion of quartz is increased. Even at 200 °C, the β-C_2S had not completely reacted in the neat cement pastes, but with quartz : cement ratios of 1 or more, complete reaction of both C_3S and C_2S was always attained at 150 °C or over. As with neat cement pastes, C_3A was remarkably persistent. It seems usually to persist for at least 1 day at temperatures up to about 100 °C, irrespective of cement : quartz ratio. There are indications that in the presence of quartz, C_3A may react less rapidly than in neat cements. It was found after 1 day at 145 °C for a quartz:cement ratio of 0.45, and after 4 hr at 155 °C (table 2).

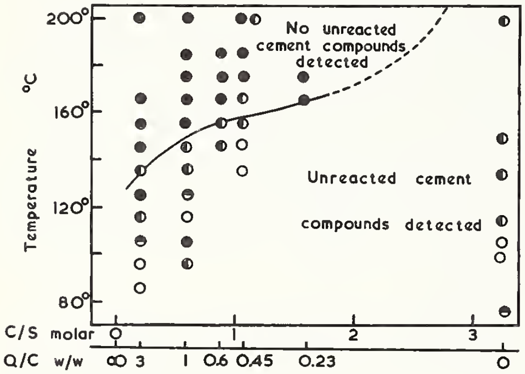

FIGURE 4. *Occurrence of unreacted cement compounds in cement and cement-quartz pastes cured for 25 hours.*

○, C_3S, β-C_2S, and C_3A detected. ◓, C_3S, β-C_2S detected. ◐, β-C_2S, (?) C_3S detected. ●, No anhydrous phases detected.

Conditions of Formation of Individual Phases in Cement-Quartz Pastes

CSH *gel*—Detection of this phase in quartz-cement pastes was not satisfactorily achieved by the methods used. A poorly crystallized phase structurally related to tobermorite was probably present in most or all of the products.

Tobermorite—Figure 3 shows the field of temperature and composition in which this phase was detected after 25 hours' curing. The minimum temperature needed for its formation in detectable quantity in pastes having about the same C/S ratio as to tobermorite is about 125 °C. This temperature probably depends on the cement: quartz ratio. Tobermorite was often a major product. The maximum yield seems likely to be attained at overall C/S ratios of about 0.8 (quartz : cement about 0.65) and temperatures around 180 °C. At higher temperatures, xonotlite tends to form, probably at the expense of tobermorite.

C_2S *α-hydrate*—This compound is formed at overall C/S ratios of 1 or more (quartz:cement ratios below about 0.5), above about 125 °C (fig. 3 and table 2). This minimum temperature of formation seems not to be much influenced by the quartz:cement ratio within this range. C_2S α-hydrate was often a major product.

Xonotlite was a minor product in pastes of high quartz:cement ratio cured at 180 °C or above (fig. 5).

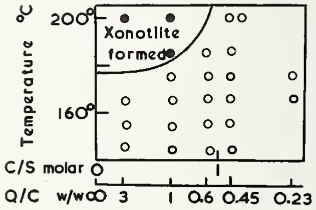

FIGURE 5. *Occurrence of xonotlite in cement-quartz pastes cured for 25 hours.*

●, Xonotlite detected. ○, No xonotlite detected.

$Ca(OH)_2$—As already noted, formation of this compound is largely suppressed in the presence of quartz. The minimum temperature needed to avoid its formation probably decreases with rising quartz:cement ratio. The curve shown in figure 2 is partly conjectural; more data would be needed to establish its position definitely. At quartz:cement ratio 1 and curing time one day, $Ca(OH)_2$ was not detected at autoclave temperatures above about 105 °C.

CSH(A)—This phase appeared irreproducibly in a field centered on overall C/S 1.0, temperature 180 °C (table 2 and fig. 6). It was often formed within 1 day, and in one case within 4 hours. The lack of reproducibility contrasts with the situation regarding the phases so far mentioned. This supports the view (Buckner, Roy, and Roy, [7]) that CSH(A) is a quaternary phase containing CO_3^{2-}, essentially the same as scawtite, and is formed only in the presence of CO_2. McConnell and Murdoch's studies on natural scawtites [8] suggest that the minimum amount of CO_2 needed to permit formation of this phase may be low. The tendency to form scawtite is possibly greater in small laboratory specimens than in the interiors of the much larger ones used in commercial practice.

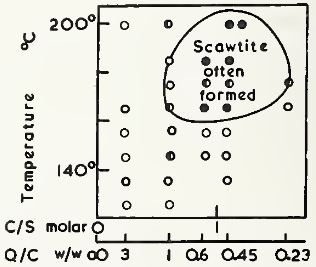

FIGURE 6. *Occurrence of scawtite or CSH(A) in cement-quartz pastes cured for 25 hours.*

●, Scawtite detected. ◐, Scawtite doubtful. ○, No scawtite detected.

Hydrogarnet-type phases—Some evidence was obtained of the formation of a phase related to C_3AH_6 and the hydrogarnet family in a number of specimens. These lay in a field centered on an overall C/S ratio of 0.9, and a temperature of 165 °C (fig. 7 and table 2). As with CSH(A), the phase appeared irreproducibly. The evidence consisted of the presence of a weak powder line of spacing 5.05 ± 0.1 A. This is in the correct range for one of the strongest reflections for phases belonging to this family, although it is probably significantly lower than the value of 5.14 A reported for C_3AH_6.

With a few specimens, other, unidentified weak powder reflections were observed. The most important of these was of spacing 6.0–6.1 A. It was shown by several specimens with quartz: cement ratio 0.4–1.0 and curing temperature 155 to 200 °C.

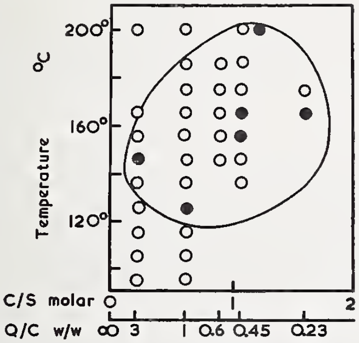

Figure 7. *Possible occurrence of hydrogarnet-type phase in cement-quartz pastes cured for 25 hours.*

●, Hydrogarnet-type phase probably occurs. ○, No hydrogarnet-type phase detected. Ring outlines field in which this phase appears to be formed.

The Course of Reaction in Cement-Quartz Pastes at 85 to 200 °C

The primary reaction is probably always the hydration of the cement to give a lime-rich CSH gel and $Ca(OH)_2$. It seems probable that if any hydrated aluminate or sulfoaluminate phases are formed at all they are quickly decomposed, their components becoming incorporated in the CSH gel. There is some evidence that above 120 °C the Al_2O_3 may separate again partly or completely from the gel, giving a phase of hydrogarnet type. In general, the Al_2O_3 seems to have only a minor influence on the subsequent behavior of the CSH gel.

If no quartz is added, the CSH gel tends above 125 °C to recrystallize, giving C_2S α-hydrate; above 165 °C, tricalcium silicate hydrate can also form. This latter phase can form only as a result of reaction between the gel and $Ca(OH)_2$ crystals that have previously separated from it. Its formation probably represents a beginning of equilibrium crystallization.

The first effect of the quartz is to restrict the separation of $Ca(OH)_2$; one or more poorly crystallized tobermoritelike phases is presumably formed. So long as unreacted quartz grains remain, there is probably a zoning of these phases around them, material of low C/S ratio, possibly similar to CSH(I), forming nearest the quartz grains, and more lime-rich material, perhaps CSH(II), farther away. Very little quartz is needed to prevent formation of tricalcium silicate hydrate at 165 °C or above; a quartz : cement ratio of 0.1 is probably enough.

At 120 to 180 °C, the important processes are the recrystallization of lime-rich gel to give C_2S α-hydrate, and of lime-poor gel to give tobermorite. These processes can occur simultaneously over a limited range of overall C/S ratios. Formation of tobermorite is favored by a high quartz:cement ratio, but if this rises above about 0.7 ($C/S \leq 0.8$) the product is likely to contain a substantial amount of unreacted quartz.

At the higher temperatures the process is complicated by the formation of additional phases. CSH(A) and xonotlite (figs. 5 and 6) are probably formed by recrystallization of tobermorite. Other phases, such as hillebrandite or "Phase F" may be similarly formed from C_2S α-hydrate or from CSH(II) at low quartz:cement ratios; not enough suitable runs were made to establish if this formation does in fact occur.

Comparison With Results of Other Investigators

In the main, these results agree well with those of Kalousek [2], Sanders and Smothers [6], and Neese, Spangenberg, and Weisskirchner [9]. This agreement is especially good as regards formation of tobermorite and of C_2S α-hydrate. None of the earlier workers reported the formation of xonotlite or of CSH(A), but this can be attributed to the narrower range of conditions studied. A more important divergence lies in the probable detection of a hydrogarnet-type phase in the present case, though this cannot yet be considered as certain. The present results do not support Neese's view that nekoite is formed under certain conditions.

The results may also be compared with those obtained for lime-quartz pastes (Aitken and Taylor, [1]. On the whole, there is a close similarity, the cement behaving essentially as a source of both lime and silica, but certain differences are apparent:

(1) Tobermorite is formed over a wider range of overall C/S ratios (0.2–1.6) with cement than with lime (0.33–1.08). The minimum temperature at which it was detected was also slightly lower with cement (115 °C) than with lime (125 °C). These differences can possibly be attributed to the presence of Al_2O_3 in the cement; according to Kalousek [10], Al_2O_3 favors the formation of tobermorite.

(2) Gyrolite was not found when cement was used. Its absence is possibly not significant, as its formation in lime-quartz pastes is slow, and

not many runs were made with cement where the combination of time and temperature was such that formation of gyrolite might have been expected.

(3) Xonotlite was formed less readily with cement. The lowest temperature at which it was found was 180 °C, against 165 °C with lime. This can possibly be attributed to the presence of Al_2O_3 in the cement (Kalousek, [10].

(4) In general, reaction seems to be slower with cement. In every run, unreacted quartz was found in the product, though sometimes only in small amounts; with the lime-quartz pastes, the quartz often reacted completely. Because of this slower reaction, there is a tendency with cement for any given hydrated compound to form most readily when the overall C/S ratio is less than that of the compound, as with tobermorite (fig. 3) or xonotlite (fig. 5). This was not observed with lime.

(5) CSH(A) was formed with cement but not with lime; hillebrandite and "Phase F" were formed with lime but not with cement. These differences may not be significant.

This work was carried out as part of a Fellowship for research on the steam curing of cement and asbestos-cement products supported by the Johns-Manville Corporation, whose generous assistance is gratefully acknowledged. We also thank A.P.C.M., Ltd., for the cement specimen.

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Paper III–S7. Two Different Ways of Hydration in the Reaction of β-Ca_2SiO_4 With Water at 25 to 120 °C[*]

Herbert Funk

Synopsis

β-Ca_2SiO_4 is transformed into tobermorite-like calcium silicate hydrates in two different ways:

(1) By reaction with pure water, β-C_2S is able to hydrate directly to give needle-shaped tobermorite. The needles originated from a single crystal of β-C_2S are oriented to each other. In this course of hydration β-C_2S crystals take up H_2O directly, being altered continuously with increasing water content. This is shown by X-ray diagrams as well as by optical observations of the intermediate products which no longer contain anhydrous β-C_2S and are not yet completely formed tobermorite.

(2) β-C_2S forms foil-like or platy tobermorite through the solution phase. Exclusively this course of reaction is observed, if certain additives are used ($CaCl_2$, supersaturated solution of $Ca(OH)_2$, seed crystals). Unlike the products of the direct hydration (1) the partly hydrated products of the solution-phase reaction consist of mixtures of foil-like tobermorite and residual anhydrous β-C_2S. Addition of seed crystals of tobermorite foils to the mixture of β-C_2S and water stops the slower direct hydration reaction, and foils of tobermorite, rather than needles, are formed through the solution phase.

(3) β-C_2S as well as γ-C_2S is practically quantitatively transformed into dicalcium silicate α-hydrate, $Ca_2OH(HOSiO_3)$, at 100 to 200 °C through the solution phase, if seed crystals of this compound are added. After addition of tobermorite seed crystals at 100 °C β-C_2S as well as γ-C_2S is transformed into tobermorite through the solution phase.

Résumé

β-Ca_2SiO_4 se transforme en hydrates de silicate de calcium comparable à un tobermorite, de deux façons différentes:

(1) Par réaction à l'état solide, β-C_2S est transformé par H_2O en tobermorite aciculaire, dans lequel les aiguilles sont orientées les unes envers les autres. Dans cette réaction solide les cristaux de β-C_2S absorbent H_2O, continuellement modifiés par l'accroissement de la teneur en eau. Les diagrammes de rayons X indiquent ce fait aussi bien que les observations optiques. Il y a formation de produits intermédiaires qui ne contiennent plus de β-C_2S anhydre et ne sont pas encore des tobermorites complètement formés.

(2) β-C_2S forme un tobermorite en feuilles ou en plaques dans la phase de solution. Ce cours de réaction est atteint à l'aide de certains additifs ($CaCl_2$, solution sursaturée de $Ca(OH)_2$, grains de cristaux). A la différence du produit de la réaction solide, les solides en partie hydratés consistent en mélange de tobermorite en feuille et de β-C_2S anhydre résiduel. L'addition de grains de cristaux de feuilles de tobermorite arrête l'hydration plus lente à l'état solide, et ce sont des feuilles de tobermorite, plutôt que des aiguilles, qui sont formées dans la phase de solution.

(3) β-C_2S comme γ-C_2S est presque quantitativement transformé en α-hydrate de silicate dicalcique, $Ca_2OH(HOSiO_3)$, à 100–200 °C dans la phase de solution, si des grains de cristaux de ce composé sont ajoutés. Après addition de grains de cristaux de tobermorite à 100 °C, β-C_2S ainsi que γ-C_2S est transformé en tobermorite dans la phase de solution.

Zusammenfassung

β-Ca_2SiO_4 kann auf zwei verschiedenen Wegen tobermoritähnliche Calciumsilikathydrate bilden:·

(1) β-C_2S kann mit reinem Wasser direkt unter Bildung von Tobermoritnadeln reagieren. Die aus einem Einkristall von β-C_2S entstehenden Nadeln sind optisch zueinander orientiert. Bei diesem Hydratationsweg nehmen die β-C_2S-Kristalle direkt H_2O auf, wobei sie mit steigendem Wassergehalt kontinuierlich verändert werden, wie es sowohl die Röntgendiagramme als auch die optischen Beobachtungen zeigen. Es werden Zwischenprodukte gebildet, die kein wasserfreies β-C_2S mehr und noch keinen fertig gebildeten Tobermorit enthalten.

(2) β-C_2S kann über die Lösungsphase folien- oder plattenförmigen Tobermorit bilden. Dieser Reaktionsweg wird ausschließlich beobachtet, wenn bestimmte Zusätze beigefügt werden ($CaCl_2$, übersättigte Lösung von $Ca(OH)_2$, Impfkristalle). Im Unterschied zu den Produkten der direkten Hydratation (1) bestehen die teilweise hydratisierten Produkte der Lösungsphasenreaktion aus Gemischen, die Tobermoritfolien und restliches wasserfreies β-C_2S enthalten. Durch Impfkristalle aus Tobermoritfolien wird die langsamere direkte Hydratation des β-C_2S unterbrochen und es entstehen durch die Lösungsphase Tobermoritfolien anstelle von Nadeln.

(3) β-C_2S wird ebenso wie γ-C_2S praktisch quantitativ bei 100–200 °C durch die Lösungsphase in Dicalciumsilikat-α-Hydrat, $Ca_2OH(HOSiO_3)$, umgewandelt, wenn Impfkristalle dieser Verbindung zugefügt werden. Durch Zugabe von Tobermorit-Impfkristallen wird sowohl β-C_2S als auch γ-C_2S bei 100 °C durch die Lösungsphase in Tobermorit umgewandelt.

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[*] Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Institut für anorganische Chemie, Deutsche Akademie der Wissenschaften zu Berlin, Germany.

Introduction

By hydration of the cement components C_3S and β-C_2S, tobermorite-like calcium silicate hydrates have been observed as foils, needles, plates, or laths, or mixtures of them. The X-ray diagrams of these different forms are either extraordinarily similar or identical; for brevity they are designated as tobermorite, but it would be better to call them tobermorite-like phases.

In a previous work [1] [1], the formation of the needle-shaped tobermorite-like phase with the composition $2CaO{\cdot}SiO_2{\cdot}2H_2O$ at 100 °C from β-C_2S with water has been found to occur by direct hydration of β-C_2S. To differentiate this direct hydration of β-C_2S crystals by H_2O (as liquid or vapor) from the phase formed by reaction through the solution, it was called "direct" or "solid-state" hydration. Formerly, also McConnell [2, 3] had observed that the hydration of β-C_2S (larnite) and of α'-C_2S (bredigite), both occurring in nature, led to the tobermorite-like phase (plombierite) in the oriented form.

Hydration of β-C_2S in the Solid State With the Formation of Needle-Shaped Tobermorite

Sufficiently stabilized β-C_2S [2] was allowed:

(1) to mix with water (1:10 up to 1:50) at 25 °C by rotation in polyethylene bottles, or

(2) to stand with water, or saturated $Ca(OH)_2$ solution in pasty consistency (1:2.5), in silver crucibles at 25 or 100 °C.

These conditions led to the formation of needle-shaped tobermorite-like calcium silicate hydrate as a final product, which had a composition of $1.5CaO{\cdot}SiO_2{\cdot}1.5H_2O$ (at 25 °C) to $2CaO{\cdot}SiO_2{\cdot}2H_2O$ (at 100 °C).

Optical Investigation

From time to time, samples were taken from the reaction mixtures (β-C_2S with H_2O), and changes occurring at the crystals were microscopically observed. On the surface of the crystals, taken from partly hydrated intermediates, there was a zone of decreased refractive index which extended progressively into the crystal. With a water content of $\sim 1H_2O/SiO_2$ (after having been dried in vacuo over P_2O_5) most crystals practically became optically uniform again. The refractive index decreased from $n=1.71$–1.73 (β-C_2S), to $n=1.67$–1.68 (intermediate product with $\sim 1H_2O/SiO_2$). After the hydration up to a content of $\sim 1H_2O/SiO_2$ the crystals remained optically active and still rotated the plane of polarized light uniformly. Amorphous portions which might consist of fine-grained tobermorite, have not been found during this solid state hydration. Portions of amorphous, optically nonoriented tobermorite are to be seen only in case of hydration proceeding through the solution phase.

Electronmicroscopic Investigation

Some photographs, characteristic for changes observed in the crystals, show that the β-C_2S crystals (fig. 1(a)) have a more layer-like structure after the action of water. After three days action of water at 100 °C, e.g., about 1.1 H_2O/SiO_2 has been bound (fig. 1(b)). After four days at 100 °C the substance contains 1.4 H_2O/SiO_2; with this or higher water content, crystals often split off columnar or needle-shaped fragments (fig. 1(c)). Beta-dicalcium silicate crystals treated with water for 20 days at 100 °C have the composition, e.g., $1.9CaO{\cdot}SiO_2{\cdot}2.0H_2O$; their X-ray pattern is similar to that of tobermorite (see following section). Tobermorite needles arising from a β-C_2S crystal often still hold together, and the contour of the starting crystal is still to be seen (fig. 1(d)).[3]

Crystals of an intermediate product with $<1H_2O/SiO_2$, obtained after two days action of water on β-C_2S at 100 °C, seem only little changed in their appearance. But on treating this substance with ultrasonics of low intensity the hydrated crystals disintegrate into needles (fig. 1(e)), showing them also to have been changed in their interior by the water; anhydrous β-C_2S remains completely unchanged when treated in the same way.

Amorphous tobermorite had not been found in the intermediates and therefore the water content was assumed to be found in the crystals; this assumption corresponds to the results of optical observation. The water taken up by the β-C_2S crystals extends also into the interior of the crystals indicated by the decreased refractive index, and also by the easy splitting into needles by ultrasonics. That this alteration occurs in the β-C_2S crystals remaining undissolved becomes once more evident by the changes of the X-ray pattern described below.

X-ray Investigation

Debye photographs of intermediate substances formed of β-C_2S containing 0.5 to 1 H_2O/SiO_2 show only an increase of background. With a counter-tube goniometer we have recognized in these substances:

(1) a general decrease of the intensities of the reflections of β-C_2S,

(2) a change of the relative intensities of reflections of β-C_2S, proceeding to the vanishing of certain reflections.

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] One percent by weight of Na_2SO_4, or 0.3 percent by weight of $Ca_3(BO_3)_2$ was added to γ-C_2S (diameter of crystals, 10–50 μ). In the case of stabilization with 1 percent of Na_2SO_4, the mixture was heated three times for one hour to 1,100 °C in a platinum dish with a lid, and well mixed afterwards. Insufficiently stabilized β-C_2S may be re-transformed into γ-C_2S by action of water, if the grain size is about 0.01 mm or more [4].

[3] Thin, long laths of tobermorite have been observed to grow from small needles, if these have been allowed to stand—especially at 100 °C—with water (for instance if needles were used as seed crystals).

X-ray photographs according to the Guinier method demonstrate the change of intensity most distinctly. The reflections in the diagram of β-C_2S do not become weaker equally, as the substance is progressively hydrated (see fig. 2c, d). Only certain reflections vanish, which often are not those weakest in intensity (in fig. 2 marked by arrows). On the other hand, the pattern of the hydrated substance has left unchanged other, weaker, reflections (in fig. 2 marked by x). The diagram of the hydrated intermediate substance, therefore, does not contain a symmetrically weakened diagram of β-C_2S, although there are many reflections common to both. The new reflection appearing at 1.82 A, also present in tobermorite, is marked by a double arrow.

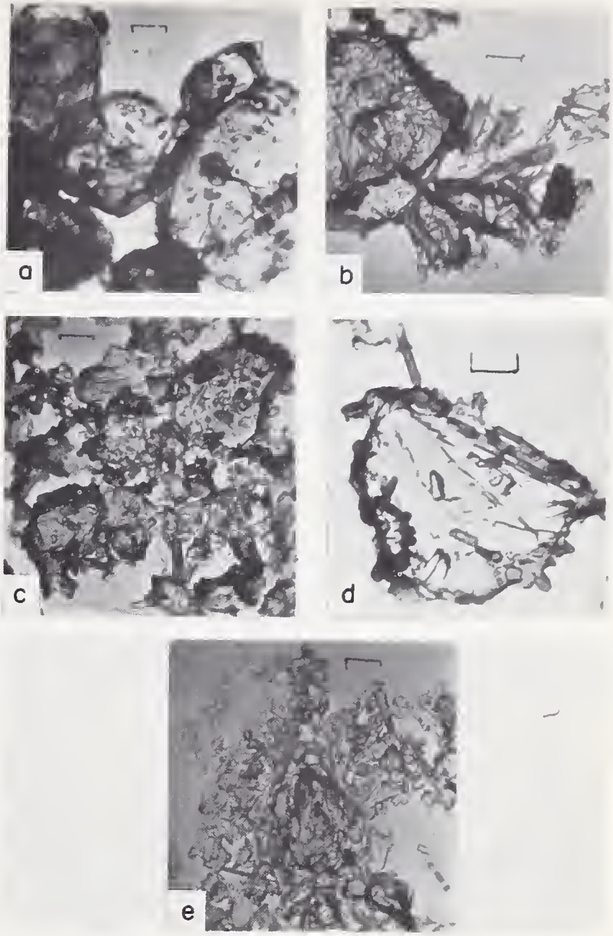

Figure 1. *Electron-micrographs of β-C_2S in different stages of hydration.*

a. β-C_2S (stabilized with 1% Na_2SO_4).
b. β-C_2S, 3 days 100 °C (1.1 H_2O/SiO_2).
c. β-C_2S, 4 days 100 °C (1.4 H_2O/SiO_2).
d. β-C_2S, 20 days 100 °C (1.9 $CaO \cdot SiO_2 \cdot 2.0\ H_2O$).
e. β-C_2S, 2 days 100 °C (0.9 H_2O/SiO_2) treated with ultrasonics.

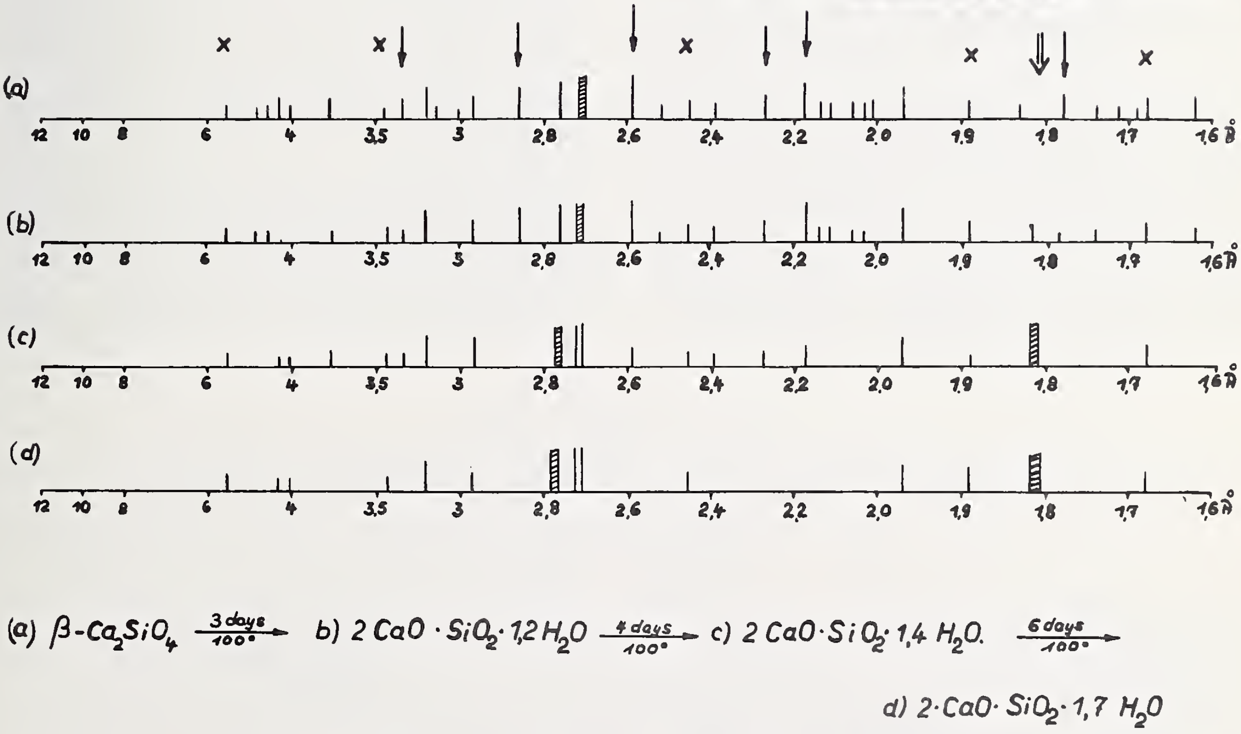

Figure 2. *X-ray patterns of β-C_2S in various stages of hydration.*

Conclusion

The changes of the X-ray patterns of the intermediate substances, corresponding to optical and electronmicroscopical observations, must be interpreted in the following way: β-C_2S remaining undissolved hydrates by the action of water that probably reacts as H^+ and OH^- ions. Every β-C_2S crystal is continuously altered according to the increase of its water content. This change may be observed by optical methods and by the continuous alteration of the X-ray patterns of the products on progressive hydration.

β-C_2S Hydrated Through Solution by the Formation of Foil-Like or Platy Tobermorite

Hydration of β-C_2S under special conditions yields tobermorite also in the form of foils or plates. The special conditions are those in which additives are supplied either to the water added ($CaCl_2$, supersaturated solutions of Ca $(OH)_2$) or to the reaction mixture (as seed crystals). There is evidence that foil-like or platy tobermorite, formed by additives in a shorter time of reaction, occurs through the solution phase.

β-C_2S Hydration in Shorter Time by Additives

Mixtures with additives were prepared in the same way as described before, in the form of pastes or by rotating them with the respective solutions. A survey of the times of hydration of β-C_2S by different solutions is given in table 1.

Pure water as well as lime water (saturated with 1.6 g $Ca(OH)_2$/l) leads to tobermorite needles after a hydration time of 140–200 days, as shown in columns 1 and 2, respectively. The fact that that needles are formed by hydration in the solid state is shown, as previously stated, by the variable diagram of intermediate substances which are incompletely hydrated. A supersaturated solution of $Ca(OH)_2$ (2.2 g/l, column 3), such as may occur in contact with C_3S, and therefore usually is present in the cement paste, shortens hydration time to about 100 days, during which the tobermorite phase is formed in foils. Complete hydration takes place in 30 to 40 days if a 15-percent $CaCl_2$ solution is applied.

If samples, still incompletely hydrated, are taken (see columns 3 and 4, reactions in which foil-like tobermorite is formed), microscopic observation shows mixtures of optically amorphous masses with residual anhydrous β-C_2S. X-ray diagrams also show that tobermorite is present with anhydrous β-C_2S. Formation of these nonoriented tobermorite crystals (seen in the electronmicroscope as foils) mostlikely occurs through the solution phase. The characteristic difference from the direct hydration of β-C_2S to give needle-like tobermorite is the fact that the intermediate products of the solution reaction contain foils and give no X-ray photograph with an altered diagram of β-C_2S. If it is true that tobermorite foils are formed through solution, then this reaction may be expected to be induced by addition of seed crystals of foil-like tobermorite to β-C_2S with pure water.

Tobermorite Foils as Seed Crystals: Hydration of C_2S Through the Solution Phase

Undissolved β-C_2S is hydrated by pure water at 25 and 100 °C to yield needle-shaped tobermorite as described before. If, however, 10 percent by weight of tobermorite foils are added, β-C_2S will be completely transformed into foil-like tobermorite after 60 to 70 days at 25 °C. After approximately 30 days the reaction product contains only half of the water content of the final product. Optical, electron-optical, and X-ray examinations of such incompletely hydrated products show that the greatest part of the substance is tobermorite foils, the rest being anhydrous β-C_2S. This means that the addition of seed crystals causes hydration of β-C_2S through the solution phase. Parallel runs, under the same conditions but without addition of tobermorite foils, always yielded needles formed by the solid-state hydration.

If the hydration products consist of tobermorite foils, the mass seems to be less stiff than if needles are formed by solid-state hydration. Tobermorite foils as seed crystals frequently lead not only to more foils but to relatively large, platy crystals (approximately 10–100 μ long). Besides foil-like

TABLE 1. *Hydration of β-C_2S*

β-C_2S (stabilized by 1% of Na_2SO_4; particle size 5—40μ); allowed to stand with aqueous solution (1:3) at 25 °C.

	1	2	3	4	5
	Pure water	$Ca(OH)_2$ solution, saturated (1.60 g/l)	$Ca(OH)_2$ solution supersaturated (2.2 g/l)	$CaCl_2$ solution 15%	Seeded with tobermorite foils
Completely hydrated after	~200 days	~140 days	~100 days	30–40 days	~70 days.
Crystal shape of tobermorite (electron microscope).	Needles	Needles	Foils	Foils and plates (lamellar).	Foils.
X-ray pattern of an incompletely hydrated sample.	Intermediate pattern (variable).	Intermediate pattern (variable).	β-C_2S+tobermorite	β-C_2S+tobermorite	β-C_2S+tobermorite.

and platy tobermorite, with a 10-percent $CaCl_2$ solution, frequently a shrouding zone around the β-C_2S crystals occurs, having a gel-like and shapeless appearance in the electronmicroscope.

Gamma-dicalcium silicate as well as β-C_2S is completely transformed into tobermorite foils in 10 days at 100 °C after addition of a 15-percent $CaCl_2$ solution or seed crystals of tobermorite foils. Seed crystals of dicalcium silicate α-hydrate, $Ca_2OH(HOSiO_3)$, completely yield dicalcium silicate α-hydrate from β-C_2S or γ-C_2S at 100 to 200 °C.

Conclusions

β-C_2S hydrates in two different ways:

(1) In a slow direct hydration, β-C_2S crystals, remaining undissolved, take up H_2O. After 140 to 200 days, an oriented transformation into tobermorite needles is observed.

(2) At a certain minimum concentration of $CaCl_2$ or $Ca(OH)_2$ in aqueous solution, namely,

(a) 1 molar in $CaCl_2$, or

(b) 0.03 molar in $Ca(OH)_2$ (supersaturated), exclusively foil-like or platy tobermorite rather than needles is spontaneously formed from β-C_2S at 25–100 °C through the solution phase.

Tobermorite foils are also formed from β-C_2S with water at 25 and 100 °C by the addition of tobermorite foils under conditions in which, without seed crystals and with pure water, only the formation of needle-shaped tobermorite is observed. Both types of tobermorite are able to form setting masses. The formation of tobermorite needles from β-C_2S with water at 100 °C does not occur in preference to a formation of $Ca_2OH(HOSiO_3)$ (C_2S α-hydrate) if seed crystals of C_2S α-hydrate are added or spontaneously formed.

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Paper III–S8. Infrared Absorption of Some Compounds in the CaO-SiO_2-H_2O System*

Charles M. Hunt

Synopsis

Infrared absorption spectra of γ-C_2S, β-C_2S, C_3S, and the hydration products of C_3S have been obtained in the 300 to 5000 cm^{-1} region, using the KBr pressed-pellet technique. Spectra of okenite, gyrolite, Loch Eynort tobermorite, afwillite, and hillebrandite, in the form of natural minerals, and a synthetic xonotlite have also been measured. The vibrations associated with the SiO_4 groups are of great value for identifying the compounds but because of their complexity are difficult to interpret in terms of structure. The OH bending vibrations near 1650 cm^{-1} are either weak or absent in these compounds. This would be consistent with crystal structures in which water is largely, or in some cases entirely, in the form of OH groups. The position of the OH stretching vibrations suggests some degree of hydrogen bonding and also unbonded OH in some of these hydrates. None of the compounds, however, appears to contain hydrogen bonds of the diversity and strength of those reported in afwillite.

Résumé

Les spectres d'absorption infrarouge de γ-C_2S, β-C_2S, C_3S, et les produits d'hydratation de C_3S ont été obtenus dans la région de 300 à 5000 cm^{-1}, en employant la technique KBr de granules comprimées. Les spectres d'okenite, de gyrolite, de tobermorite de Loch Eynort, d'afwillite, et d'hillebrandite, sous forme de minéraux naturels, et un xonotlite synthétique ont également été mesurés. Les vibrations associées aux groupes de SiO_4 sont de grande valeur pour l'identification des composés, mais à cause de leur complexité il est difficile de les interpréter en termes de structure. Les vibrations OH dues à la flexion dans le voisinage de 1650 cm^{-1} sont faibles ou absentes dans ces composés. Ceci serait compatible avec les structures cristallines dans lesquelles l'eau se présente pour une grande part, ou dans certains cas entièrement, sous forme de groupes OH. La position des vibrations OH dues à la tension suggère qu'il y a dans une certaine mesure un lien d'hydrogène ainsi que OH non-lié dans certains de ces hydrates. Aucun des composés, cependant, ne paraît comporter de liens d'hydrogène ayant la diversité et la résistance de ceux notés dans l'afwillite.

Zusammenfassung

Ultrarotabsorptionsspektra des γ-C_2S, des β-C_2S, des C_3S und der Hydratationsprodukte des C_3S wurden von 300 bis 5000 cm^{-1} unter Benutzung zusammengepreßter KBr Kügelchen aufgenommen. Die Spektra des Okenits, des Gyrolits, des Loch-Eynort-Tobermorits, des Afwillits und des Hillebrandits wurden als natürliche Mineralien, und außerdem auch das Spektrum eines synthetischen Xonotlits gemessen. Die Vibrationen, die zur SiO_4-Gruppe gehören, können zur Identifizierung der Verbindungen gut benutzt werden, aber wegen ihrer großen Kompliziertheit sind sie schwierig für Strukturanalyse zu benutzt werden. Die OH-Biegungsschwingungen in der Nähe von 1650 cm^{-1} sind in diesen Verbindungen nur schwach vorhanden, oder sie fehlen vollständig. Das stimmt mit den Kristallstrukturen, in denen das Wasser zum grossen Teil oder sogar nur als OH-Gruppen vorkommt, gut überein. Die Lage der Spannungsschwingungen des OH läßt vermuten, daß Wasserstoffbindung zum Teil auftritt, und daß einige dieser Hydrate nicht gebundene OH-Gruppen haben. Aber man gewinnt den Eindruck, daß keine dieser Verbindungen Wasserstoffbindungen der Mannigfaltigkeit und Stärke besitzt, wie man sie vom Afwillit kennt.

Introduction

In their review papers for this symposium, Brunauer and Greenberg [1] [1] and Taylor [2] have briefly discussed the infrared absorption of the calcium silicate hydrates. The present paper undertakes to extend this discussion and introduce absorption spectra of a few of the compounds which are referred to in these papers.

Heller and Taylor [3] have compiled optical and X-ray data for a number of the calcium silicates and calcium silicate hydrates. Infrared spectroscopy offers an additional means of characterizing these materials. The spectra in the interval 300 to 5000 cm^{-1} presented here have been obtained partly for this purpose and also to study the SiO_4 and OH vibrations for information related to structure.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the National Bureau of Standards, Washington.

[1] Figures in brackets indicate the literature references at the end of this paper.

Methods and Materials

Measurement of Spectra

The compounds were measured by the KBr pressed-pellet technique [4,5]. The pellets contained a milligram of compound and approximately 250 mg of KBr. In some cases, pellets with only 0.3 to 0.5 mg of compound were also measured. The spectra were obtained without a blank pellet in the reference beam, and transmission values are uncorrected for losses caused by reflection and scattering. A small spurious absorption appears at 2940 cm^{-1} and is marked in the figures by an asterisk. Others have noted similar absorption in KBr pellets [6]. The spectra at 620 to 5000 cm^{-1} were obtained immediately after heating the pellets in vacuum at 100 °C, overnight or usually much longer. Those at 300 to 620 cm^{-1} were measured without this treatment.

The spectra were obtained with a Beckman IR–4 double-beam spectrometer. Cesium bromide prisms were used for the range 300 to 620 cm^{-1}, and NaCl prisms for the range 620 to 5,000 cm^{-1}.

Materials

Gamma dicalcium silicate was prepared from calcium carbonate and silica gel. The mixture was heated to 1,410 °C and then formed into pellets under pressure and reheated twice. The product was finally heated to 660° to complete reversion to the γ-form.

Beta dicalcium silicate was prepared the same way as γC_2S, except that 0.4 percent of boric acid was added to stabilize the compound, and the heating at 660° was omitted.

Tricalcium silicate was prepared by heating a mixture of calcium carbonate and silica at 1,400 °C. The product was reground, made into a paste with water, and carefully reheated to 1,400 °C. This process was repeated two more times.

Microscopic examination of the synthetic calcium silicates indicated that they were predominantly homogeneous materials containing small amounts of impurities. The powder X-ray patterns were in agreement with ASTM patterns.

Paste-cured C_3S was obtained by reacting equal weights of water and C_3S for a period of 14 months at 100 °F. The product contained 20 percent of water after vacuum-drying at 100 °C.

Loch Eynort tobermorite was obtained from Dr. G. F. Claringbull of the British Museum of Natural History. The sample is designated as part of B.M. 1937, 1490 and has been described by Claringbull and Hey [7], and also Gard and Taylor [8].

The other natural minerals were obtained from Dr. G. S. Switzer of the National Museum, Washington, D.C. They are listed with nominal chemical formula [3], source, and identifying museum number as follows:

Okenite, $CaO{\cdot}2SiO_2{\cdot}2H_2O$, from Disco Island, Greenland, museum No. 94,524,

Truscottite, $CaO{\cdot}2SiO_2{\cdot}1/2H_2O$, from Redjang Lebong mine, Sumatra, museum No. 95,872,

Gyrolite, $2CaO{\cdot}3SiO_2{\cdot}2H_2O$, from Disco Island, Greenland, museum No. 112,506,

Afwillite, $Ca_3(SiO_3OH)_2{\cdot}2H_2O$, type specimen from Dutoitspan mine, Kimberley, South Africa, museum No. 95,237,

Hillebrandite, $2CaO{\cdot}SiO_2{\cdot}H_2O$, from type location, Ternates mine, Velardena, Durango, Mexico, museum No. 95,767.

Microscopic examination of afwillite and gyrolite indicated nearly homogeneous materials. Hillebrandite was predominantly homogenous, but contained a few isolated particles of different refractive index. Okenite and truscottite contained noticeable amounts of intimately distributed material of different refractive index.

Powder X-ray patterns of afwillite and hillebrandite were in excellent agreement with those of Heller and Taylor [3]. The other minerals showed all of the principal lines of the compound in question, but gyrolite had a small extraneous line at 4.43 A, okenite had some calcite lines, and truscottite had some quartz lines and a few other unidentified lines.

Xonotlite was prepared by E. S. Newman of the National Bureau of Standards. It has been previously described [9].

Results

The absorption spectra of the compounds investigated are shown in figures 1 and 2. Figure 1 shows the spectra of γ-C_2S, β-C_2S, and C_3S and also paste and ball-mill-hydrated C_3S. Figure 2 presents the spectra of compounds in the CaO-SiO_2-H_2O system, arranged in the order of increasing CaO/SiO_2 ratio. With the exception of xonotlite, all of the specimens in figure 2 are natural minerals.

Discussion

General Spectral Features

Gamma dicalcium silicate, β-C_2S, and C_3S show broad absorption in the 700 to 1200 cm^{-1} region. This feature is common to the spectra of most silicates [10], and is associated with a number of vibrational modes associated with Si—O linkages. D. M. Roy [11] has also measured γ-C_2S and β-C_2S in this region and obtained patterns between 700 and 1200 cm^{-1} somewhat similar to the ones in figure 1. She found γ-C_2S to give an altered spectrum in KBr pellets, which suggests that under some circumstances this compound may be subject to anion exchange or other effects sometimes observed in KBr [12, 13, 14, 15, 16]. However, the 700-to-1200-cm^{-1} part of the spectrum in figure 1 resembles Roy's spectrum in nujol mull rather than her KBr spectrum. Possibly this may be due to the short (15 seconds) mixing time used in preparing the pellets. Launer [17] has also measured the spectrum of β-C_2S at 620 to 5000 cm^{-1}. The comparable parts of Roy's and Launer's patterns are slightly sharper than the one shown in figure 1. The very small band at 1260 cm^{-1} is very possibly due to the boric acid stabilizer in the compound [18]. It is absent from Launer's β-C_2S which was prepared without a stabilizer. The method of preparation is described by King [19].

When C_3S is hydrated as a paste, the spectral detail in the 700-to-1200-cm^{-1} region is lost, and the center of this broad absorption shifts to higher frequency. This particular preparation shows no band at 12.1 μ where Van Bemst [20] reported an absorption band in CSH-II. In the region 3000 to 4000 cm^{-1} there is a sharp band at 3620 cm^{-1}, due to $Ca(OH)_2$ in the product, and a broader band near 3450 cm^{-1} somewhat similar to the one found in Loch Eynort tobermorite. The OH bending vibration near 1650 cm^{-1} is broad in hydrated C_3S but comparatively sharp in Loch Eynort tobermorite. Also noteworthy are the spectral differences between these materials in the range 300 to 600 cm^{-1}.

Kalousek and Roy [21] have prepared a synthetic tobermorite with a CaO/SiO_2 ratio of 0.8 and a spectrum in the interval 620 to 5,000 cm^{-1} similar to that of Loch Eynort tobermorite. On the other hand, their calcium silicate preparations of larger CaO/SiO_2 ratio bear more resemblance to paste-hydrated C_3S. According to Brunauer and Greenberg [1], the tobermorite obtained by hydration of C_3S or β-C_2S resembles a high-lime tobermorite far more than a low-lime tobermorite. This is also true of the infrared spectra.

The similarity between Kalousek and Roy's hydrates having a large CaO/SiO_2 ratio and paste-hydrated C_3S also includes the strong band between 1400 and 1600 cm^{-1} which is due to the 0.5 percent of CO_2 found in the material. A carbonate contamination in $Ca(OH)_2$ or a high-lime calcium silicate hydrate produces stronger absorption in the region 1400 to 1600 cm^{-1} than a comparable amount of carbonate in a low-lime material [22].

Brunauer, Copeland, and Bragg [23] have shown that C_3S hydrated in a ball mill gives afwillite as a hydration product. Figure 1 shows the infrared absorption spectrum of a ball-mill preparation made in their laboratory. The spectrum may be compared with that of natural afwillite shown in figure 2. The patterns show some differences in detail, but there is good correspondence between the positions of the principal absorption bands. The bands are less sharp in ball-mill-hydrated C_3S than in the natural mineral, particularly in the region of longer wavelengths. The ball-mill-hydrated product shows a sharp band at 3620 cm^{-1} due to $Ca(OH)_2$. This band is absent from the natural material.

Examination of the spectra of the calcium silicate hydrates in figure 2 shows that most of the patterns are sufficiently distinctive to be of value in identifying the minerals. The bands at 1500 and 875 cm^{-1} in okenite and gyrolite clearly show the presence of calcite as a contaminant. Hillebrandite, truscottite, and xonotlite also show a small absorption near 1500 cm^{-1}.

Kalousek and Roy [21] have determined the spectrum of a natural xonotlite in the region 620 to 5000 cm^{-1}. Their spectrum resembles the corresponding part of the spectrum in figure 2 quite closely, except that their pattern shows slightly less detail near 680 and 980 cm^{-1}, and the band at 3430 cm^{-1} is weaker. They also have noted that this latter band is weaker in natural than in synthetic xonotlite, particularly in preparations made at lower temperatures.

Berkovich, Keiker, Gracheva, Zevin, and Kupreeva [24] have measured the spectrum of a synthetic tobermorite in the interval 830 to 5000 cm^{-1}. Their product shows less spectral detail than the natural mineral or Kalousek and Roy's preparation, but it does not resemble the hydrated C_3S.

SiO_4 Vibrations

It would be possible to account for considerable complexity in the absorption spectra of the silicates from the fundamental vibrations of the SiO_4 tetrahedra, even neglecting possible absorptions due to harmonics, combination bands, and lattice vibrations. This may perhaps best be shown by briefly reviewing the vibrational behavior of the free tetrahedron and considering the modifications of the vibrations as the tetrahedron is incorporated in a crystal. According to the theory of molecular vibrations [25a, 26, 27], any nonlinear molecule of five atoms should have nine fundamental vibrations. However, in XY_4 molecules of tetrahedral symmetry only four fundamental frequencies appear [10, 25b, 28], because a number of vibrations have the same frequency, that is to say are degenerate. Of the four fundamental vibrations of the tetrahedron, only two are infrared active. This is summarized briefly in table 1.

TABLE 1. *Fundamental vibrations of tetrahedral XY_4 molecule*

Vibrational species	Number of vibrations	Frequencies of SiO_4 ion[a]	
		cm^{-1}	
A_1 nondegenerate	1	800	Raman active.
E doubly degenerate	1	500	Raman active.
F_2 triply degenerate	2	625, 1050	Infrared and Raman active.

[a] Data from Landolt Bornstein, vol. I, pt. 2, p. 258, based on Raman spectra of glasses.

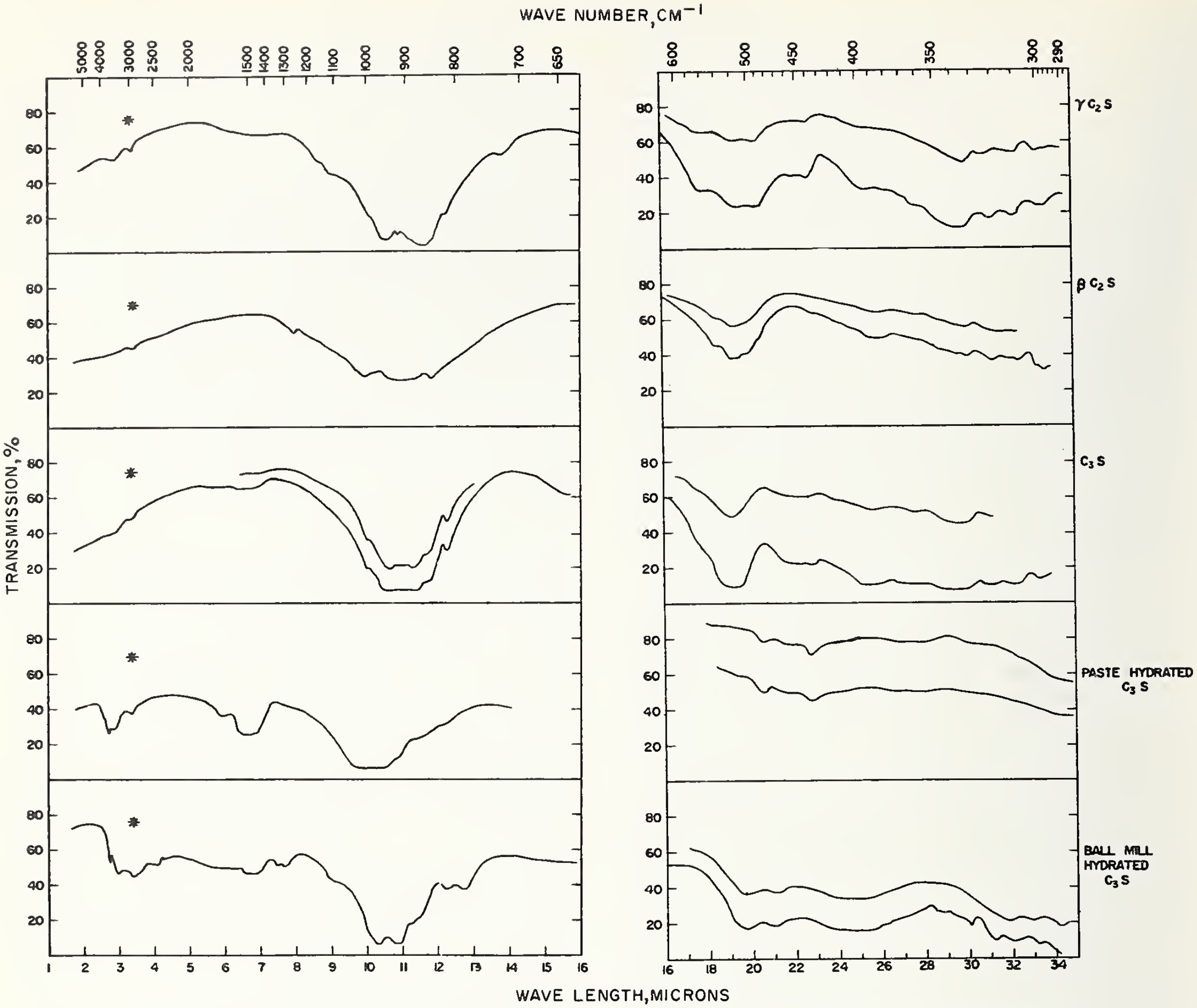

FIGURE 1.—*Infrared absorption spectra of* γ-C_2S, β-C_2S, C_3S *and paste- and ball-mill-hydrated* C_3S.

The pellets corresponding to the lower curves contained 1 mg of compound in 250 mg KBr, and those for the upper curve, where two curves are shown, contained 0.3–0.5 compound in 250 mg KBr. *Denotes there is small absorption in the spectrum of the KBr in this position.

If the SiO_4 group is part of a crystal lattice, the crystal plays a dominant role in determining which vibrations appear in the spectrum. If the oxygens are no longer equivalent, as is usually the case in a crystal, instead of vibrating as a tetrahedron the SiO_4 group vibrates as a body of lower symmetry. This means that degenerate vibrations may be split into separate frequencies, and vibrations which are inactive in the free tetrahedron may be infrared active in the crystal.

Schaeffer, Matossi, and Wirtz [10] have suggested that absorption between 8 and 12 μ in the spectrum of silicates arises from one of the triply degenerate vibrations of the SiO_4 tetrahedron. If this hypothesis is correct, one of the reasons why absorption in this region is broad and complex in so many silicates may be that splitting of these vibrations occurs.

Halford [29] has outlined a method for predicting the number of fundamental vibrations of a crystalline solid when the space group symmetry and number of molecules per unit cell are known It has been quite successful with some simple compounds. In γ-C_2S, which has space-group symmetry Pbnm and cell contents $4(Ca_2SiO_4)$ [3, 30, 31], the SiO_4 group occupies sites having mirror-plane symmetry. According to Halford's method it should vibrate according to the selection rules for a body having only mirror-plane symmetry. Under these circumstances, the SiO_4 group should have nine fundamental vibrations, all of which are infrared and Raman active. The absorption spectrum of γ-C_2S in figure 1 shows at least this number of vibrations, disregarding absorptions below 400 cm^{-1} which include, or might be entirely due to, translational lattice vibrations From single-crystal measurements [30], as well as analogy with Na_2BeF_4 [31], γ-C_2S has the olivine structure in which the SiO_4 groups are present as isolated tetrahedra, but because of the restrictions of the crystal they do not vibrate as free tetrahedra. However, it would be possible

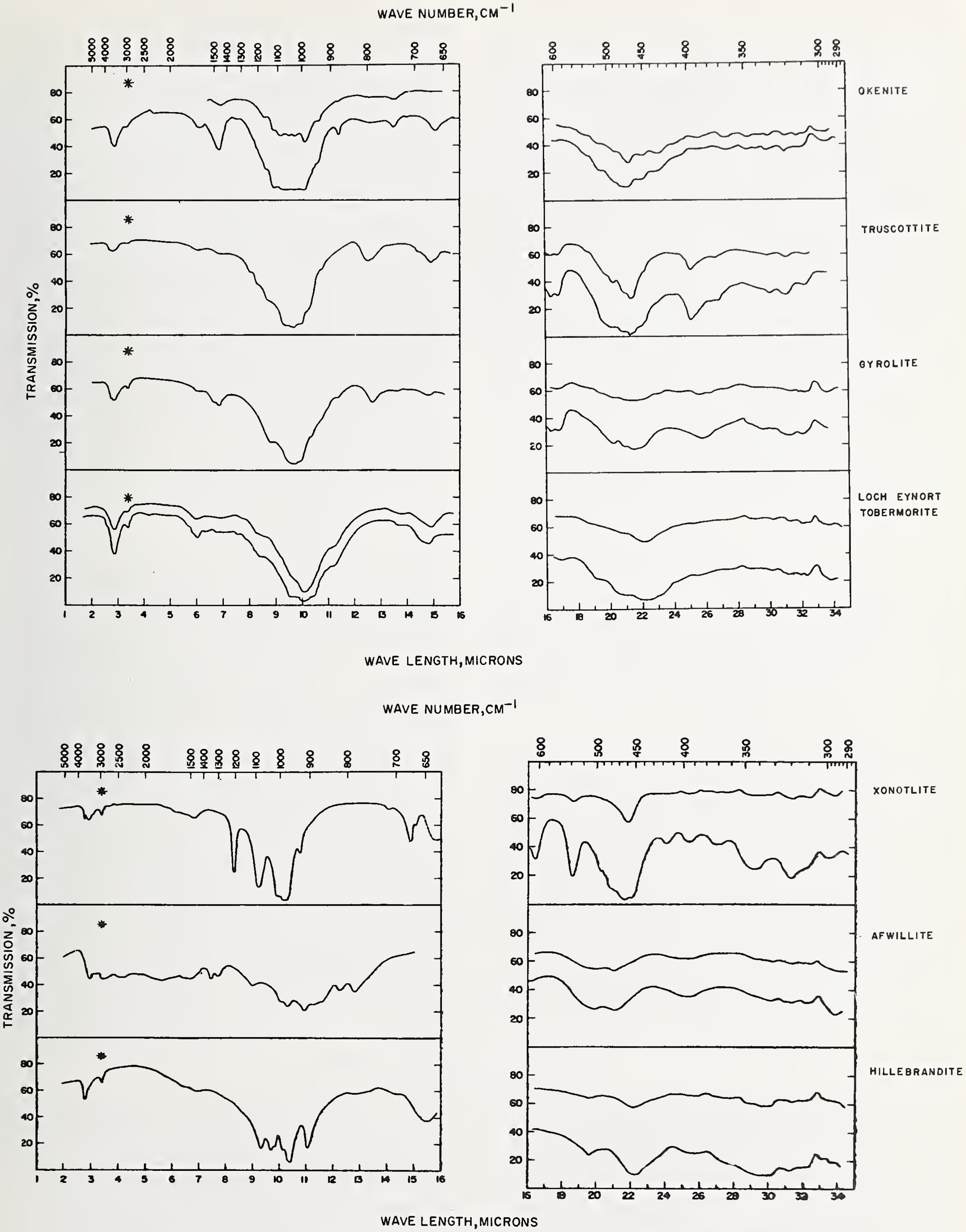

FIGURE 2.—*Infrared absorption spectra of minerals in the* CaO-SiO_2-H_2O *system.*

The pellets corresponding to the lower curves contained 1 mg of compound in 250 mg KBr, and those for the upper curve, where two curves are shown contained 0.3–0.5 mg of compound in 250 mg KBr. *Denotes there is small absorption in the spectrum of the KBr in this position.

to make some plausible correlations between the absorption bands in γ-C_2S and the four frequencies of the free tetrahedron if the three closely grouped bands at 861, 917, and 948 cm^{-1} arise from the splitting of one triply degenerate vibration, the bands at 490, 512, and 560 $cm^-{}_1$ arise from splitting of the other triply degenerate vibration, the bands at 440 and 454 arise from splitting of the doubly degenerate vibration, and the band at 726 cm^{-1} is due to the nondegenerate vibration. Bands unaccounted for in this assignment would be harmonics, combination bands, and lattice vibrations.

Beta dicalcium silicate has space-group symmetry $P2_1/n$ and four molecules per unit cell [3, 32]. According to the structural analysis of Midgley [32], the SiO_4 tetrahedra are in general positions. Therefore, the site symmetry cannot be used directly to determine the selection rules for the vibrations of SiO_4 in β-C_2S as in γ-C_2S. The spectrum of β-C_2S in figure 1 contains a group of vibrations at 503, 518, and 539 cm^{-1} and another group of vibrations at 844, 909, and 1010 cm^{-1}. These two groups of bands may plausibly be interpreted as derived from splitting of the two triply degenerate vibrations in the free tetrahedron. However, the spectra of Roy [11] and Launer [17] suggest that there may possibly be more spectral detail to account for in well-crystallized material.

For the more complicated silicates, correlation of bands in the 350 to 1250 cm^{-1} region with crystal structure remains empirical. Descriptively speaking, a structure in which the SiO_4 tetrahedra are all equivalent might be expected to have fewer bands than a structure in which SiO_4 is present in more than one kind of environment. However, since a single SiO_4 group could account for as few as two infrared active fundamentals or as many as nine, depending on crystal symmetry, the number of bands in the spectrum affords a rather insensitive test of the complexity of a silicate structure. Furthermore, in ring, chain, and sheet structures, where covalent bonds between SiO_4 groups may be present, the model of SiO_4 tetrahedra subject to the modifying effects of a crystal field is not applicable.

OH Vibrations

Some of the OH absorptions in the calcium silicate hydrates are weak, and KBr is somewhat hygroscopic. This hygroscopicity offers no problem in detecting strong OH absorptions but makes the measurement of weak bands difficult. It is common practice to use a blank pellet in the reference beam to compensate for absorbed water in KBr. Another procedure, suggested by Baker [13], is to heat the pellets in vacuum for several hours. This treatment removes absorbed water from KBr rather effectively, and because rediffusion is slow permits measurement of a spectrum. This procedure provides spectra of unhydrated compounds more nearly free of OH absorption than the reference-pellet technique and has been adopted in the present measurements. It unquestionably removes adsorbed water, and in some cases, loosely held combined water from the compounds themselves. Nevertheless, useful empirical comparisons can be made with this procedure, as has been done in figures 1 and 2.

The OH bending vibration which appears near 1650 cm^{-1} in water is weak or absent from the spectra of truscottite, xonotlite, and hillebrandite. Kalousek and Roy [21] have previously noted the absence of this band in xonotlite. According to Lecomte [33, 34] the absence of absorption at this frequency is characteristic of hydroxides. If the OH is attached to a heavy atom by a covalent bond, as for example in methyl alcohol [25c], the OH vibration is shifted to slightly lower frequency. If the OH is in an ionic crystal and is not attached by a covalent bond, as in $Ca(OH)_2$, the bending vibration, if it exists at all, would be more in the nature of a hindered rotation and would appear in a completely different region of the spectrum.

Okenite, tobermorite, and possibly also gyrolite' retain a small OH bending vibration after evacuating the pellets at 100 °C. Kalousek and Roy [21] have reported absorption at 1650 cm^{-1} after heating a synthetic tobermorite at elevated temperature. They have attributed this absorption to interlayer water. As previously mentioned, the hydration product of C_3S also retains an absorption in this position, but it is broad rather than sharply defined as in the better-crystallized tobermorites of smaller CaO/SiO_2 ratio. According to Brunauer and Greenberg [1] the hydration product of C_3S or β-C_2S has a density consistent with a *c*-spacing of 9.3 A after drying at a water vapor-pressure of 5×10^{-4} mm mercury. This spacing should accommodate no interlayer water. Nevertheless, in the case of hydrated C_3S, a small bending vibration is retained after heating in vacuum.

The structure of afwillite contains H_2O molecules as well as OH groups [35]. There is undoubtedly absorption at 1650 cm^{-1} in the spectrum of afwillite, but there is no sharp band in this position. From this point of view, the water in afwillite is different from the water of crystallization of a typical salt hydrate.

The OH stretching vibrations are of particular interest, because they appear at smaller wave numbers in hydrogen-bonded systems [36]. Unbonded OH has a stretching absorption near 3700 cm^{-1}, while hydrogen-bonded OH absorbs at lower frequencies. In the case of water, for example, this change has been demonstrated by comparing the spectrum of a dilute solution of water in carbon tetrachloride with the spectrum of the pure liquid [37]. In the case of crystalline solids, data collected for a large number of compounds show a correlation between the shift in OH stretching frequency and the distance between oxygen atoms in O—H—O bonds [38–45]. Gorman [46] has reviewed much of this evidence. However, simple application of this principle to unfamiliar compounds is complicated by the fact that a few bands which are probably not OH stretching fundamentals have also been found in this region of the spectrum. A spectrum of powdered $Ca(OH)_2$ in KBr shows a predominant sharp band at about 3620 cm^{-1} [22], which would be a very reasonable frequency for an OH stretching vibration without hydrogen bonding. However, Petch and Megaw [47] and Busing and Morgan [48] have shown that oriented single crystals of portlandite have a number of bands. A similar complexity has been observed with brucite [49]. Roy and Roy [50] have raised the question as to which absorption maximum should be chosen for correlation with O—O distance in such cases. The existence of more than one absorption maximum would be expected if OH groups are not equivalent and more than one O—O distance exists in the crystal. However, such an explanation would not apply to portlandite or brucite. In view of the large number of examples in which interatomic distance has been correlated with frequency shift [38–45] the principle has validity, but a certain amount of ambiguity is introduced by the fact that bands other than OH stretching fundamentals appear in the region of the spectrum where these fundamentals occur.

Under the resolution obtained in the present measurements, okenite, truscottite, and tobermorite show single broad stretching absorptions. The frequency displacement of approximately 200 cm^{-1} suggests hydrogen bonding of strength comparable with that found in liquid water.

The spectrum of paste and ball-mill-hydrated C_3S both show a sharp absorption near 3620 cm^{-1} due to $Ca(OH)_2$ which contains no hydrogen bonds. They also show broad absorption at longer wave lengths due to the presence of hydrogen bonds of moderate strength in the calcium silicate hydrates. The spectra of gyrolite and xonotlite show somewhat analogous double absorption, suggesting the presence of OH groups both with and without hydrogen bonding in the compounds themselves.

Hillebrandite shows a double peak near 3600 cm^{-1}. This position does not suggest very strong hydrogen bonding. However, broadening of the band near the top suggests some perturbation of the OH stretching frequency.

The spectrum of afwillite between 2000 and 3600 cm^{-1} has been carefully studied by Petch, Sheppard, and Megaw [51], with a CaF_2 prism. They have measured both powdered material and oriented single crystals. They have also used polarized radiation to determine the direction of vibrations where possible. From crystal-structure considerations [35], they postulate six positions where hydrogen bonds occur. Three of these have interatomic distances close to 2.7 A, which would correspond to absorptions at wave numbers of the order of 3000 cm^{-1}, and three have interatomic distances close to 2.5 A, which would correspond to much smaller wave numbers. In powdered afwillite they found bands at approximately 2400, 2800, 3130, and 3340 cm^{-1} as well as absorption at smaller wave numbers which was difficult to resolve. The spectrum in figure 2 shows the bands at 2400, 2800, and 3340 cm^{-1}, but the 3130 cm^{-1} band is not resolved. This spectrum also shows that unresolved absorption extends well below 2000 cm^{-1}. If the absorption between 1500 and 3400 cm^{-1}, both resolved and unresolved, results from the six hydrogen bonds suggested by Petch, Sheppard, and Megaw [51], comparison with the other calcium silicate hydrates in figure 2, suggests that none of these compounds have as many or as strong hydrogen bonds as those found in afwillite.

The author is indebted to Professor Ellis R. Lippincott of the University of Maryland for helpful discussions of the theory and interpretation of infrared spectra, and to Dr. Deane K. Smith of the Portland Cement Association Fellowship at the National Bureau of Standards for discussion of X-ray crystallography of β-C_2S and γ-C_2S. The author is also indebted to those mentioned in the text who provided specimens for this study.

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Discussion

Rustum Roy

In recent studies of the infrared spectra of the hydrated magnesium and aluminum silicates Stubican and Roy[1, 2] have adopted an empirical approach which takes advantage of the ability to control precisely by synthesis the cations (including H^+, D^+) involved in the structure. In connection with the present paper it is only relevant to point out that many of the assumptions regarding the selection rules in solids do not prove to be of any real value. Furthermore, it has been shown that only with Si^{4+} (or other tetravalent metal ions) is there any meaning to the assignment of a particular frequency to a metal-oxygen stretching or bending mode. Even with Al^{3+}, and especially with divalent ions, the rest of the structure and the contrapolarizing effect of the cations in the second sphere of coordination have such large effects on the frequency at which a particular vibration mode appears, that assignment at fixed frequencies is not very meaningful in most cases. The present state of the most definite assignments in layer silicates showing the range of their variation with substitution is shown in summary form in figure 1. It may be of some help in suggesting interpretations of some of the spectra presented by Dr. Hunt. One of the most interesting results, part of which appears in figure 1, is the verification of the previous tentative assignment of the 11μ band in kaolinite as the bending mode of O-H. It will be noted that this vibration is labelled H-O-Al to indicate the importance of the cation to which the $(OH)^-$ is attached: for example it will be seen that the same vibration appears at about 12μ in

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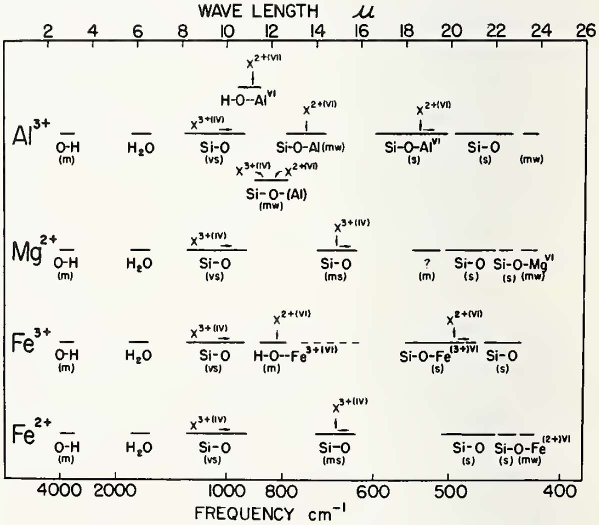

FIGURE 1. *Infrared absorption in layer silicates.*

H-O-Fe^{3+}. These bands are all shifted by about a 1.37 ratio when *D* is substituted for *H*. They also respond to Ga^{3+} substitution and presumably appear only at much longer wave lengths with divalent cations such as Mg^{2+}. Therefore, H-O-Ca bending moments may not appear at low enough frequencies to be detected here.

Exceptions to this scheme may occur in the case of strongly polarizing ions such as Zn^{2+} or Cd^{2+} in which case the absorptions may well appear below 15μ.

(Note—This discussion is Contribution Number 60-58 of the College of Mineral Industries, The Pennsylvania State University.)

Closure

C. M. Hunt

The problem of identifying the vibrational modes and assigning frequencies is difficult when dealing with polymeric materials. The concept of symmetry and its role in determing the number and kind of vibrations, which is applicable to simple molecules, is mainly of descriptive value when applied to more complex structures. However, even on a descriptive basis it serves as a reminder that a change in crystal symmetry could lead to a change in the number, kind, and position of bands in the infrared absorption spectrum. More empirical study of compounds of known structure is needed, and the work with synthetic layer minerals referred to by Dr. Roy is an important step in this direction.

Aside from considerations of symmetry, the "ionic" or "covalent" character of the M—O bonds themselves is also important in determining the vibrational characteristics of the crystal. Miller and Wilkins [1] concluded from the examination of spectra of a number of sulfates, nitrates, carbonates and other polyatomic anions that their absorption frequencies were sufficiently characteristic to have analytical value, even though the cation also exerted some effect on the spectrum. The N—O, S—O, and C—O bonds in these anions have considerable directional or "covalent" character. Al—O, Fe—O, and Mg—O bonds undoubtedly have more "ionic" or nondirectional character than bonds in these typical polyatomic anions or Si—O bonds in silicates. The "ionic" or "covalent" character of the bonds would be more important than valence per se in determining the presence or absence of characteristic frequencies.

Returning to figures 1 and 2 in the original paper, Roy's comments also point up the desirability of examining deuterium analogs of the calcium silicate hydrates in the figures to identify Si—O—H bending modes which at present have not been distinguished from Si—O frequencies.

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Paper III–S9. Crystalline Solubility and Zeolitic Behavior in Garnet Phases in the System $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$*

Della M. Roy and Rustum Roy

Synopsis

The earlier confusion on the formation of hydrogrossularites from the grossularite composition is shown to be due to failure to attain equilibrium. Anhydrous grossularite can be synthesized with water catalysis at least as low as 600 °C. Stable solid solutions have been prepared only from C_3AH_6 to $C_3AS_2H_2$, the latter being the most stable (360 °C at 2000 atm). Phases with lattice constants only slightly larger than grossularite (up to 11.90 A) can be prepared from silica-rich members of the series, but these are thought to be metastable.

Solid solution along the join $C_{12}A_7$-C_3AS_3 was very limited in extent, although some change in the lattice constant and refractive index of $C_{12}A_7$ was observed in mixtures on the join.

Data obtained by means of a recording balance demonstrate clearly a zeolitic behavior of "$C_{12}A_7$", as the phase adsorbs varying amounts of H_2O with varying temperature. This phase is more accurately described as a hydrous phase under atmospheric condition with the composition of about $C_{12}A_7H$. Metastable "hydrogrossularite" formed through very short runs at intermediate temperatures showed a similar behavior, but rehydration was no longer complete after dehydration above 800 °C.

Résumé

Il est indiqué que la confusion antérieure sur la formation d'hydrogrossularites à partir de la composition du grossularite a pour cause l'insuccès à atteindre l'équilibre. La synthèse du grossularite anhydre peut être réalisé avec catalyse de l'eau à une température au moins aussi basse que 600 °C. Les solutions solides stables n'ont été préparées que de C_3AH_6 à $C_3AS_2H_2$, ce dernier étant le plus stable, (360° à 2000 atm.). Les phases avec constantes de réseau seulement légèrement plus grandes que celle du grossularite (jusqu'à 11.90A) peuvent être préparées à partir de membres de la série riches en silice, mais on a des raisons de penser que ceux-ci sont métastables.

La solution solide était très limitée le long de la ligne $C_{12}A_7$-C_3AS_3, cependant on observa des changements concernant la constante de réseau et l'indice de réfraction de $C_{12}A_7$ dans les mélanges sur la ligne.

Les résultats obtenus au moyen d'une balance enregistreuse démontrent clairement un comportement zéolitique de "$C_{12}A_7$", puisque la phase absorbe des quantités variables de H_2O avec la température variable. Cette phase est décrite plus précisément comme phase aqueuse sous condition atmosphérique avec la composition approximative de $C_{12}A_7H$. "L'hydrogrossularite" métastable formé pendant de très courts intervalles à des températures intermédiaires se comportait de la même façon, mais la réhydratation n'était plus complète après une déshydratation au-dessus de 800°.

Zusammenfassung

Die widersprechenden Angaben in der älteren Literatur über die Bildung der Hydrogrossularite aus Grossularitzusammensetzungen müssen darauf zurückgeführt werden, daß in den älteren Arbeiten die Gleichgewichte nie erreicht worden sind. Wasserfreier Grossularit kann mit Wasserkatalyse bei 600 °C synthetisiert werden, und vielleicht auch bei tieferen Temperaturen. Stabile feste Lösungen sind nur von C_3AH_6 bis $C_3AS_2H_2$ synthetisiert worden, und die letztgenannte Verbindung ist die stabilste (360 °C bei 2000 Atmosphären). Phasen mit Gitterkonstanten, die nur ein wenig größer als die des Grossularits sind (bis 11.90 Å), können von den silikatreichen Gliedern der Reihe hergestellt werden, aber es sieht so aus, als ob diese metastabil sind.

Feste Lösungen an der Verbindungslinie $C_{12}A_7$-C_3AS_3 kommen nur in einem kleinen Bereiche vor, aber einige Veränderungen der Gitterkonstante und des Brechungsindex des $C_{12}A_7$ wurde in den Mischungen an dieser Linie gefunden.

Messungen, die mit Hilfe einer Registrierwaage erhalten wurden, zeigen deutlich, daß $C_{12}A_7$ sich wie ein Zeolith benimmt, da diese Phase schwankende Mengen Wassers als Funktion der Temperatur aufnimmt. Diese Phase sollte doch unter atmosphärischen Bedingungen besser als ein Hydrat beschrieben werden, daß ungefähr die Zusammensetzung $C_{12}A_7H$ hat. Der metastabile, sogenannte Hydrogrossularit, welcher in kurzzeitigen Experimenten bei nicht zu hohen Temperaturen dargestellt wird, zeigte dasselbe Verhalten, aber er hat nicht mehr den alten Betrag Wassers gebunden, nachdem er einmal bei 800° C dehydratisiert worden ist.

Introduction

The knowledge of phase equilibrium relationships between the hydrogarnet C_3AH_6 and its silica-bearing counterpart grossularite, C_3AS_3, is important in understanding processes of hydration in aluminous cements. In addition to these two cubic garnets, a third closely related cubic compound $C_{12}A_7$, stable at relatively high temperatures is involved in the equilibria. The system $CaO\text{–}Al_2O_3\text{–}H_2O$, extensively investigated at low temperatures, has been studied by Majumdar

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the College of Mineral Industries, Pennsylvania State University, University Park, Pennsylvania.

and Roy [1][1] at elevated temperatures, and a review of literature up to 1956 included. They showed that at elevated pressures (~1000 atm) C_3AH_6 is the only stable calcium aluminate hydrate within the temperature range 100–200 °C, and that above this temperature $C_4A_3H_3$ $+Ca(OH)_2$ are in equilibrium with H_2O at elevated pressures (in contrast to the ready formation of $C_{12}A_7$ through dehydration of C_3AH_6 at atmospheric pressure). $C_4A_3H_3$ in turn decomposes to $C_{12}A_7+Ca(OH)_2+H_2O$ above 710 °C. A review of more recent literature on the system CaO $-Al_2O_3-H_2O$ is given in the present symposium [2].

The data available on the equilibria involved with the addition of silica are less complete. Yoder [3] attempted to synthesize grossularite from the C_3AS_3 composition at various temperatures and pressures, presumably forming "hydrogarnets" from the single composition. Flint, McMurdie, and Wells [4] produced garnets along the join C_3AH_6–C_3AS_3 and discussed the relationship of such hydrogarnets and those containing iron to sulfate resistance in cements, showing that both Fe_2O_3 and SiO_2 were important in increasing the resistance to sulfate attack [5]. Carlson [6] contemporaneously with work by the authors [7] formed crystalline garnets ranging from pure C_3AH_6 to C_3AS_3, but found that the cell constant of the garnet formed was a function of both temperature and compostition, as well as time, and the results were complicated by the presence of nonequilibrium phases.

The present investigation was begun with the hope of reconciling certain inconsistencies and obtaining new data as follows:

(1) From a single composition, C_3AS_3, Yoder claimed to have obtained a variety of products. How can this represent equilibrium?

(2) No data supported the existence of a complete solid-solution series between C_3AS_3 and C_3AH_6 at a single temperature. Does such a series exist, and if so, what are the temperature limits?

(3) The effects of time, temperature, and pressure as separate parameters in the crystallization of these phases were not well defined.

(4) The equilibrium relationships of $C_{12}A_7$ in the C–A–S–H system are not well established.

Experimental Procedure

Essentially amorphous mixtures of compositions along the C_3A–C_3AS_3 and $C_{12}A_7$–C_3AS_3 joins as shown in figure 1 were made by decomposition of alcohol-water solutions of calcium and aluminum

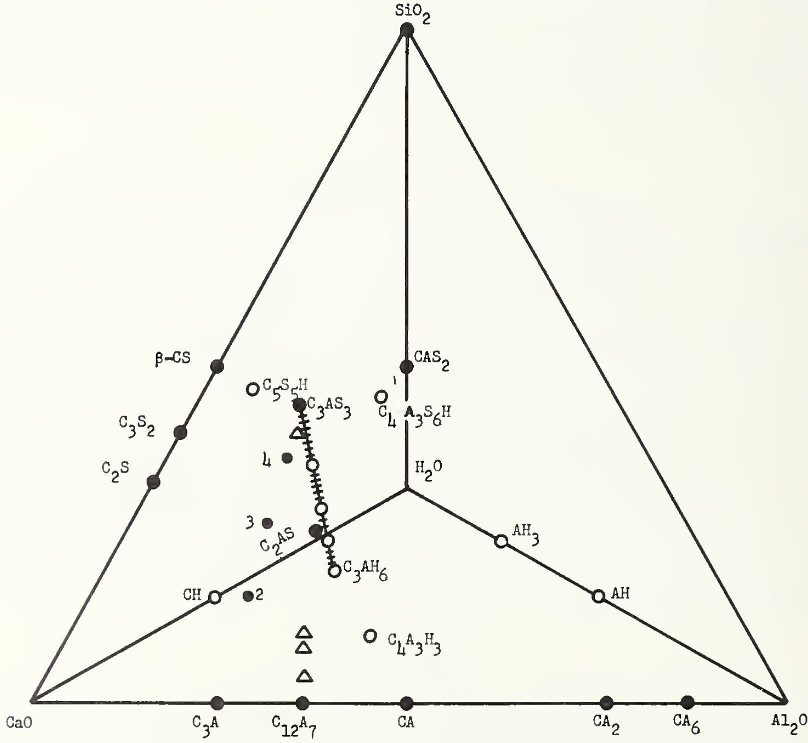

FIGURE 1. *Tetrahedron of the* C–A–S–H *system.*

Solid dots represent anhydrous compositions on the C_3A-C_3AS_3 join studied, open circles the correponding hydrated phases. Triangles represent $C_{12}A_7$-C_3AS_3 join compositions.

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[1] Figures in brackets indicate the literature references at the end of this paper.

nitrates with ethyl orthosilicate or Ludox (colloidal silica) (see Roy [8], Koizumi and Roy [9]). Some glasses were also used for the grossularite composition. Mixtures were treated hydrothermally (Roy and Tuttle, [10]) for periods of time varying from 1 hour to 3½ months. In many runs samples were held in gold-foil envelopes, but since it was desired to prevent transfer of material, many samples were contained in sealed gold or palladium tubes.

Grossularite Composition Crystallized at Different Temperatures

While several studies of the crystallization of presumed hydrogrossularites have been made starting with the grossularite composition C_3AS_3, it is clear that such a process is beset with unnecessary problems. When a hydrogrossularite appears from a total composition of C_3AS_3 it is usually assumed that silica has been leached out. Our results using hermetically sealed systems, however, gave the same result and directly disproved this suggestion. Furthermore a series of longer and longer runs made with the grossularite composition showed conclusively that one is dealing for the most part merely with failure to obtain equilibrium in short runs. In figure 2 the effect of length of run on the unit cell of the garnet formed demonstrates this point. Moreover, in runs under equivalent conditions, gels yield a more nearly anhydrous garnet than do glasses, indicating the danger of metastability when using glassy starting materials. Next, the cell dimension and index of refraction of the garnet formed from the grossularite composition at different temperatures was studied, and the results are shown in figure 3. Duration of the runs in most cases was at least one week, and the pressure was 2000 atm. Essentially pure grossularite with negligible water content, having n=1.736 and a_0=11.86 A is formed between 550 °C and 860 °C. Above 860 °C at 1000 atm. grossularite decomposes to wollastonite + anorthite + gehlenite. In the range 550 °C to 400 °C the garnet lattice is slightly expanded (a_0= ~11.92A max.) with a corresponding decrease in index of refraction, although the latter is higher than the range of hibschite, plazolite, and most of the naturally-occurring "hydrogrossular" minerals which are indicated on the left scale. The significance of the slightly expanded structures obtained below 550 °C is discussed in more detail in a later section. Anhydrous grossularite is therefore a stable phase at least as low as 600 °C and does not appear to require any pressure for its formation at equilibrium, the water pressure merely catalyzing the reaction. Anhydrous grossularite crystallized at 750 °C could not be rehydrated at 525 °C or 325 °C.

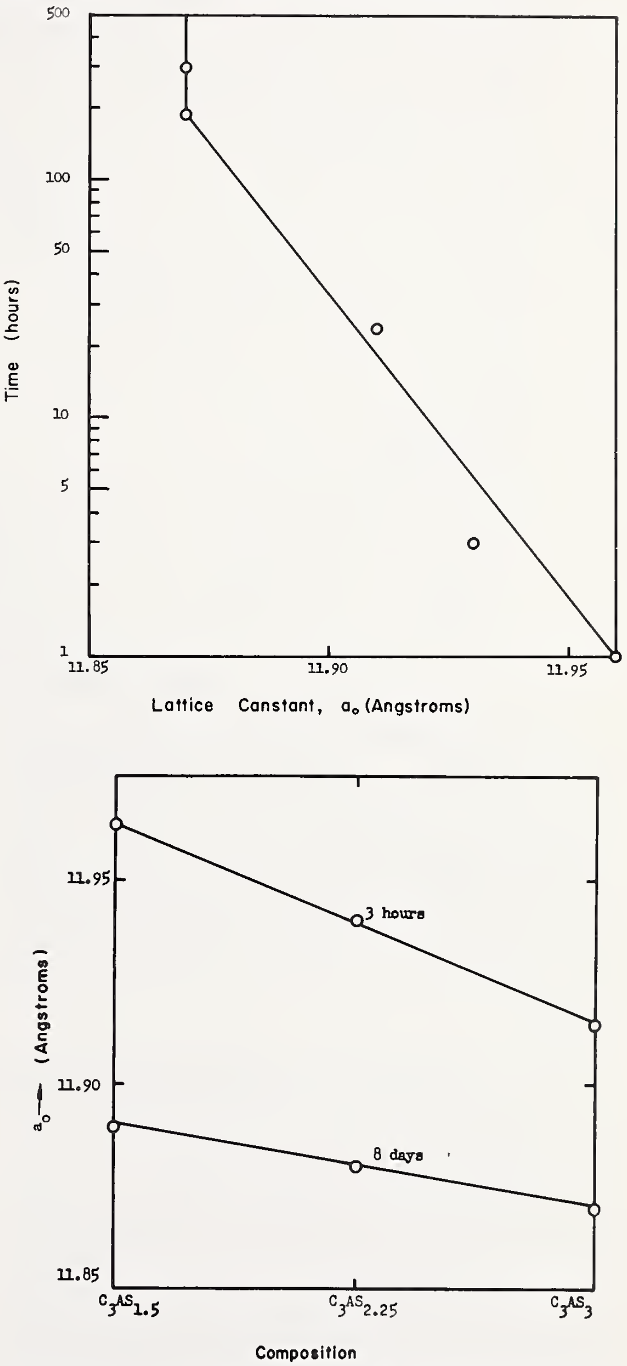

FIGURE 2. (a) *Lattice constant a_0 of grossularite formed from C_3AS_3 at 550 °C and 10,000 psi as a function of time.* (b) *Lattice constant obtained from various compositions in short and long runs.*

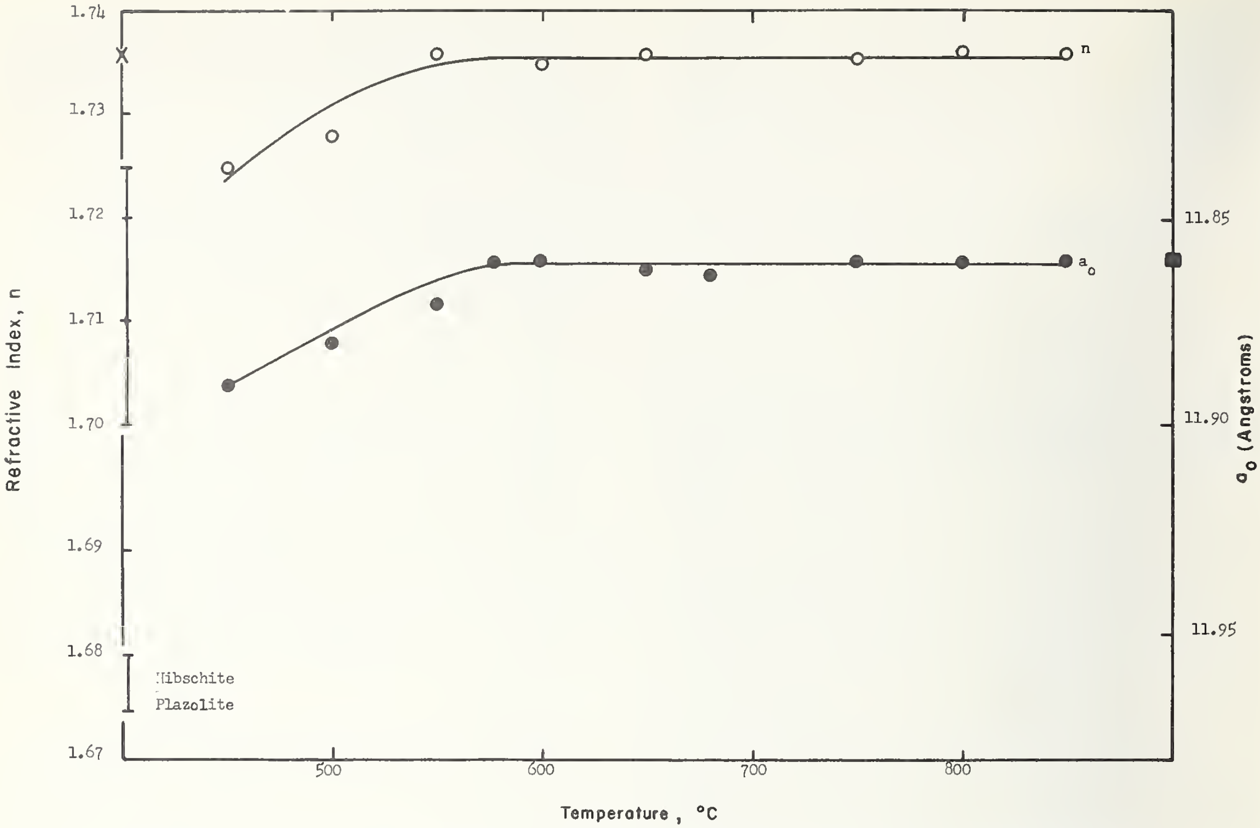

FIGURE 3. *Lattice constant a_0 and refractive index n of grossularite formed at different temperatures.*

Hydrogarnet Solid Solutions

The formation of a complete series of solid solutions from C_3AH_6 to C_3AS_3 was never achieved at a single temperature, and the evidence strongly suggests that the complete series is not stable. Two possible types of "hydrogarnets" are formed—one apparently a stable series extending from C_3AH_6 to about $C_3AS_2H_2$ at relatively low temperatures, and the other at intermediate temperatures (300–600 °C) probably metastable and limited in extent from grossularite to about $C_3AS_{2.75}H_{0.5}$. These assumptions are based on the data obtained as follows:

Runs up to the maximum stability temperature of C_3AH_6 (about 300 °C at 2000 atm.) yielded single-phase solid solutions extending beyond about $C_3AS_{1.5}H_3$, probably as far as $C_3AS_2H_2$, but other phases in addition to hydrogarnet were formed from mixtures richer in silica. The stability of such phases was tested by increasing the duration of the runs in a series, which did not affect the product materially. Typical results are given in figure 4, which shows the lattice constant a_0 of garnet or hydrogarnet formed as a function of composition at certain significant temperatures. The cell constant of the hydrogarnet solid solution formed at 300 °C between C_3AH_6 and $C_3AS_2H_2$ can be expressed by an almost straight line interpolation between the values for C_3AH_6 and C_3AS_3, although, as mentioned above, the solid-solution series was not complete. Instead of crystallizing grossularite, high-silica mixtures yielded hexagonal anorthite plus the appropriate calcium silicate hydrate in addition to a hydrogarnet.

Runs at the next higher temperature 350 °C yielded from the 1.5 SiO_2 composition a nearly single-phase hydrogarnet having, however, a much smaller a_0 than that formed at 300 °C. Compositions on either side yield a hydrogarnet which has very nearly the same cell dimension as that from the $C_3AS_{1.5}$ composition, mixed with other phases. These data suggest a maximum thermal stability of a hydrogarnet near the 1.5 mole SiO_2 composition (perhaps as high as 2.0 SiO_2 and stable only below about 360 °C). At 450 °C grossularite containing very little H_2O and having $a_0=11.89$ A was obtained from C_3AS_3, as well as in other compositions up to $C_3AS_{1.5}$, in which it was mixed with other phases. At 500 to 600 °C the garnet formed was essentially anhydrous, with $a_0=11.86$–11.88 A.

In addition to changes in lattice constant, changes in the intensity pattern of the X-ray reflections from hydrogarnet solid solutions obtained at 300 °C are observed, and typical patterns of different compositions are given in table 1. Increase in silica content diminishes the intensities of the low-angle reflections.

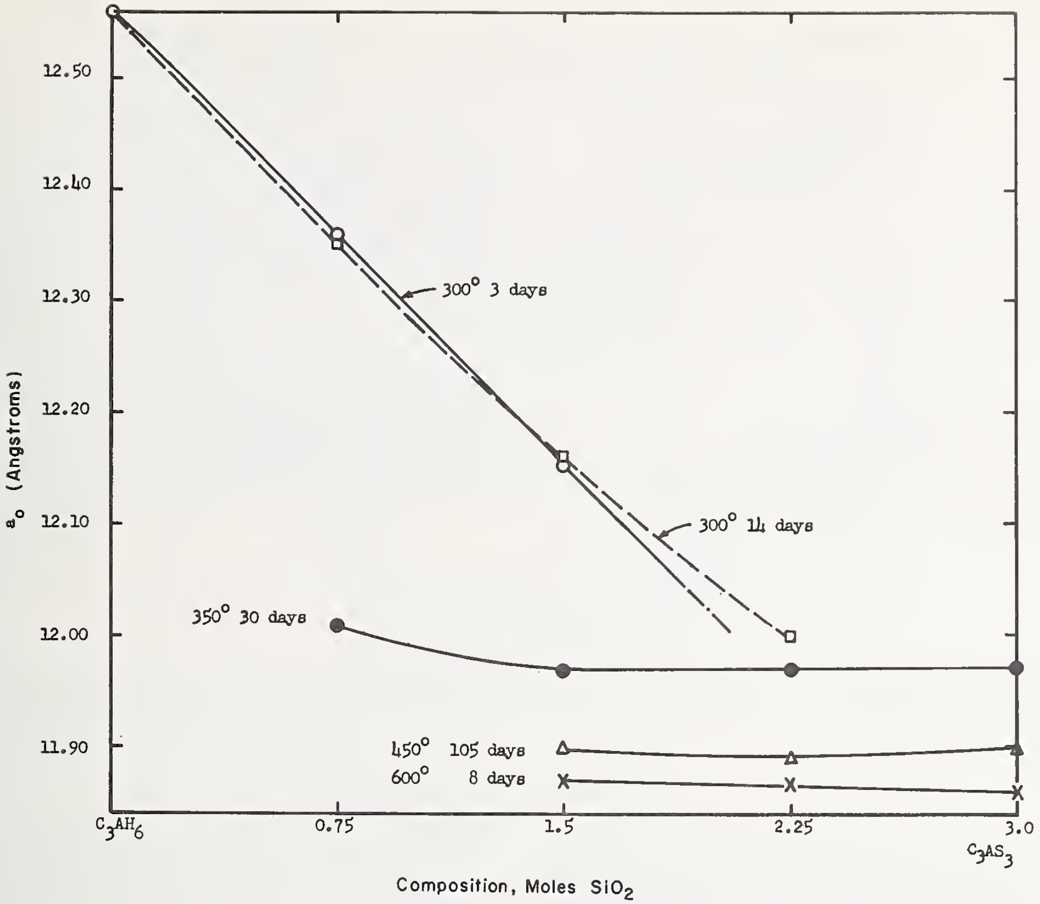

FIGURE 4. *Lattice constant of garnet formed on* C_3AH_6-C_3AS_3 *join at different temperatures.*

TABLE 1. *Intensities of reflections in hydrogarnets formed at 300 °C*

Composition	Mol. ratio				*hkl*											
	CaO	Al_2O_3	SiO_2	H_2O	211	220	310	321	400	420	332	422	431, 510	521	440	611, 532
1141	3	1	0.75	(4.5)	4	2	--------	2.5	5	10	(vw) 2	2.5	2.5	5	--------	6
1142	3	1	1.5	(3)	2	1.5	--------	--------	5	10	--------	2	2	3	--------	3
1157	3	1	2	(2)	1	--------	--------	--------	4.5	10	--------	1.5	1	2.5	--------	2.5

Temperature-Composition Diagram for C_3A–C_3AS_3 Mixtures

The results of studies along the C_3AH_6-C_3AS_3 join are summarized in a temperature-composition diagram in figure 5, illustrating the phases formed under water pressures of 1000 to 2000 atm from the anhydrous compositions indicated on the abscissa. A single-phase area is shown as existing stably only from $C_3A(H_6)$ to about $C_3AS_2(H_2)$; the hydrogarnet of maximum thermal stability is near the latter composition, stable to about 360 °C while higher-silica compositions yield this hydrogarnet + hexagonal anorthite + (probably) xonotlite. Grossularite or a slightly expanded hydro-grossularite (metastable?) mixed with $C_4A_3H_3$ and $Ca(OH)_2$ are formed at intermediate temperatures, while $C_{12}A_7$ is formed above the decomposition temperature of $C_4A_3H_3$. Above 860 °C grossularite decomposes to wollastonite + gehlenite + anorthite. The join CS–$C_{12}A_7$ furthermore appears to be stable at high temperatures. Dashed lines indicate probable relations. The alternative explanation of our data would entail moving the horizontal line at 360° to about 550 °C which would mean that a complete series of stable solid solutions could form and that the low-temperature silica-rich assemblages were metastable.

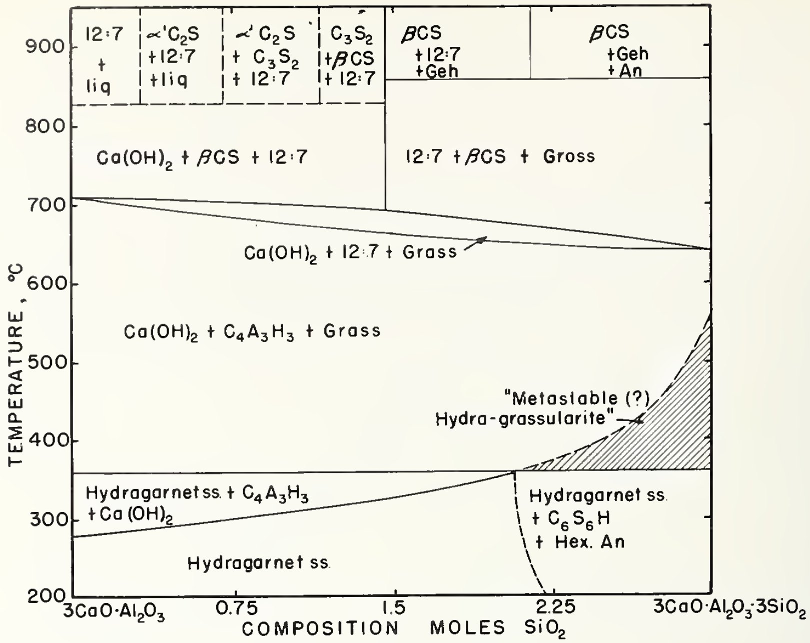

FIGURE 5. *Temperature-composition diagram for the* C_3A-C_3AS_3 *join at 2,000 atm* H_2O *pressure.*

An alternative interpretation would be to move the phase boundary at 360° to 550°, making the silica-rich hydro-grossularite stable, and the silica-rich low temperature assemblages metastable.

The Join $C_{12}A_7$–C_3AS_3

Early results obtained on the join C_3AS_3–C_3AH_6 indicated that the $C_{12}A_7$ formed at higher temperatures from decomposition of members near C_3AH_6 was variable with respect to index of refraction, lattice constant, and the intensity pattern of the X-ray reflections. Solid solubility of C_3AS_3 in $C_{12}A_7$ might be postulated to explain the differences. The compound $C_{12}A_7$ has a unit cell size only slightly larger than that of grossularite, and it was thought probable that the open structure of $C_{12}A_7$ [11] would enable it to incorporate silica into its lattice without any very drastic effects.

In order to test this theory, mixtures along the join $C_{12}A_7$–C_3AS_3 were made at molar ratios of 90:10, 80:20, 75:25 and 10:90, using $C_{36}A_{21}$ and $C_{24}A_8S_{24}$ as equivalent formulas for $C_{12}A_7$ and C_3AS_3, respectively.

The results unfortunately were not unequivocal. While in a single run a very slight decrease in cell constant with increasing C_3AS_3 was observed, from one run to another the values overlapped. Furthermore, even in the 10 percent C_3AS_3 mixture a second phase was usually detected (gehlenite), and no clear determination of refractive index changes in the $C_{12}A_7$ could be made because of the very small crystal size obtained in sealed tubes. The indices are, however, higher than those usually reported, being 1.610±0.002 for a sample prepared hydrothermally at 750° and 1,000 atm and in mixtures where SiO_2 was present were as high as 1.624±0.003, which would suggest some incorporation of SiO_2 into the structure. Certain differences in the intensity pattern of the X-ray reflections were observed, but were not entirely consistent. The overall results can merely be taken to suggest a small extent of crystalline solubility of C_3AS_3 in $C_{12}A_7$.

Zeolitic Behavior of H_2O in "$C_{12}A_7$"

One of the most unexpected findings of this study was the remarkable dehydration behavior of "$C_{12}A_7$" and the hydrogarnet series (e.g., $C_3AS_{1.5}H_3$). In contradistinction to normal discrete hydrates in which above a certain temperature for a certain partial pressure of H_2O the composition of the phase(s) remains constant, zeolites absorb and desorb water as a function of temperature (with p_{H_2O} fixed) without structural change. It was found that $C_{12}A_7$ can absorb water even at 1000 °C at a p_{H_2O} of 16 mm. Figure 6 shows the recording balance records of adsorption and desorption of water at a pressure of 16 mm as the temperature is varied. The solid curve was run at a heating rate of 3 °C per minute, while the circles show the relative weight of the sample after holding at the indicated temperature for several hours (in all cases except the

1200 °C point). All the steps indicated are reversible on heating and cooling.

Furthermore, there appears to be a correlation of the index of refraction and lattice constant of $C_{12}A_7$ with water content: Anhydrous $C_{12}A_7$ prepared at 1330 °C and examined immediately had $n=1.616 \pm 0.002$, while that prepared hydrothermally at 750 °C and 2,000 atm had $n=1.610 \pm 0.002$. A slight increase in cell dimension with increasing H_2O content was observed as follows: for the d_{642} spacing: 1330 °C=1.6006; 300 °C (at $p_{H_2O}=16$ mm)=1.6012; and 750 °C, 2,000 atm=1.6019 (all ±0.0002 A). The effect of water on the $C_{12}A_7$ properties therefore appears to be more consistent than the effect of solid solution with C_3AS_3. Indeed it is clear that $C_{12}A_7$ under ordinary atmospheric condition is not an anhydrous phase at all but rather a hydrate fairly close to the composition $C_{12}A_7H$.

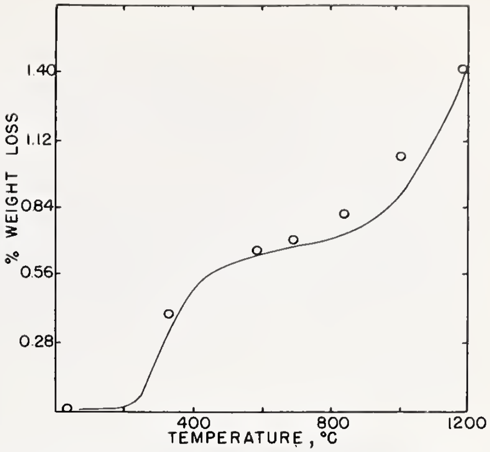

FIGURE 6. *Recording balance data for* $C_{12}A_7$.
Heating curve at 3 deg per minute.

"Hydro-Grossularite"

In line with the conclusion that hydrogarnet solid solution was limited to the C_3AH_6–$C_3AS_2H_2$ region, and that such solid solutions were stable to only about 360 °C, an attempt was made to determine the nature of the slightly hydrated product obtained near the C_3AS_3 composition at intermediate temperatures. First, the time study made at 550 °C and 10,000 psi (see fig. 2) revealed that expanded hydrated structures were obtained at first in very short runs, but that increased time resulted in a product approaching grossularite, both for C_3AS_3 and intermediate compositions (in the latter case mixed with other phases).

The hydration-dehydration behavior of some of these apparently metastable products was studied by means of the recording balance. Figure 7 shows some of the results from a phase formed at 520 °C, 10,000 psi for 2½ hours, a garnet with $a_0=11.91$ A. The curve was obtained by heating at 6 °C per minute at $p_{H_2O}=16$ mm, while the circles represent values after heating for several hours. The arrows from the 600° and 625 °C points indicate reversibility, but the 850° product rehydrated only partly on cooling to 300°, as shown by the dashed line. In this respect the "hydro-grossularite" differs from $C_{12}A_7$, although the "zeolitic behavior" persists at least as high as 625 °C, and involves approximately 3 percent reversible loss or gain.

Additional runs were made in attempt to rehydrate crystalline grossularite which had been synthesized at 750 °C and 30,000 psi. The results were negative at 325 °C and 30,000 psi and 525 °C and 55,000 psi. Results of other runs to determine whether or not a little H_2O could be stably incorporated into the structure of an intermediate composition, $C_3AS_{2.6}$, were not too conclusive. An expanded lattice with $a_0=11.92$ A was formed after 24 hours at 525 °C and 55,000, but decreased with increasing time.

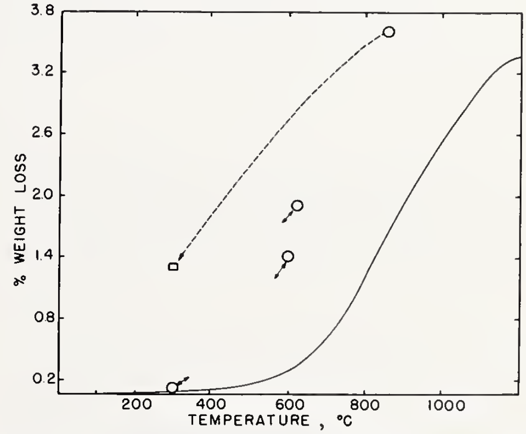

FIGURE 7. *Recording balance data for "Hydro-grossularite."*
Heating curve at 6 deg per minute.

From all our data it is clear that in glasses and gels of composition near grossularite, the calcium-aluminum-rich phases always crystallize first metastably, leaving some silica which then reacts very slowly to give the equilibrium phase. In addition the possibility of quite a different type than the tetrahedral hydroxyls may also enter the structures.

This study is part of a research program on polymorphism and subsolidus phase equilibria sponsored by National Science Foundation grants G–1000 and G–4648.

(This paper is Contribution Number 60-13, Experiment Station, College of Mineral Industries, The Pennsylvania State University).

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Paper III–S10. Calcium Exchange in Systems of xCaO·SiO$_2$·yH$_2$O-Ca(OH)$_2$-H$_2$O*

T. Thorvaldson, F. W. Birss, and K. G. McCurdy

Synopsis

The exchange of calcium between hydrated C_3S and solutions of $Ca(OH)_2$ in equilibrium with it was studied. Two types of exchange seem to occur, one a rapid and the second a slow process. Comparisons are made between the exchange behavior of hydration products formed in the unsaturated range, a hydration product formed in supersaturated calcium hydroxide, and afwillite.

Résumé

Etude est faite de l'échange de calcium entre le C_3S et les solutions de $Ca(OH)_2$ en équilibre. Deux types d'échange semblent se produire, l'un est un procédé rapide et l'autre un procédé lent. Des comparaisons sont établies entre le comportement d'échange des produits d'hydratation formés dans le domaine non saturé, d'un produit d'hydratation formé dans la solution de l'hydroxide de calcium sursaturé, et de l'afwillite.

Zusammenfassung

Der Kalziumaustausch zwischen hydratisiertem C_3S und $Ca(OH)_2$-Lösungen, die im Gleichgewicht stehen, ist untersucht worden. Augenscheinlich ereignen sich zwei Arten des Austausches: eine vollzieht sich schnell, die andere aber langsam. Die Austauschverhalten der hydratisierten Produkte, welche von der ungesättigten Lösung gebildet werden, des Hydrates, welches in übersättigten Kalziumhydroxyd geformt wird, und des Afwillits, werden verglichen.

Introduction

The very interesting paper of Brunauer and Greenberg on the hydration of C_3S and β-C_2S presents a clear account of the problems and the difficulties met with in the study of the hydration of the silicates of portland cement and gives an excellent report of the progress to date in that field.

The experiments which we wish to describe have been in progress somewhat intermittently during the last eight years. They grew out of attempts to determine the molar ratio of CaO/SiO$_2$ (referred to as r in what follows) in the hydration products of C_3S and β-C_2S without carrying the hydration to completion [1].[1] C_3S and β-C_2S labeled with the radioactive isotope Ca-45 were hydrated, with agitation, in a solution of calcium hydroxide near saturation or in the metastable region of supersaturation, and the fraction of the isotope appearing in the solution was plotted against moles of lime liberated per mole of the silicate. The curve obtained was then compared with theoretical curves for various r values, derived on the assumption that the silicate passes through the solution in the process of hydration. A general equation connecting the fraction of the isotope liberated to the solution and the r-value of the hydrated silicate was developed. This equation was developed on the assumption that exchange of calcium between the solution and the hydration product, after its precipitation from the solution, was negligible during the time of the experiment. A similar method was used for determining the value of r by using unlabeled C_3S, hydrated in a solution of lime labeled with Ca-45.

Considering the poor crystalline condition of the solid hydration product and the variation of its CaO/SiO$_2$ ratio with the concentration of calcium hydroxide in solution, one would expect at least a moderately rapid exchange of calcium ions between the solution and the hydrated solid. This exchange would affect the radioactive count of the solution and therefore also the curve for the radioactivity of the solution against lime liberated per mole of silicate. The amount of change in the curve would vary with the time of the experiment. The two extreme cases, no exchange and complete equilibrium exchange of the isotope, are readily subject to mathematical treatment. The object of the original work was to develop an experimental method by which r could be determined without completing the hydration of the silicate and to obtain evidence as to whether its probable value in a saturated or slightly supersaturated solution of lime at 21 °C. approximated 1.5 or 2.0. It so turned out that even with the extreme condition of complete exchange the theoretical curves were not altered sufficiently to affect the conclusion that the value of r in a saturated solution of calcium hydroxide, at 21 °C., under the conditions of the experiments approached 1.5. However, if one is to use the

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the University of Saskatchewan, Saskatoon, Canada. (Co-author Birss is now at the University of Alberta).

[1] Figures in brackets indicate the literature references at the end of this paper.

theoretical expressions for calculating exact values of r from data obtained by the tracer method under given conditions, exchange becomes of major importance. This led to a further study of exchange in such systems.

A theoretical paper has been prepared and submitted for publication by Fraser W. Birss in which mathematical expressions, by which r may be calculated, are developed on the basis of tracer methods for various mechanisms of hydration of the "through-solution" type, as well as for "direct" hydration, and for "hybrid" mechanisms combining some of the features of through-solution and direct hydration.

The tracer method has been tested by its application to the better understood mechanism of the hydration of plaster of paris, where the product is known, at least when excess of water is used, to separate from supersaturated solution as well-formed crystals of gypsum. The experimental results for the hemihydrate labeled with Ca-45 agreed well with the assumption of a through-solution mechanism for the hydration, and indicated no appreciable exchange between calcium ions in solution and the calcium in the crystals of gypsum after formation, in the time required for the hydration experiments. [2]

Experimental

In 1953 one of us decided to make a study of the exchange of calcium between a solution of calcium hydroxide, labeled with Ca–45, and completely hydrated C_3S. The hydrations were carried out by placing C_3S and carbon-dioxide-free water in sealed steel tubes lined with pure silver or fine gold and revolving the tubes, end over end, at 30 revolutions per minute for long periods of time in a room thermostated at 21 °C (and in later experiments at 25° and 8 °C).

The tubes were then centrifuged and two 25-ml portions of the clear supernatant liquid titrated with 0.06 M HCl using modified methyl red as indicator. The liquid removed was replaced by a solution of exactly the same concentration of calcium hydroxide containing the labeling agent Ca–45, and the tubes replaced on the shaker. From time to time they were centrifuged and 3 replicate samples of 0.5 ml were removed for counting. The counting times for each sample were such as to give 1 percent standard deviation (about 10,000 counts). Each replicate was counted three times and the 9 results averaged. Corrections were made for background, radioactive decay, and for coincidence if necessary. The above applies to all the experiments unless otherwise stated.

The HCl was standardized against individual samples of CaO, freshly prepared from purified low-alkali $CaCO_3$ (less than 0.002 percent of Na_2O). The value obtained by titration was checked by gravimetric determination of calcium with excellent agreement. The two samples of C_3S used were prepared, in platinum, from highly purified silica and the $CaCO_3$ described above, in an induction furnace. The analysis follows:

Sample	*CaO (Total)* %	SiO_2 %	R_2O_3 %	*CaO (free)* %
1–37	73.75	26.21	0.07	0.04
1–53	73.71	26.22	nil	0.03

The first three tubes were on the shaker for 10½ to 11 months. They gave final concentrations of 3.15, 10.20, and 20.45 millimoles CaO per liter and calculated r-values of 1.00, 1.272, and 1.392, respectively. Dissolved SiO_2 was determined, and correction was made in calculating the lowest r-value. No silica was found in the liquid in the other tubes. Later control experiments, the tubes containing solutions of calcium hydroxide but no C_3S, showed no change in titer after being shaken for several months.

The exchange experiments gave a rapid loss in the activity [2] of the solution during the first 12 hours, indicating rapid exchange of calcium, the percentage loss during this period increasing with the r-value of the hydrate. After 12 hours the rate of loss of activity decreased greatly. Calculations of the ratio of the moles of lime not exchanged per mole of SiO_2 indicated that this ratio, in the case of $r=1.27$ and 1.39, reached a gently sloping plateau at a value slightly above 1 in two to five days. For $r=1.00$ the plateau was not so evident, and the exchange continued at a more rapid pace.

The calculations were made by means of the expression x (the moles of lime in the solid hydrate which at a given time have reached exchange equilibrium with the solution) $=a\left(\frac{T}{A}-1\right)$ where a=moles of lime in the solution; T=total activity in the system; A=total activity in the solution.

The moles of lime not exchanged per mole of silica $=\frac{m-x}{s}$, where m=moles of lime and s=moles of silica in the solid hydrate. T and a were corrected for the removal of activity and lime from the solution due to a previous sampling. The results are given in figure 1 [3].

Other hydrations were carried out on the shaker, at 25 °C, for periods of from 10 to 31 months. After adding the isotope the change in activity with time was treated graphically. (Four 0.5 ml replicates were taken at each sampling and counted as above, and the 12 values for activity were averaged.)

The specific activity of the lime in solution was calculated at each sampling. The log of the specific activity was then plotted against time. This plot gave a straight line, after a short initial period, and by extrapolation to zero time (i.e., the time of the introduction of the isotope) one

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[2] The term "activity" will be used to denote radioactive count.

can separate the effect on activity of the slow and the initial fast exchange, the latter usually being complete in 2 to 3 days. Figure 2 for a hydrate of $r=1.404$, and figure 3 for one with $r=1.05$, are examples of the curves obtained.

From the initial activity of the solution and the extrapolated value for the slow process, one may calculate the exchange of activity with the solid during the fast process and the amount of calcium in the solid which reached exchange equilibrium with the calcium in the solution (i.e., equal specific activity). As the weights of calcium and silica in the hydrated silicate are known from the hydration data, one may then calculate the molar ratio of the lime *not exchanged* to the silica in the solid.

This calculation may be accomplished in a single step by substituting the experimental values in the equation

$$r_0=\frac{(a_0+m)A_1-a_0A_0}{sA_1}$$

where

r_0=molar ratio of the calcium *not exchanged* by the fast process to the total silica in the hydration product

A_0=initial activity of the solution (reg/0.5 ml/min)[3]

A_1=the extrapolated activity of the solution-time curve at zero time (reg/0.5 ml/min)

a_0=total CaO in the solution at the beginning of the exchange reaction (millimoles)

m=total CaO in the hydration product (millimoles)

s=total SiO_2 in the hydration product (millimoles).

As an alternative to the above one obtains the same result by plotting the logarithm of the specific activity of the CaO in the solid hydrate against time, extrapolating the curve for the slow reaction to zero time and calculating r_0.

Table 1 gives a summary of the results of the hydration and exchange experiments.

TABLE 1. *Summary of results*

Experiment	Weight C_3S	Time of hydration	Final conc. $Ca(OH)_2$ in solution [a]	Overall molar CaO/SiO_2 ratio	Calc. r_0	Temperature
	g	*mo*	*mM*			*°C*
121 [b]	0.0257	11	3.15	1.00	0.76	21
122	.1007	10.5	10.20	1.272	1.09	21
123	.2168	11	20.45	1.392	1.14	21
502	.1007	14	10.30	1.261	-------	21
503	.2168	14	20.40	1.391	-------	21
56 [c]	.1000	11	12.39	1.323	1.05	25
58	.1000	24	12.54	1.296	0.95	25
57	.1000	31	12.39	1.328	1.06	25
62	.1850	11	19.88	1.405	0.98	25
59	.1850	10.3	19.89	1.404	.94	25

[a] Saturated solution of $Ca(OH)_2$ at 21 °C—20.95 millimoles/liter
at 25 °C—20.15 millimoles/liter [7].

[b] Experiments 121–123, 502 and 503: C_3S 1–53 was hydrated in 75 ml H_2O.

[c] Experiments 56–59 and 62: C_3S 1–37 was hydrated in 75 ml of solution containing 2.55 millimoles CaO/liter.

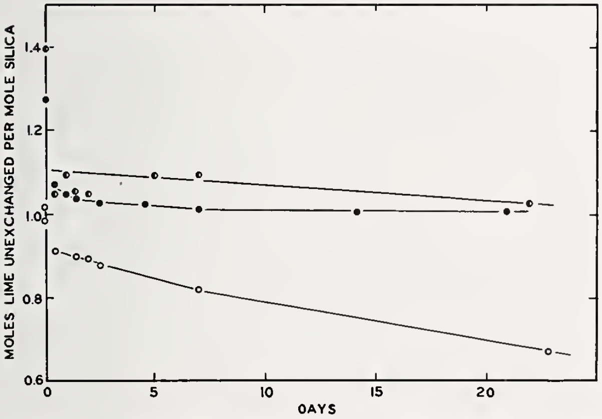

FIGURE 1. *Calcium exchange in an equilibrium system: Labeled* $Ca(OH)_2$ *solution-solid hydrated* C_3S *at 21 °C.*

◑, $CaO/SiO_2=1.39$; ●, $CaO/SiO_2=1.27$; ○, $CaO/SiO_2=1.00$.

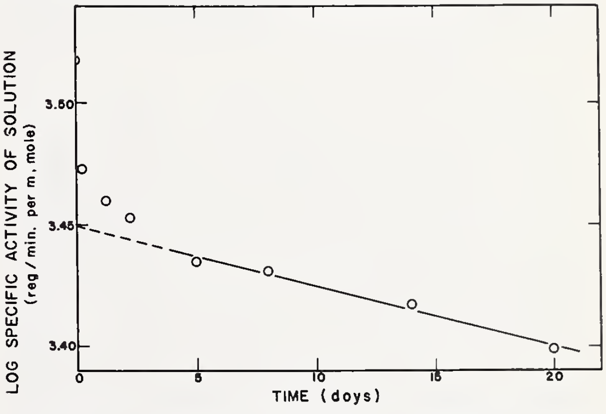

FIGURE 2. *Calcium exchange in an equilibrium system: Labeled* $Ca(OH)_2$ *solution-solid hydrated* C_3S *at 25 °C.*

CaO/SiO_2 ratio=1.40.

Accelerated Hydration of C_3S

The long time, and the uncertainty as to the time required, for complete hydration represent difficulties in studying the hydration products of C_3S. Ball-mill hydration and quantitative X-ray analysis used by Brunauer and Greenberg (paper III–1, this Symposium) are partial remedies for these difficulties. The authors have accelerated hydration greatly by introducing a mass of crumpled thin pure silver foil into the silver lined reaction tubes. Such baffling of the flow of liquid with movable foil caused formation of colloidal silver in the liquid, but blanks indicated that this did not materially affect the titer of the lime solutions. The hydration of C_3S in some instances appeared to be complete in less than 3 weeks, but most of the hydrations by this method were continued up to 2 months. Consistency was not quite as good as in the experiments of table 1, and the titers tended to be higher, giving lower r-values, possibly due to variation in the size of the particles of the

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[3] One register (reg.)=64 counts.

hydration product. The presence of the colloidal silver and the fine subdivision of the hydrate made the accurate determination of refractive index more difficult, but no material of refractive index higher than 1.60 was discovered, indicating the absence of afwillite. The results obtained by this method are given in table 2.

Parallel exchange experiments were made with afwillite.[4] Its behavior is entirely different from that of the hydration products of C_3S. In solutions of high concentration there is at first a very slight and equivalent drop both in concentration and activity of the solution with no further significant changes. This is further evidence that the products in table 2 were similar to those of table 1 and that appreciable amounts of afwillite were not present.

TABLE 2. *Accelerated hydrations of C_3S, using baffles*

Experiment at 25 °C	Weight of C_3S No. 1–37	Time of hydration	Final conc. $Ca(OH)_2$	r	r_0
	g	*mo*	*mM/liter*		
5–59 [a]	0.1850	0.75	20.4	1.36	0.96
6–59	.1850	.75	20.5	1.35	0.90
8–59	.1850	1.5	20.2	1.38	1.06
9–59	.1850	2.0	19.9	1.41	0.89
10–59	.1850	2.0	20.3	1.37	1.03
11–60	.1600	3.5	18.1	1.35	1.04
5–60 [b]	.0265	2.0	3.1	1.05	0.85
6–60	.0458	2.0	5.1	1.10	.82
at 8 °C [c]					
1–60	.2350	5.0	22.43	1.37	1.08
2–60	.2350	5.0	22.67	1.36	0.97
3–60	.1175	5.0	12.13	1.24	1.05

[a] Experiments 5–, 6–, 8–, 9–, 10–59 and 11–60 were hydrated in 75 ml of a solution containing 2.66 millimoles CaO/liter.

[b] Experiments 1–, 2–, 3–, 5– and 6–60 were hydrated in 75 ml of water.

[c] Saturated solution of $Ca(OH)_2$ at 8 °C—22.5 millimoles/liter [7].

Discussion

When interpreting the experimental results one should bear in mind that the system remains in chemical equilibrium during the exchange of calcium between the liquid and solid phases. The hydroxyl concentration of the liquid phase as determined by titration and that of calcium as determined by semi-micro quantitative analysis, remain unchanged and chemically equivalent. The isotope effect of Ca-45 may be considered negligible. The change in the distribution of the radioisotope between the solution and the hydrate is thus a measure of the exchange of calcium between the two phases.

At first it was the intention to eliminate the calculation of the decay of the radioisotope by counting a control solution stored in a pyrex glass container. It was found that the loss in activity of the control solution was greater than that calculated from the half-life of Ca-45. Solutions stored in the gold and silver lined tubes did not show this discrepancy. Apparently there was appreciable exchange of calcium between the solution and the glass of the container. The decay was therefore calculated on the basis of a half-life of Ca-45 of 165 days, the value determined experimentally. This is in good agreement with the latest figures found in the literature.

From the experimental results it is obvious that a large part of the calcium present in the solid hydration product of C_3S is subject to comparatively rapid exchange with calcium present in the equilibrium solution and that the amount of this labile calcium increases with the ratio of lime to silica in the hydration product. The remainder of the calcium exchanges at a very slow rate.

The similarity of the exchange curves to those for the adsorption of a solute from an aqueous solution by a solid powder may suggest that one is simply dealing with the attainment of equilibrium by an exchange of the calcium-45 ions in the solution with the ordinary calcium ions already present in a typical adsorbed layer on the surface of the hydrated silicate. However, for a number of reasons it is difficult to accept this view:

(1) The reader is referred to the evidence for the preferential adsorption of water and low adsorption of lime by tobermorite in paper III–1 by Brunauer and Greenberg.

(2) Our experiments on hydration of C_3S under greatly varying conditions support this finding. By microscopic measurements it was found that the average diameter of the crystalline aggregates of the hydrate in experiment 57 (at 31 months) was about twice that of the particles of experiment 56 (at 11 months, table 1). There was, however, no significant difference between the equilibrium concentrations of lime (or the r-values) of the two experiments. Our baffled hydrations, which gave very finely divided hydration products, tended to give r-values somewhat lower than the corresponding long-term hydrations. Thus, there is no indication of an increase in the adsorption of lime with decrease in particle size, which might be expected to give rise to an increase in surface area.

(3) Hydrations at 8 °C gave markedly lower r-values for the solid hydrate than those at 25 °C. This would mean *less* adsorption at the lower temperature.

(4) Exchange of radioactive ions in solution with ions in the surface layers of ionic crystals usually reaches equilibrium in a few minutes. Paneth and Vorwerk [5] found that when a finely divided precipitate of lead sulfate was shaken with a saturated solution containing some Pb-112, a steady state was attained in about one minute.

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[4] The sample of afwillite was kindly supplied to the senior author in 1929 by John Parry [4] and was composed of pure crystalline material from the original discovery at Kimberley. Our analysis gave CaO, 49.30%; SiO_2, 34.12%; and H_2O, 16.44% after drying at 100 °C.

Singleton and Spinks [6] added a small amount of Sr-90 to precipitated strontium sulfate in equilibrium with its solution and found that, with shaking, the primary exchange reaction was complete in less than one minute, while a slower secondary process or processes continued for one to two hours. This compares to days required in the case of the hydration product of C_3S.

(5) In several of our exchange experiments the initial activity of the solution (i.e., at zero time), calculated on the basis of the law of mixtures, was compared with the experimental value obtained after violent shaking by hand for one minute with subsequent centrifuging (10 min). For C_3S hydration products of medium r-values the two agreed within the expected 1 percent statistical variation while for products with high r-values the drop in activity was slightly in excess of this. Had there been a large amount of adsorbed lime on easily accessible solid surfaces one would expect a rapid drop in the activity of the solution during the first minute. The above applies only to aged precipitates. It is well known that fresh precipitates behave differently, probably because of recrystallization on aging.

One is thus tempted to suggest that the exchange experiments distinguish between two categories of calcium with a marked difference of chemical bonding in the crystal lattice and that the exchange takes place throughout the whole mass of the hydration product, therefore being much slower than ordinary adsorption, but still quite fast compared to exchange with the lime of the basic crystal lattice.

Some experimental difficulties were encountered. On centrifuging, the hydrated silicate tends to form a solid cake which may be difficult to disperse by mechanical shaking. The slowing up of the fast exchange (e.g., fig. 2) may result. A possible remedy would be ultrasonic dispersion. After the preliminary experiments the number of samplings were reduced to the minimum required to define the curve for the slow exchange (e.g., fig. 3). Test samples were also removed by filter sticks without centrifuging.

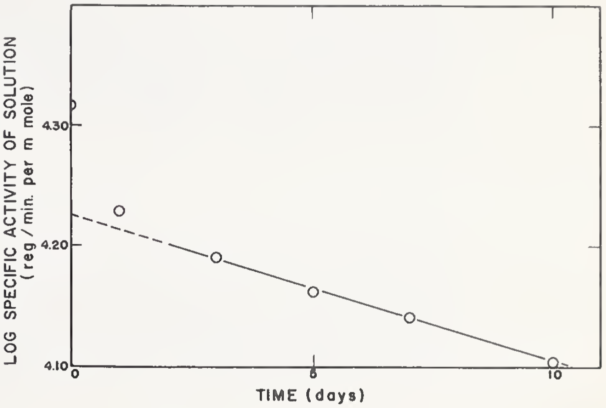

FIGURE 3. *Calcium exchange in an equilibrium system· Labeled* Ca(OH)₂ *solution-solid hydrated* C_3S *at 25 °C.* CaO/SiO_2 ratio=1.05.

Exchange in Hydration Products Formed in the Supersaturated Region

Two hydrations at 21 °C. (without baffling) were begun with the object of maintaining the concentration, by periodic dilution, in the metastable region just above saturation. Actually, during the 12-month hydration, the supersaturation varied from 2 to 22 percent. The CaO/SiO_2 ratios in the solids were 1.99 and 1.98. The rapid exchange indicated ratios of CaO (not exchanged) $/SiO_2$ of between 0.5 and 0.6 in 12 hours, and of less than 0.5 in 3 days, followed by slow exchange. Thus, instead of a hydration product giving the typical exchange curves of figures 1 to 3, the initial rapid exchange accounted for three-fourths of the total lime in the solid phases. White's test for calcium hydroxide was strongly positive and microscopic examination of the hydration products disclosed many large crystals of calcium hydroxide. Exchange experiments with finely divided calcium hydroxide crystals indicated that the slow secondary exchange may have been due to the calcium hydroxide in the hydration product.

These experiments indicate that hydration of C_3S under conditions of supersaturation, and in the presence of the calcium hydroxide phase, may produce a hydration product which exchanges all its lime very rapidly. The experimental result should, however, be considered subject to confirmation.

It should be noted that in these two experiments there was appreciable absorption of carbon dioxide due to the many openings of the reaction vessels for titration in order to follow the degree of supersaturation. The other hydration products (tables 1 and 2) were free from contamination of carbon dioxide at the start of the exchange experiments, and only in those used for the determination of an excessive number of points on the exchange curves could any material of high birefringence be detected in the hydration products.

The authors are greatly indebted to William A. G. Graham, Roger Kelly, and Betty-Gene Lepine for assisting from time to time with the preparation of the hydration products used in the exchange experiments. They also wish to express their appreciation to Dr. K. J. McCallum for valuable advice, and to Dr. A. R. Byers, Professor of Geology, University of Saskatchewan, who on many occasions made microscopic examinations of both the original silicates and the reaction products.

Thanks are also due to the National Research Council of Canada for financial support.

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Paper III–S11. Kinetics of Reaction in the System $CaO–SiO_2–H_2O$*

P. E. Halstead and C. D. Lawrence

Synopsis

The kinetics of the reaction between colloidal silica powder and lime solution, in the temperature range 10 to 50 °C, indicate a through-solution mechanism with the dissolution of silica as the slow step. The activation energy obtained for the process is 16.7 kcal/mole.

It has been found possible to express the concentration of silica and lime in solution during the reaction, and in the equilibrium system CSH—solution finally produced, in terms of a solubility product relationship.

Résumé

La cinétique de la réaction entre la poudre de silice colloidale et la solution de chaux, dans la gamme des températures 10 à 50 °C, indique un mécanisme qui s'opère par la voie de la solution, la dissolution de la silice constituant le stade lent. L'énergie d'activation obtenue pour ce processus est de 16,7 kilocalories/molécule-gramme.

On a constaté que la concentration de la silice et de la chaux en solution pendant la réaction, et dans le systéme d'équilibre CSH—solution finalement produite, peut être exprimée en fonction du produit de solubilité.

Zusammenfassung

Die Kinetik der Reaktion zwischen kolloidalem Siliciumoxyd-Pulver und Kalklösung, im Temperaturbereich 10 to 50 °C, deutet auf einen Mechanismus hin, der sich durch Vermittlung der Lösung vollzieht, wobei die Auflösung des Siliciumoxydes die langsame Stufe darstellt. Die bei diesem Vorgang erhaltene Aktivierungsenergie beträgt 16,7 Kilocal/Mol.

Dabei war es möglich, die Konzentration des Silicium-oxydes und des Kalkes in der Lösung während der Reaktion, sowie im Gleichgewichtssystem CSH—endgültig gebildete Lösung, in eine das Löslichkeitsprodukt enthaltende Beziehung auszudrücken.

In recent years considerable attention has been paid to the composition of the solid phase in the system $CaO–SiO_2–H_2O$ and in particular to the lime:silica ratio of the solid in equilibrium with calcium hydroxide solution of various concentrations. Comparatively little work has been reported on the composition of the liquid phase in equilibrium with calcium silicate hydrates. This paper reports the results of some measurements of reaction kinetics in the system and of the composition of the liquid phase.

In 1934 Cummins and Miller [1] [1] followed the reaction between saturated calcium hydroxide and siliceous powders by conductivity measurements, and at equilibrium, by analysis. In these experiments the reaction velocities were affected considerably by the nature of the siliceous particles, and in general equilibria were only established after a period of several days.

Also in 1934, Flint and Wells [2] made an extensive study of the solubility of silica in calcium hydroxide solutions and obtained curves relating the concentrations of $Ca(OH)_2$ and SiO_2 in equilibrium in aqueous solution. Families of curves were obtained, of the same general form but differing according to the source of the solutions, i.e., whether obtained by reaction of $Ca(OH)_2$ and SiO_2, or by decomposition by hydrolysis of various calcium silicate hydrates. A month was allowed for the systems to reach equilibrium.

In 1950 Taylor [3] reported a few measurements of the silica concentration in solution in equilibrium with solid calcium silicate hydrates of various lime:silica ratios. In these experiments also, the time taken to attain equilibrium was days or months.

In the work reported here, experiments similar to those mentioned above have given similar results but in a much shorter time and with fewer apparent anomalies. An interpretation of the results is offered on the basis of classical solution theory.

Experimental

The mechanism of the reaction between silica powder and calcium hydroxide solution is relatively complicated on account of the presence of divalent calcium ions and the fact that the reaction product is comparatively insoluble in water. As an exploratory step, therefore, the simpler reaction between silica and sodium hydroxide solution was studied. In other experiments calcium hydroxide solution was substituted for the sodium hydroxide solution.

The apparatus used for the reactions consisted of a Pyrex three-necked flask of either 30-ml or

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Research and Development Division of the Cement and Concrete Association, London, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

1-liter capacity immersed in a constant-temperature water bath.

The larger vessel was used for both the sodium hydroxide and calcium hydroxide experiments, and samples of solution were withdrawn from it for silica determination through a porous polyvinyl chloride filter equivalent in porosity to a No. 4 sintered glass filter. Since, for the measurement of calcium hydroxide concentration it was not necessary to withdraw samples of solution, the smaller vessel was used for calcium hydroxide reactions when only calcium hydroxide concentrations were to be measured.

A known volume of calcium hydroxide or sodium hydroxide solution was introduced into the vessel, precautions being taken to prevent contact with atmospheric carbon dioxide.

After the solution had reached the temperature of the water bath, a weighed amount of silica powder (B.D.H. "Colloidal Silica Powder" of specific surface ca. 220 m^2/g.) was introduced as quickly as possible. A magnetic stirrer in the vessel kept the silica powder in suspension and the concentration of the solution uniform.

Measurement of Concentration of Calcium Hydroxide in Solution

The method of measuring the concentration of the calcium hydroxide in solution consisted of measuring its electrical conductivity using a dip cell (Mullard type E. 7591) and a Wheatstone bridge fed from an alternating current supply of frequency 1 kc. Earphones were used to balance the bridge. From the conductivity and a previously constructed calibration curve, the concentration of the solution could be determined.

The electrical conductivity of calcium hydroxide solution is essentially due to the hydroxyl ions present and in the range of concentrations encountered in this work provides an easier and more accurate method of measuring small changes in $Ca(OH)_2$ concentration than titration with versenate or acid solutions. Conductivity measurements are particularly convenient in that they permit analysis to be made without removal or loss of material and without exposure to atmospheric CO_2. It is important, however, to keep the temperature of the solution closely controlled.

Measurements of the conductivity of calcium hydroxide solutions and of the lime-silica reaction were made over the range 10–50 °C and a range of concentration of 0.0025–0.025 mole/liter. The corresponding range of conductivity was such that the measured resistance of the solution lay between 200 and 2,000 ohms. The results of these measurements were in close agreement with the empirical relationship

$$\Lambda_t=\Lambda_{25}[1+x(t-25)]$$

where Λ_{25}=equivalent conductivity at 25 °C
and x=empirical constant=0.017.

A figure of $x=0.018$ has been quoted by Glasstone [4].

The Debye-Hückel-Onsager equation applied to $Ca(OH)_2$ solutions at 25 °C gives:

$$\Lambda_c=252-210\sqrt{c}$$

At $c=0.0034$ g equivalents/liter, $\Lambda_c=239.5$. The experimental value obtained was 240.

Measurements of Concentrations of Sodium Hydroxide in Solution

The conductivity measurements which provided a convenient method of measuring the concentration of calcium hydroxide solution were used in a similar fashion to measure the concentration of sodium hydroxide in the reaction solutions in the range 0–40 mm/liter.

Measurement of the Concentration of Silica in Solution

Samples of solution withdrawn through the filter from the reaction vessel were analyzed colorimetrically for silica content.

The standard procedure [5] was followed. Citric acid was added to prevent interference by calcium ions and 1:2:4 aminonaphthol-sulfonic acid was used as reducing agent. The optical density of the molybdenum blue coloration was measured in a Spekker absorptiometer using 4-cm cells and Ilford No. 608 red filters (transmitting only light of wavelength 6400 A or longer) with a mercury vapor lamp.

Five minutes were allowed for the yellow molybdate complex to develop before adding the citric acid and reducing agent. Development of the molybdenum blue complex took a further twenty minutes, and thereafter the optical density remained constant for several hours. Using a standard silica solution a straight-line calibration graph of concentration against optical density was obtained over the range 0–0.03 mM silica/liter. The concentration range obtained in this work was 0–12 mM/liter, and samples were diluted to bring them within the calibrated range.

It was found that a suspension of the silica powder in water gave no blue coloration when subjected to the above procedure; therefore, traces of silica powder which might have passed through the filter were unlikely to have caused any errors in the determination.

Results and Discussion

In the experiments involving reaction between sodium hydroxide and silica powder, the results obtained fit the expression

$$1-(x)^{1/3}=Kt$$

where x=fraction of silica remaining in solid form after time t, by assuming that the rate-determining step was dissolution of silica from the surface of spherical particles. The rate of solution was independent of hydroxyl-ion concentration in the range 15–40 milliequivalents/liter. The average activation energy for the reaction was found to be 18±1 kcal/mole over the range 25 to 45 °C. In the particular conditions of the experiment, approximately 55 percent of the silica enters solution in the first hour at 35 °C. The progress of the reaction as silica enters solution is accompanied by a corresponding decrease in sodium hydroxide, or more precisely, hydroxyl-ion concentration. The relationship between dissolved silica and decrease in hydroxyl ion could not be explained by the formation of any simple silicate ion in solution. The number of moles of silica entering into solution was at all times greater than the number of gram-equivalents of hydroxyl ion removed.

On examining the results from similar experiments in which the sodium hydroxide was replaced by calcium hydroxide, a very different pattern of reaction was observed (figs. 1 and 2). The characteristic features are:

(1) A sharp initial fall in calcium hydroxide concentration, occurring in the first minute of reaction, followed by a steady fall in the next few hours at approximately one tenth of the rate of reaction found for the sodium hydroxide reaction and independent of the calcium hydroxide concentration, with an average activation energy of 16.7 kcal/mole over the temperature range 10–50 °C.

The rate of reaction fell as the reaction progressed in a similar way to the sodium hydroxide reaction.

(2) An initial very rapid rise in silica concentration in solution, followed by a less rapid fall to a concentration which remained stable for a short period and then rose slowly as the reaction proceeded.

We interpret these phenomena in the following way:

(1) The initial sharp fall in the calcium hydroxide concentration represents adsorption of $Ca(OH)_2$ by the silica particles. The amount of $Ca(OH)_2$ adsorbed is roughly equivalent to a layer of Ca^{2+} ions on the surface of the silica particles one ion thick.

A similar initial reaction was observed by Cummins and Miller [1] and ascribed to the formation of a superficial layer of highly hydrated calcium silicate on the surface of the silica particles.

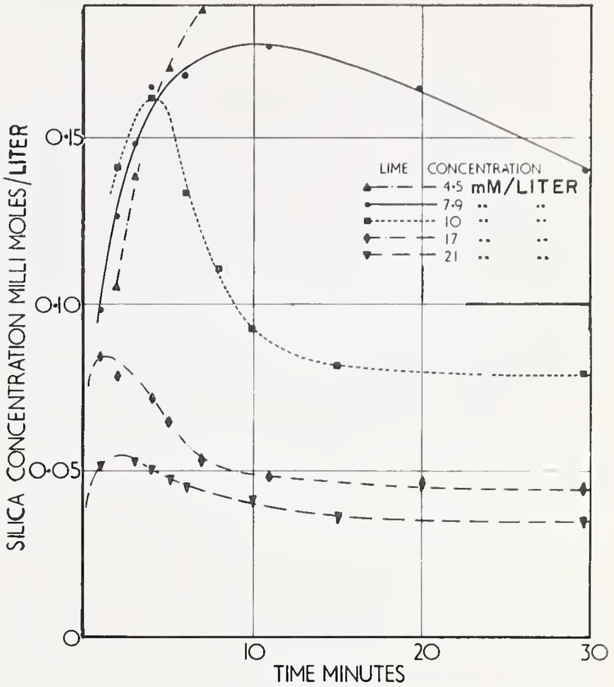

FIGURE 1. *Initial stage of the reaction of colloidal silica and lime solution at 45 °C.*

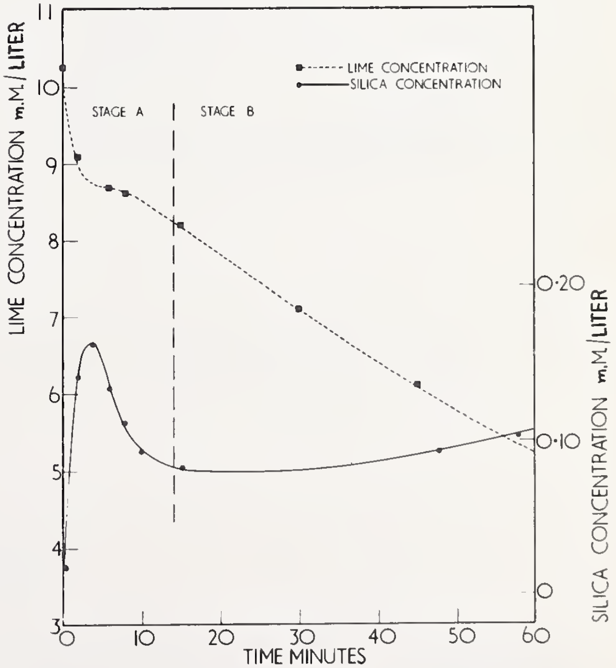

FIGURE 2. *Reaction of colloidal silica and lime solution at 45 °C.*

The continuing fall in calcium hydroxide concentration takes place as the main chemical reaction precipitates calcium silicate hydrate from solution.

(2) The initial rapid rise in silica concentration represents simple solution of the silica and occurs at a rate comparable with that obtained in the sodium hydroxide experiments. The fall in silica concentration occurs at a point of critical supersaturation with respect to calcium silicate hydrate in solution. The silica concentration thereafter is controlled at the saturation point of calcium silicate hydrate, i.e., silica is entering and leaving solution at the same rate. The saturation concentration of silica in solution rises as the calcium hydroxide concentration of the solution is reduced by the progress of the reaction.

On this interpretation, the rate-determining step is the same in both reactions studied. In support of this theory, the activation energies of the two processes are nearly identical, and the rate of reaction is independent of hydroxyl-ion concentration in both reactions. The very much lower rate obtained using calcium hydroxide may be explained by the more ready adsorption of calcium ions onto the surface silicate groups. If, as seems likely, only silicate groups can undergo depolymerization, the adsorption of a calcium ion, removing the negative charge on the surface silicate group, removes the possibility of that group entering solution. In effect, the surface area of the particles available for dissolution is reduced in the presence of calcium ions.

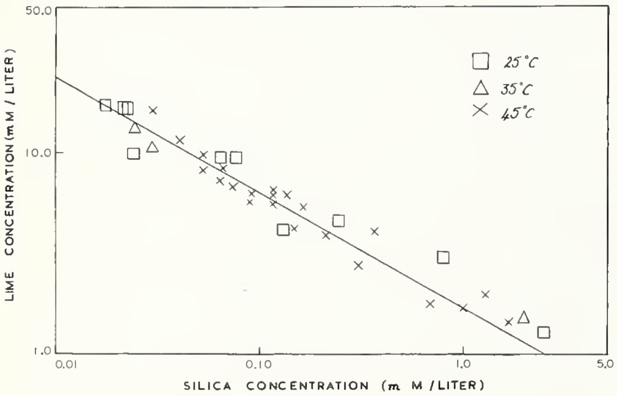

Figure 3. *Solution concentrations during lime-silica reaction.*

The form of the graph of lime and silica contents of the reaction solution, after the initial stage, led us to examine the relationship between lime and silica content of solutions in equilibrium more generally and we have found that the experimental values taken over a wide range of conditions fit the relationship:

$$[Ca(OH)_2]^x \, [SiO_2]=K$$

remarkably closely. (See fig. 3.)

The regression of $[Ca(OH)_2]$ on $[SiO_2]$ gives a "best fit" at $x=1.9$ and $K=3.4$ with correlation coefficient $r=-0.95$. It is particularly interesting to find that lime-silica concentrations measured after 15 min fit the above curve as well as measurements on the equilibrium system. We have found no suggestion of an inflection of the curve at low lime concentrations, indicative of a reduced silica concentration below a peak occurring at about 0.075 g CaO/liter as reported by Flint and Wells [2].

The similarity of this result to a solubility product suggests that in solution something resembling a salt such as C_2SH may exist, i.e., $Ca_2SiO_4 \cdot aq$. This accords with the suggestion of Flint and Wells [2] that in the system $CaO-SiO_2-H_2O$ at 30 °C, the calcium silicates present are salts of orthosilicic acid H_4SiO_4 which would by progressive replacement of hydrogen by calcium ions form hypothetical calcium silicates hydrates of C:S ratio of 1:2, 1:1, 3:2, and 2:1.

The significance of the "solubility product" in cement hydration seems to be that in a cement and water paste any increase in $Ca(OH)_2$ concentration must force elimination of silica from solution in the liquid phase.

Thus whilst there exists a discrete liquid phase the formation of hydrated calcium silicates can reasonably be explained by a through-solution mechanism.

At $Ca(OH)_2$ concentrations above about 2 mM/liter the equilibrium concentration of silica in solution is exceedingly small and the $CaO:SiO_2$ ratio in solution at a $Ca(OH)_2$ concentration of 20 mM/liter must be about 90:1. It is possible that the peculiarities of crystal growth of calium silicate hydrates may be a consequence of the great difference in $CaO:SiO_2$ ratio in the solids and in the "mother liquor" from which they separate.

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Discussion

Sidney A. Greenberg

The work reported in the paper is very interesting. It is clear to all that the kinetics and mechanisms of solution of colloidal silicas in basic solutions are important to an understanding of the processes proceeding in concrete mixtures. However, the authors do not refer to some recent work which has been published on this subject. The conclusions of the authors, nevertheless, are in complete agreement with the previously published work.

In a paper by O'Connor and Greenberg [1] it was shown that silica dissolves in sodium hydroxide solutions according to the equation

$$C_p^{1/3}=C_{p0}^{1/3}-k_3t \qquad (1)$$

where C_p and C_{p0} are the amounts of silica at time t and at zero time, respectively, and k_3 is a constant. This equation was derived on the assumptions that the rate of solution is proportional to the surface area and that the particles are spheres. It was later reported [2] that silica reacts with calcium hydroxide solutions with concentrations greater than 0.0036 molar according to eq (1). The mechanism proposed for the reaction is the same as that given by Halstead and Lawrence.

A detailed study of the initial chemisorption reaction of calcium hydroxide by silica has been discussed in detail [3]. It was shown that the surface of silica is covered by acidic silanol groups, SiOH, which react immediately with calcium hydroxide in an acid-base reaction.

The nature and amount of silicic acid dissolved in sodium hydroxide and calcium hydroxide solutions have been discussed [4–6] and the subject is reviewed by Brunauer and Greenberg [7]. It was shown that several equations explain the composition of the silicate solutions. One is for electroneutrality.

$$2[Ca^{++}] \text{ or } [Na^+]=[OH^-]+[H_3SiO_4^-]+2[H_2SiO_4^{--}] \qquad (2)$$

and another is for material balance

$$[SiO_2]_t=[H_4SiO_4]+[H_3SiO_4^-]+[H_2SiO_4^{--}] \qquad (3)$$

where the quantities in brackets are concentrations in moles/l. The relative quantities of the three species of silicic acid are controlled by the dissociation constants of the acid [4, 5]. The relationship between the calcium and silicic acid concentrations for solutions in contact with hydrates of C/S mole ratio 1/1 and above is controlled by the activity product,

$$K=a_{Ca^{++}}a_{H_2SiO_4^{--}} \qquad (4)$$

which is equal to 10^{-7} at 25 °C [6, 7].

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Paper III–S12. The Influence of High-Pressure Steam on the Process of Hardening of Calcium and Magnesium Silicates and Cements of Different Compositions*

P. I. Bozhenov, V. I. Kavalerova, V. S. Salnikova, and G. F. Suvorova

Synopsis

Autoclave curing of building units made of cellular concrete, dense concrete, and silicate concrete is one of the progressive technologic methods which makes possible the production of precast building elements in a comparatively short time (12 to 14 hours). In the practical production of building units, autoclaving is widely used at a pressure of 8 to 12 atm, and corresponding temperature of 174 to 191 °C.

The authors give details of investigations carried out in the USSR, which show the influence of high pressure steam (up to 200 atm) on the processes of hydration and hardening of cementing materials containing calcium and magnesium silicates.

The investigations show that under the conditions of increasing steam pressure and temperature, the hydration of the cementing material, the processes of concrete hardening, and the interaction of cementing material with aggregates occur more intensively. There is an optimum limit of pressure and an optimum regime of autoclave curing for each kind of cementing material, depending on its mineralogical composition. For example, cementing materials of the type of belite cements (with high C_2S contents), which includes some industrial wastes, such as nepheline slurry, blast furnace slags and Martin slags, and slate ashes, require intensive curing within the range of 16 to 25 atm and reduced regimes of autoclaving.

Autoclaving the materials with high contents of MgO or magnesium silicates at steam pressure of 25 to 50 atm gives new high-quality materials.

The use of high pressure steam (16 to 25 atm) in autoclave technology permits a reduction of the general technological cycle of autoclave treatment by as much as 5 to 7 hours.

The examples given show that autoclaving with high pressure steam provides solutions of such important problems in the building industry as reducing the time required for hardening precast concrete products and widening the raw material base by use of industrial wastes and natural rock minerals containing magnesium.

Résumé

L'autoclavisation des éléments constructifs en béton cellulaire, béton plein et béton de silicates se présente comme un des procédés les plus avancés qui permet d'obtenir les éléments préfabriqués en un laps de temps relativement court.

La production des éléments constructifs comprend une large utilisation de l'autoclave (vapeur à haute pression et température 8–12 atm et 174–191 °C).

Le rapport fait part des recherches effectuées en URSS qui montrent l'influence de la vapeur à haute pression sur les procédés d'hydratation et de durcissement des liants contenant les silicates calciques et magnésiques.

Les recherches affirment que, lorsque la pression et la température de la vapeur s'augmentent, on arrive à une intensification de l'hydratation des liants, des procédés de durcissement des bétons, et des réactions entre les liants et les agrégats.

Chaque sorte de liant, selon sa propre composition minéralogique, présente une limite optimum de pression et son propre régime d'autoclavisation.

Ainsi, les liants du type des ciments bélites (avec une forte teneur en C_2S), y compris certains déchets industriels—par exemple, le laitier de haut fourneau et la scorie Martin, le schlamm de néphéline, les cendres volantes des schistes, exigent un traitement intensif, compris entre les limites de 16–25 atm et des régimes réduits d'autoclavisation.

On obtient des nouveaux matériaux de construction de haute qualité à l'aide de l'autoclavisation à vapeur sous pression de 25 à 50 atm des matières contenant une forte teneur en MgO ou en silicates magnésiques.

L'utilisation de la vapeur à haute pression (16–25 atm) durant l'autoclavisation permet de réduire le cycle technologique général jusqu'à 5–7 h.

L'exposé du rapport démontre que l'autoclavisation à vapeur de haute pression donne la possibilité de résoudre des problèmes d'importance magistrale pour l'industrie du bâtiment, tels que la réduction du délai de durcissement des éléments préfabriqués et l'extension de la base des matières premières, grâce à l'utilisation des déchets industriels et des minéraux de roches naturels contenant le magnésium.

Zusammenfassung

Die Dampfhärtung von Bauteilen aus Leichtbeton, Schwerbeton und Silikatbeton ist ein sehr modernes Verfahren, welches die Möglichkeit gibt in relativ kurzer Zeit fertige Bauteile zu erhalten.

Die Herstellung von vorgeformten Bauteilen mit Dampferhärtung unter Druck von 8–12 Atm (bei 174–191°) ist weit verbreitet.

Der Vortrag gibt eine Übersicht von den Untersuchungen in USSR, die den Einfluss von Dampfdrücken bis zu 200 Atm auf die Vorgänge der Hydratation und Härtung von solchen Bindemitteln zeigen, die Silikate von Calcium und Magnesium enthalten.

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*Fourth International Symposium on the Chemistry of Cement, Washington, 1960. Contribution from the Academy of Construction and Architecture, Leningrad, U.S.S.R.

Die Untersuchungen zeigen, dass mit steigendem Dampfdruck und Temperatur die Hydratation von Bindemittel, der Verlauf der Härtung des Betones, und das Aufeinanderwirken der Zuschlagstoffen mehr intensiv stattfindet.

Jedes Bindemittel zeigt abhängig von seiner mineralogischer Zusammensetzung ein optimales Dampfhärtungsverfahren.

Zum Beispiel, Bindemittel wie Belitzemente (mit hohem C_2S Gehalt) sowie eine Reihe von industriellen Abfällen, Hochofen und Martin-Schlacke, Nephelin-Schlämme, Schiefer, Flugasche, erfordern eine intensive Dampferhärtung innerhalb der Grenze von 16–25 Atm.

Bindemittel mit einem hohen Gehalt von MgO oder Magnesiumsilikaten bei einer Dampferhärtung von 25–50 Atm, liefern neue hochwertige Baustoffe.

Die Hochdruck Härtetechnik, 16 bis 25 Atm, macht es möglich die Zeitdauer des Dampfhärte-Verfahrens um 5 bis 7 Stunden zu verkürzen.

Die vorgeführten Beispiele zeigen, dass das Dampfhärte-Verfahren mit hohen Dampfdrücken die Lösung von solchen Aufgaben, die in der Bauindustrie auftreten, wie die Verkürzung der Härtezeit von vorgeformten Betonteilen und die Erhöhung der Auswahl von Rohmaterialien, ermöglichen, sodass industrielle Abfälle und unverarbeitetes Gestein, das Magnesium enthält, verwendet werden können.

The production of precast building units, based on the technical properties of calcium silicate hydrate, is a rather young but rapidly developing building-materials industry.

There are certain scientific and practical achievements in the production of concrete and reinforced-concrete products, but a number of important problems of technology must be investigated, that is, the choice of cementing material, which takes an active part in the development of the structural properties of hardened concrete.

The quality of concrete, hardened at normal temperature, from 1 to 45 °C, greatly depends on cement "activity."

The development of technical properties of concrete by hydrothermal curing depends upon some other conditions and is defined by the physicochemical properties of cementing material and aggregates, and particularly the autoclave regime (duration of curing, temperature, and steam or water pressure, in which milieu hardening takes place).

The investigations, carried out by the Leningrad Building Institute and the Academy of Architecture and Building (Leningrad filial), showed that under certain circumstances of hydrothermal curing it is possible to produce high-quality precast members from various cementing materials, that is, from sand and lime, from a number of industrial waste products which contain calcium and magnesium silicates, and lastly by suitable technological curing of some rocks.

In the concise reports of Bernal, "The Structures of Cement Hydration Compounds," of Steinour, "The Reactions and Thermochemistry of Cement Hydration at Ordinary Temperature," and of Kalousek, "The Reactions of Cement Hydration at Elevated Temperatures," delivered at the Third International Symposium on the Chemistry of Cement, there are data that furnish a basis for judgment on the conditions of formation of hydrosilicates. In the period since the third Symposium took place, the formation of hydrosilicates has become of great interest and there are many new facts characterizing the dynamics of calcium silicate hydrate formation.

N. A. Toropov considers that as of 1959 the conditions of formation of the following calcium silicate hydrates have already been studied to some degree.

1. low-temperature:
   $CSH(I)\ 0.8CaO{\cdot}SiO_2{\cdot}aq$
   $C_2SH(II)\ 1.5\text{–}2.0CaO{\cdot}SiO_2{\cdot}aq$
2. tobermorite group of minerals:[1]
   $5CaO{\cdot}6SiO_2{\cdot}nH_2O$
3. gyrolite—$2CaO{\cdot}3SiO_2{\cdot}2H_2O$
4. afwillite—$3CaO{\cdot}2SiO_2{\cdot}2H_2O$
5. foshagite—$4CaO{\cdot}3SiO_2{\cdot}H_2O$
6. xonotlite—$6CaO{\cdot}6SiO_2{\cdot}H_2O$
7. hillebrandite (β-hydrated dicalcium silicate)
8. α-hydrated dicalcium silicate—$2CaO{\cdot}SiO_2{\cdot}H_2O$
9. c-hydrated dicalcium silicate—$2CaO{\cdot}SiO_2{\cdot}0.3\text{–}1.0H_2O$
10. tricalcium hydrosilicate—$3CaO{\cdot}SiO_2{\cdot}2H_2O$

Besides these, the following calcium silicate hydrates are also known:

11. okenite—$CaO{\cdot}2SiO_2{\cdot}2H_2O$
12. truscottite—$CaO{\cdot}2SiO_2{\cdot}0.5H_2O$
13. nekoite—$CaO{\cdot}2SiO_2{\cdot}2H_2O$

Furthermore, calcium chondrodite was recently found having a structure like that of magnesium chondrodite. And, moreover, there are some references in the literature to hydrated tricalcium silicate, foshalassite—$5CaO{\cdot}3SiO_2{\cdot}3H_2O$, di- or tetrahydrated dicalcium silicate—$2CaO{\cdot}SiO_2{\cdot}2\text{–}4H_2O$, and the hydrosilicate $6CaO{\cdot}3SiO_2{\cdot}H_2O$.

At present, 17 hydrated calcium silicates are known and somewhat studied, and it is obvious that their number will increase.

From numerous publications it is clear that the chemical composition and structure of hydrated calcium silicates can vary within broad limits. It is necessary to pay attention to the capacity of hydrated calcium silicates for change of bound water and, what is particularly important, for change in the ratio $CaO:SiO_2$ depending on the initial material and the conditions of hydrothermal curing.

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[1] Among the tobermorite group of minerals there are some hydrates differing from one another by the number of H_2O molecules in the elementary cell. These hydrates are the following:
a. 14A–hydrate, plombierite
b. 11A–hydrate, tobermorite proper
c. 10A–hydrate
d. 9A–hydrate, riversideite
(The number of angstroms standing before the word "hydrate" gives the characteristic d_{002} which distinguishes the tobermorites.)

Scientists dealing with the problems of experimental mineralogy and petrography have carried out numerous investigations, discovering the role of water during mineralogical processes, which made it possible for W. I. Vernadsky to write in 1923: "In the chemistry of the earth's crust water plays a unique role which cannot be compared with that of any other substance, and by different means it penetrates into nearly all mineral solids of the upper and partly deeper thermodynamic shells of the earth's crust, and gives with them varied types of chemical compositions of different strengths."

In fact, nature gives us numerous examples of different hydrated compositions, including hydrated silicates, having sometimes important technical properties (asbestos, hydromicas) owing to which they are assigned to the category of mineral resources.

It is necessary to mention a certain gap between theoretical investigations in which experiments are often carried out at high pressure, 100 to 3,000 atm, at temperatures from 300 to 1,000 °C, on the one hand, and the practice of hydrothermal steam curing limited to 70 to 90 °C or autoclaving at 175 to 200 °C, on the other hand.

Such a situation was created as the result of the underestimating, by practicing engineers, of the value of theoretical investigations of the physical chemistry of silicates and the thermodynamic properties of water and steam at high pressures and temperatures.

Concrete strength depends not only on cement "activity," but also on the methods of mixing and molding, and particularly on the hardening conditions.

Modern science and technology allow us to state that it is possible to develop a technology by which cement of low activity provides in a short time products with the necessary structural properties.

The results of the investigations carried out in the USSR on the problem of the influence of high-pressure-steam treatment on developing technical qualities of cement paste, depending on raw materials and regime of curing, are given in our report.

As already mentioned, there is in the technical literature enough information about hydrosilicate synthesis.

In this connection, the following names are known: Le Chatelier—1904; Michaelis—1909; Schlapfer and Niggli—1914; Thorvaldson and Shelton—1923; Lerch and Bogue—1927; Flint and Wells—1934; Keevil and Thorvaldson—1936; Lapin—1938; Michalchenko—1947; Butt—1949; Bozhenov—1952; Wolfson—1949; Toropov—1952; Taylor—1950; Bessey—1951; Kalousek—1951; Bernal—1952; Hansen—1953; Sanders and Smothers—1957; Berkovich—1958, and many others.

In these investigations, with the exception of Butt, Wolfson, Bozhenov, Sanders and Smothers and some others, the technical characteristics of the products obtained have not been studied, and there are still few data characterizing the technological conditions necessary for obtaining products with specified properties.

In many cases, industrial waste products contain large quantities of low-basic calcium and magnesium silicates. Such materials are often slow hardening under normal conditions but acquire enough strength after autoclave treatment. It is known that mixtures containing free lime and silica, after treatment with high-pressure steam, give high-strength building stone, owing to the hydrosilicates formed.

The method of hydrothermal curing in steam-curing chambers at temperatures lower than 100 °C, widespread at the present time, requires a long-run steam-curing cycle and cement of high activity.

Lately, technologists often speak of increasing the temperature and steam pressure during hydrothermal curing. The USSR, the USA, Sweden, and some other countries are moving in this direction now.

Pressure increase, and consequently temperature increase, contribute to more rapid progress of hydration and greater use of cementing-material energy, leading to reduction of the time of technological curing, and allowing one to turn out products of higher quality using less time, energy, and labor.

The results of our investigations, given below, show that autoclave curing is a powerful means of obtaining hydrosilicates from various materials that are chemically passive under normal conditions.

Calcium Silicates

Calcium-silicate-hydrate synthesis is rather difficult under normal temperature conditions. Therefore, the results of investigations are often contradictory. The majority of researchers consider that under normal conditions only two hydrosilicates, CSH(I) and $C_2SH(II)$, are formed.

At higher temperatures, calcium silicate formation occurs more rapidly and in a more complicated way than under normal conditions of temperature and humidity. Consequently, we know of many more hydrosilicates obtained by means of hydrothermal curing.

Some researchers have obtained hydrosilicates by hydrothermal synthesis, bringing together limewater or lime with silica gel or crystalline highly dispersed silica; others have studied the structure and composition of compounds appearing under various conditions as the result of calcium-silicate or portland-cement hydration.

In our laboratory, the behavior of synthetically obtained β-$2CaO{\cdot}SiO_2$, with addition to it of CaO and SiO_2, was studied during hydrothermal curing. (Bozhenov, Kavalerova, 1958.)

Mixtures in the proportions CaO:SiO_2=1:1, 3:2, 3:1, and 7:2 were prepared.

The specimens were exposed to autoclave treatment at pressures of 8, 25, and 100 atm, with curing at maximum pressure for 8 hr. Steam increase and decrease, depending on the pressure value, took about 1.5 to 2.5 hr. For autoclaved and dried specimens the compressive strength was determined; then their free lime and silica contents also were determined. The amounts of lime and silica reacting with β-2CaO·SiO_2 were determined from the difference between the amounts of added CaO or SiO_2 and the amounts found free after autoclave treatment.

It was found that during hydrothermal curing of synthetically obtained β-2CaO·SiO_2 free calcium hydroxide was liberated in the following quantities: at 8 atm—0.12 percent, 25 atm—5.64 percent, 100 atm—2.49 percent.

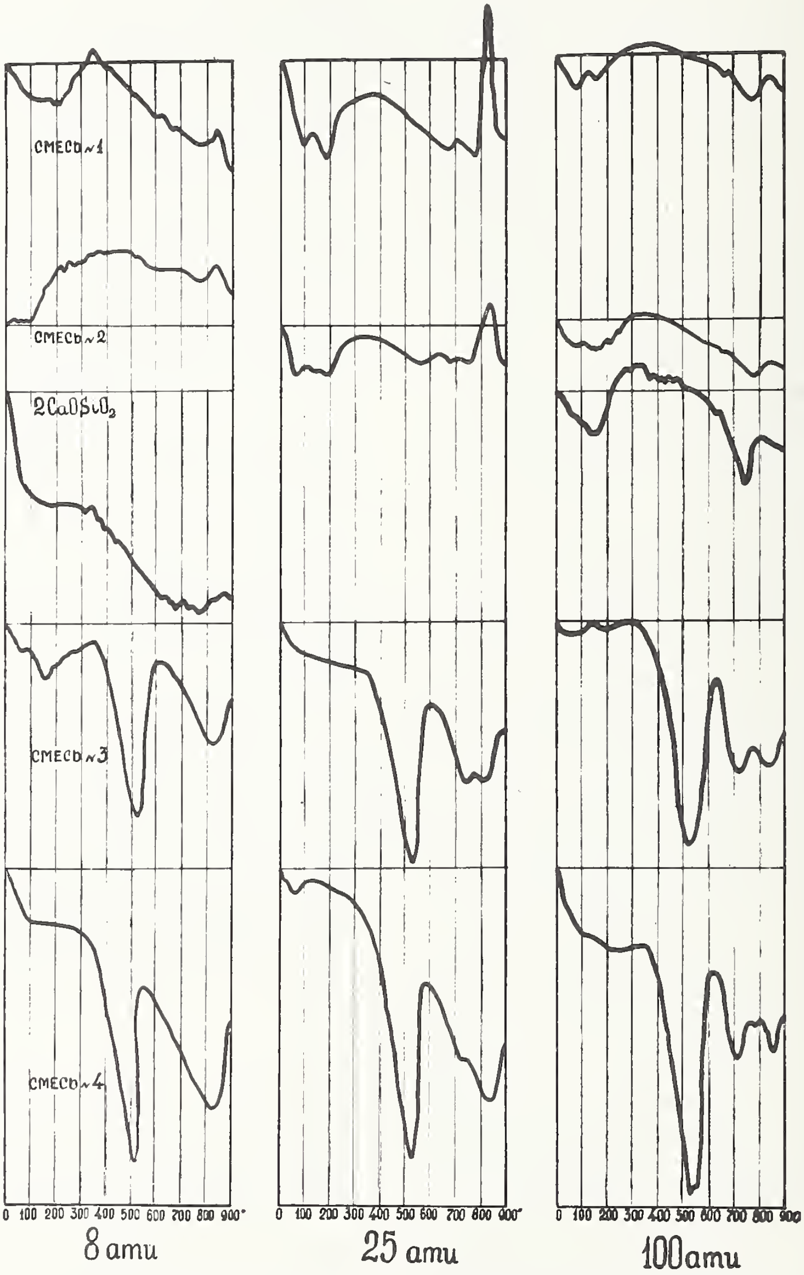

Figure 1. *Thermograms of* 2CaO·SiO_2 *and mixtures with lime or silica (autoclaved at 8, 25, or 100 atm).*

No. 1—C_2S+34.94 SiO_2=CS
No. 2—C_2S+17.44 SiO_2=C_3S_2
No. 3—C_2S+32.56 CaO=C_3S
No. 4—C_2S+48.82 CaO=C_7S_2

Table 1. *Autoclave reaction of dicalcium silicate with lime* [a]

CaO added, relative to C_2S	Lime bound in autoclave, relative to C_2S		
	Autoclave pressure		
	8 atm	25 atm	100 atm
Percent	*Percent*	*Percent*	*Percent*
32.56	19.17	17.99	17.06
48.82	32.42	30.02	30.45

[a] Maximum pressure maintained for 8 hr; pressure increase and decrease times, 1.5 to 2.5 hr.

Table 2. *Autoclave reaction of dicalcium silicate with silica* [a]

SiO_2 added, relative to C_2S	Silica bound in autoclave, relative to C_2S		
	Autoclave pressure		
	8 atm	25 atm	100 atm
Percent	*Percent*	*Percent*	*Percent*
34.94	11.40	11.24	15.07
17.44	9.50	11.00	16.34

[a] Maximum pressure maintained for 8 hr; pressure increase and decrease times, 1.5 to 2.5 hr.

As seen from tables 1 and 2, in the process of autoclave treatment β-2CaO·SiO$_2$ interacts both with CaO and SiO$_2$.

From the data of table 1 it is seen that:

a. For the same composition the quantity of bound CaO decreases somewhat with increase in pressure.

b. The quantity of CaO bound during autoclave treatment of C_2S-CaO mixtures depends on the mixture composition. Consequently, during autoclaving, chemical equilibrium is established between the hydrosilicate that is formed, and the free calcium oxide content.

Table 2 data show that β-2CaO·SiO$_2$ is able to interact with silica, forming less basic calcium hydrosilicates:

a. The higher the steam pressure in the autoclave, the more the SiO$_2$ interacts with β-2CaO·SiO$_2$;

b. At the same steam pressure the amount of bound silica is practically stable, not depending on the initial mixture composition.

The differential-thermal-analysis (DTA) curves of the products obtained show a more complicated picture than Kalousek and other investigators have observed. From figure 1, considerable change of the hydration products obtained can be noticed depending on mixture composition and autoclaving conditions. Consequently, during hydrothermal curing, activity of the C_2S increases, and as a result it energetically interacts intensively both with lime and with silica, forming calcium hydrosilicates of different compositions depending on the autoclaving conditions and the initial mixture composition.

It can be assumed that during autoclaving β-2CaO·SiO$_2$ undergoes considerable structural change, and that this change is reflected in the compositions and qualities of the products obtained.

The strength characteristics of the specimens tested, given in figure 2, show that the strength of neat β-2CaO·SiO$_2$ continuously increases as the pressure is increased. Less basic calcium hydrosilicates formed (with the addition of SiO$_2$) have

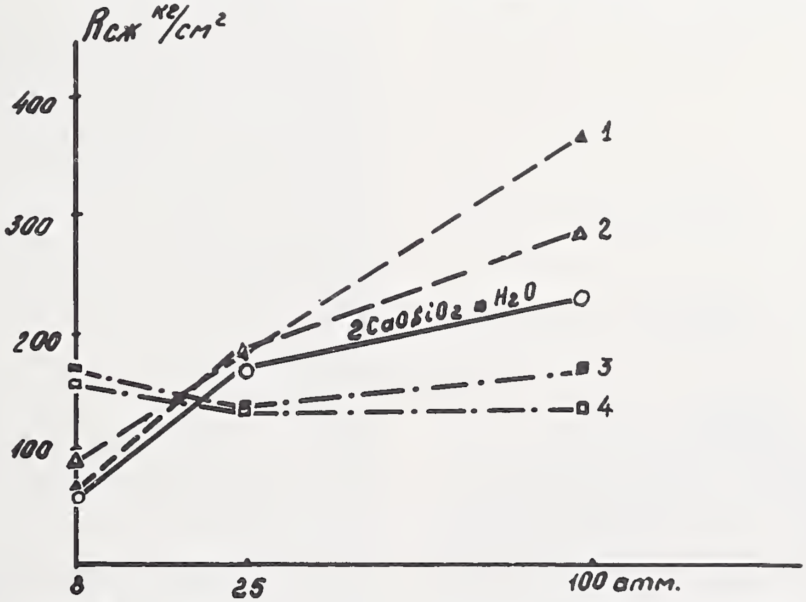

Figure 2. *Strength of* β-2CaO·SiO$_2$, *alone and with additions of* CaO *or* SiO$_2$.

No. 1—C_2S+17.44 SiO_2=C_3S_2
No. 2—C_2S+34.94 SiO_2=CS
No. 3—C_2S+48.82 CaO=C_7S_2
No. 4—C_2S+32.56 CaO=C_3S

(Ordinate: compressive strength, kg/cm². Abscissa: steam pressure, atm.)

TABLE 3. *Compressive strength of nepheline slurry with added lime or ground silica sand, after autoclaving* [a]

Composition of the cementing material			Compressive strength of paste specimens, tested at once after autoclaving
Slurry	Lime	Sand	
Percent	*Percent*	*Percent*	*kg/cm²*
100	0	0	217
87	13	0	277
85	15	0	255
83	17	0	197
80	20	0	191
100	0	0	262
95	0	5	272
90	0	10	331
85	0	15	315
80	0	20	220
65	0	35	250
25	0	75	148

[a] Maximum pressure 8 atm, maintained for 8 hr; pressure increase and decrease times, 2 hr.

TABLE 4. *Compressive strength of plant-autoclaved units made with nepheline cement and cured for various times*

Period of curing before steam treatment	Compressive strength	
	1:6 plastic mortar units, 40 x 40 x 50 cm	Concrete cubes,[a] 20 x 20 x 20 cm
Hours	*kg/cm²*	*kg/cm²*
3	65	----------
9	94	184
12	140	204
24	56	166

[a] Slurry, 80 percent; lime, 15 percent, gypsum, 5 percent.

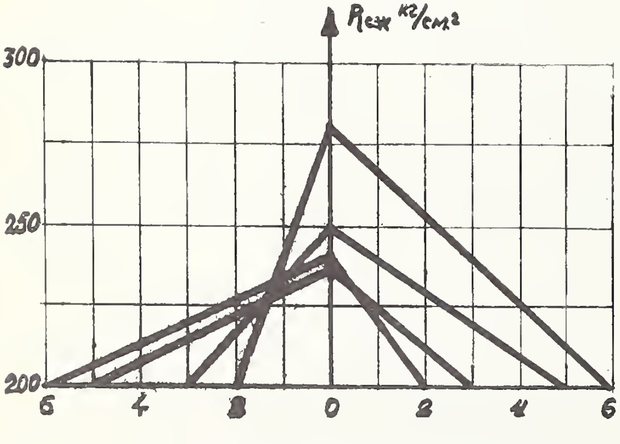

FIGURE 3. *Dependence of the compressive strength on the autoclaving regime.*

(Ordinate: compressive strength, kg/cm². Abscissa: left, period of pressure increase; right, period of pressure decrease, in hours.)

greater strength than neat belite (C_2S). This difference increases with pressure increase in the autoclave. Pressure increase from 8 to 100 atm caused a gain in strength of 4 to 5 times.

The strength of the highly-basic hydrosilicates (mixtures prepared with the addition of CaO) practically does not change as the pressure increases.

Consequently, by regulating the gross compositions of the initial mixtures and the conditions of hydrothermal curing, the structural qualities of autoclaved materials can be varied over rather a broad range.

For increasing the strength, it is expedient to prepare the mixtures that give the less basic hydrosilicates, and to increase the temperature of autoclave treatment.

In some publications there are references to the transition of β-$2CaO{\cdot}SiO_2$ to γ-$2CaO{\cdot}SiO_2$ during autoclave treatment. We have, therefore, investigated the behavior of γ-$2CaO{\cdot}SiO_2$ during hydrothermal curing. These investigations have shown that during autoclave curing γ-$2CaO{\cdot}SiO_2$ is able to react with both lime and silica, forming calcium hydrosilicates.

The results obtained were proved with precast nepheline slurry containing about 80 percent of dicalcium silicate (Bozhenov, Kavalerova—1956–1958). Nepheline slurry is a waste material from production of aluminum oxide and is a cementing material of low activity at normal hardening. The chemical analysis of the slurry showed that it contained in percent: SiO_2, 28.63; Al_2O_3, 3.13; Fe_2O_3, 4.80; TiO_2, 0.30; P_2O_5, 0.48; CaO, 52.97; R_2O, 2.18; MgO, 2.12; and ignition loss, 3.89. The existence of great amounts of β-$2CaO{\cdot}SiO_2$ in the nepheline slurry was confirmed by means of X-ray analysis.

In table 3 are shown the strength characteristics of nepheline slurry with addition of 13 to 20 percent of lime or dispersed ground silica sand in the amount of 5 to 75 percent, after autoclaving at 8 atm in accordance with the regime 2–8–2 (hours during which steam pressure was increased, maintained constant, and then decreased).

From the table it is clear that during autoclaving some quantities of lime and particularly dispersed ground silica sand increase nepheline slurry activity.

In table 4 are shown the results of plant testing of 40- x 40- x 50-cm units made with 1:6 mortar, and 20-cm cubes of nepheline-cement concrete (slurry 80%, lime 15%, and gypsum 5%).

From the table it is clear that increase of the time of curing of specimens before steam treatment to 12 hr leads to strength increase up to 20 to 25 percent.

The influence of the rate of increase and decrease of steam pressure on the compressive strength developed in the autoclave is shown in figure 3. It is seen that for the same duration of autoclave curing, rapid increase and slow decrease of pressure insure the greatest strength of the specimens.

Units of the size 40 x 40 x 50 cm prepared of 1:4 nepheline-cement mortar were cured in the autoclave with different rates of pressure increase and decrease but with equal total durations of autoclaving of 9 hr.

The data of table 5 show that the greatest strength is obtained under the conditions of rapid pressure increase and the slowest steam decrease in accordance with the regime 1–3–5.

The data obtained are in contradiction with the established views on the influence of different stages of autoclave curing. Usually operators avoid speeding up the pressure increase, apprehending the appearance of temperature stress in the products.

The influence of temperature stresses during pressure increase is overestimated, and the factors decreasing this stress are not taken into consideration. These factors are steam condensation which takes place as the result of the fact that during pressure increase the temperature of specimens is lower than the steam temperature in the autoclave, and the exothermal reaction of hydration which leads to more rapid heating of the inner layers of the specimens than would occur if only heat conduction were operative. In the stage of steam-pressure decrease, temperature stresses occur, mainly owing to the fact that during decompression a temperature difference is created between the autoclave and specimens. As the result of heat inertia the specimens appear to be overheated, leading to intensive steam generation which creates additional stresses, particularly on the specimen surface.

It appears from the above that rate of pressure increase does not play a great role in the development of strength in products during autoclave curing, but instead, the duration of decrease of steam pressure does play an important part.

The influence of the intensity of steam pressure on concrete strength of nepheline cement was studied by Stakheyev in 1955–1957. The test results given in figure 4 show that during autoclave treatment of nepheline-cement concrete, the optimum pressure is 24 atm.

Variation of the time of curing at maximum pressure from 8 to 0 hr and increase of the steam pressure from 8 to 100 atm influenced the strength of specimens in different ways. On autoclaving at 8 to 15 atm and curing for 0 hr at maximum pressure, the minimum strength of the specimens was obtained. Increase of the curing time to 8 hr at these pressures increased the strength of the specimens.

TABLE 5. *Compressive strength of 1:4 nepheline-cement mortar 40 x 40 x 50 cm specimens autoclaved under different regimes. Maximum pressure 8 atm, mixing water 13 percent*

Autoclave regime	Compressive strength at 28 Days
Hours [a]	*kg/cm* ^{2}
3–5–1	67
1–5–3	83
1–3–5	112

[a] These numbers represent the time in hours during which the steam pressure was respectively increased, maintained at the maximum, and decreased.

Quite different results were obtained with specimens autoclaved at 50 and 100 atm. In this case, the specimens exposed to autoclaving for 0 hr at maximum pressure (peak autoclaving) had the highest strength.

These experiments have shown once more that the higher the pressure the shorter the process of autoclaving must be. The reason for the strength gain and its decrease with pressure increase from 8 to 100 atm ought to be found in change of composition and structure of the hydrated products.

FIGURE 4. *Influence of steam pressure on the strength of nepheline-cement concrete.*

(Ordinate: compressive strength, kg/cm². Abscissa: steam pressure, atm.)

Magnesium Silicates

Magnesium hydrosilicate synthesis is described in the literature to a considerable degree. A number of Soviet and foreign scientists have synthesized talc, antigorite, chrysotile, and some other magnesium hydrosilicates at high temperature and pressure. Magnesium hydrosilicate synthesis was accomplished by use of the individual oxides. But in all these large and generally interesting publications, attention was not given to the study of the technical characteristics of the products obtained. The majority of these works were carried out from the point of view of experimental mineralogy and petrography.

Our investigations on the preparation of artificial hydrosilicates are of applied character, and magnesium hydrosilicates capable of reacting with water under certain conditions have been used as initial raw material, instead of the individual oxides. This procedure has practical significance, since magnesium silicates are rather widely spread in nature (serpentine, olivine).

Magnesite, $MgCO_3$, is a valuable raw material for obtaining technical products of high quality (metallic Mg, fire-proof materials and others). In nature it is found more rarely than magnesium silicates.

The main task of our work is investigation of the conditions for obtaining magnesium hydrosilicates from natural minerals and study of the technical characteristics of the products obtained.

With this aim, at the chair of building materials of the Leningrad Building Institute, systematic work has been carried out since 1954 dealing with the study of binding and some other properties of different natural magnesium silicates (Bozhenov, Salnikova—1956).

Cementing properties of magnesium silicates have been studied in the USSR by: Medvedev—1933, Syromyatnikov—1934, Jung—1946, Budnikov and Berezhnoi—1949, Budnikov and Mchedlov-Petrosyan, Mchedlov-Petrosyan—1951, 1953.

Our work showed the possibility of widening the number of usable natural silicates containing magnesium. Minerals of different chemical composition and varied crystalline structure were investigated. Taking into consideration the fact that the genesis of magnesium-containing hydrosilicates is connected in the majority of cases with the action of water vapor and high temperatures, the method of autoclaving has been used.

Minerals were investigated at different degrees of water removal because of the fact that the loss of water at the time of heating sometimes caused alteration of the crystal lattice and the appearance of active phases.

The experiments showed that the majority of minerals set in rather a short time. (See table 6.) It should be noted that the setting time varied depending on the temperature of dehydration.

Serpentine olivine, chrysotile asbestos, clinochlore, garnierite, and hydroboracite were studied thoroughly. For determination of the temperatures of dehydration in minerals, the curves of loss in weight on heating up to 1,000 °C were obtained, based on the method of dynamic weighing using a torsion balance.

Instead of the widely used method of reading the heating curves, the method of stepped increase of temperature was worked out, namely: temperature increase (5 °C per minute) was stopped as soon as a decrease in weight was noted, and the

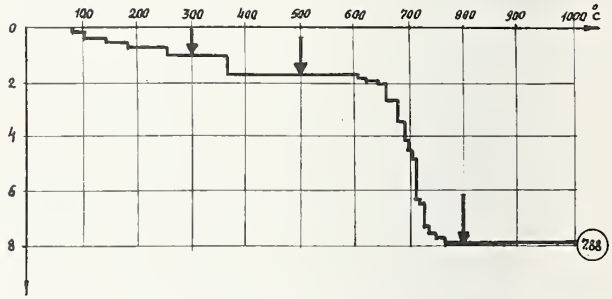

Figure 5. *Curve of dynamic weighing of serpentine olivine.* (Ordinate: weight loss, percent. Abscissa: temperature.)

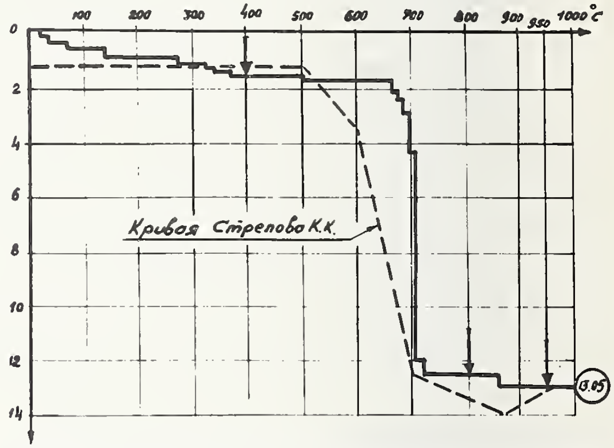

Figure 6. *Curves of dynamic weighing of chrysotile asbestos.* (Ordinate: weight loss, percent. Abscissa: temperature. Dotted curve, data of Strelov.)

Table 6. *Effect of temperature of dehydration on the subsequent setting times of water-mineral pastes*

No.	Mineral	Chemical formula	Temp. of dehydration	Setting time	
				Initial	Final
			°C	hr:min	hr:min
1	Vesuvianite	$3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	110	4:00	4:30
2	Vesuvianite	$3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	800	5:13	7:33
3	Tremolite	$2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$	110	6:10	7:30
4	Tremolite	$2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$	800	9:40	24:30
5	Actinolite	$2CaO \cdot 5(Mg,Fe)O \cdot 8SiO_2 \cdot H_2O$	110	4:53	6:30
6	Actinolite	$2CaO \cdot 5(Mg,Fe)O \cdot 8SiO_2 \cdot H_2O$	800	4:50	6:07
7	Chrysotile asbestos	$3MgO \cdot 2SiO_2 \cdot 2H_2O$	800	8:10	21:00
8	Chrysotile asbestos	$3MgO \cdot 2SiO_2 \cdot 2H_2O$	950	5:00	7:12
9	Serpentine olivine		110	7:50	20:40
10	Serpentine olivine		800	2:04	3:53
11	Talc	$3MgO \cdot 4SiO_2 \cdot H_2O$	110	(1)	(1)
12	Talc	$3MgO \cdot 4SiO_2 \cdot H_2O$	800	48:00	48:00
13	Clinochlore No. 1	$12MgO \cdot 2Al_2O_3 \cdot 7SiO_2 \cdot 10H_2O$	110	(3)	(3)
14	Clinochlore No. 1	$12MgO \cdot 2Al_2O_3 \cdot 7SiO_2 \cdot 10H_2O$	800	0:55	(1)
15	Clinochlore No. 2	$12MgO \cdot 2Al_2O_3 \cdot 7SiO_2 \cdot 10H_2O$	110	27:00	47:00
16	Clinochlore No. 2	$12MgO \cdot 2Al_2O_3 \cdot 7SiO_2 \cdot 10H_2O$	800	6:48	7:48
17	Garnierite [2]		110	(3)	(3)
18	Garnierite [2]		180	48:00	72:00
19	Phlogopite	$K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	800	(3)	(3)
20	Muscovite	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	800	10:00	23:00

[1] No setting during 72 hours.

[2] "Garnierite" is not a pure mineral.

[3] No setting during 48 hours.

Table 7. *Strengths of pressed specimens of water-mineral pastes after normal hardening*

No.	Mineral	Temp. of dehydration	Mixing water	Compressive strength				Bending strength		
				9 days	1 month	3 months	1 year	1 month	3 months	1 year
		°C	*Percent*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1	Chrysotile asbestos	800	9	6	7	14	17	3.3	3.7	4.6
2	Chrysotile asbestos	950	9	23	7	6.7	0	2.7	2.3	1.2
3	Serpentine olivine	800	7	6	18	18	20	4.8	5.1	6
4	Clinochlore	800	7	0	1.7	2.5	0	1.2	2.1	2.3
5	Garnierite	180	14	10.9	48	34	26	11.4	5.5	4.3
6	Hydroboracite	670	11	10	19	60	89	6.7	16.8	23.3
7	Hydroboracite	700	11	2	6.2	12	----------	2.3	3.7	----------

Table 8. *Strengths of pressed specimens of water-mineral pastes after autoclaving at 8 atm*

No.	Mineral	Temp. of dehydration	Compressive strength				Bending strength		
			Age of the specimens before autoclaving						
			7 days	28 days	3 months	1 year	28 days	3 months	1 year
		°C	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1	Chrysotile asbestos	800	108	126	102	90	55	38	38
2	Chrysotile asbestos	950	90	90	96	90	22	41	12
3	Serpentine olivine	800	154	138	132	126	49	45	42
4	Clinochlore	800	29	53	49	36	15.6	15.2	18.1
5	Garnierite	180	48.2	42	39	0	5.7	9.6	0
6	Hydroboracite	670	296	350	200	211	54	41	25
7	Hydroboracite	700	----------	192	87	----------	38	38	----------

specimen was cured under thermostatic conditioning until the weight was constant for 3 to 4 min. The temperature of the specimen was then again increased at the rate of 5 °C per minute until decrease of the weight of the specimen was again noted, and so on.

In figures 5 and 6 the curves obtained by this method of dynamic weighing are given. These curves have been used for establishing the temperatures for firing the specimens (in the figures they are marked with arrows).

It is clear from tables 7 and 8 that the strengths of the specimens cured in high-pressure steam exceed by many times the strengths of the specimens that were conventionally cured.

The investigations showed that the process of hardening of chrysotile asbestos and serpentine olivine occurred more intensely at higher temperatures.

These data show the possibility of the wider use of autoclaving for experimental mineralogy too, because by changing the steam-curing conditions one can judge the stability of investigated material.

The data obtained by thermal analysis (figs. 7, 8, 9, 10, 11) make it possible to form judgments about new formations. The higher the pressure of the steam in hydrothermal treatment the greater is the similarity between the hardened chrysotile-asbestos and serpentine-olivine pastes and the natural minerals. The data of petrographic analysis of hydrated samples of chrysotile asbestos and serpentine olivine provide evidence relative to the hydrated compounds formed in the process of hydrothermal curing.

Tests showed that the effectiveness of autoclaving of magnesium silicates increased with pressure increase.

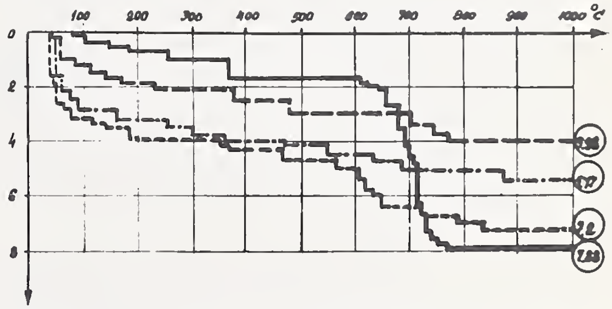

Figure 7. *Curves of dynamic weighing of serpentine olivine (temperature of dehydration, 950 °C).*

(Ordinate: weight loss, percent. Abscissa: temperature.)

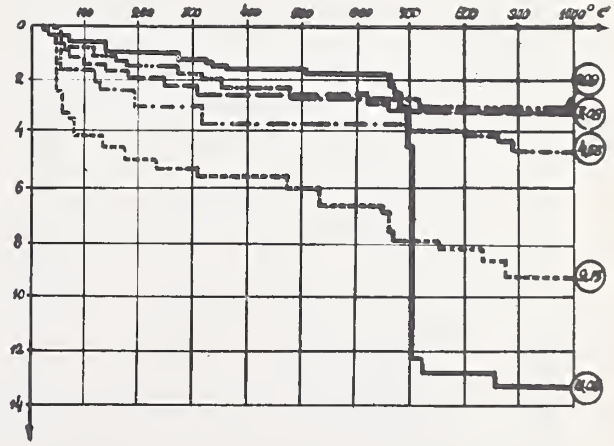

Figure 8. *Curves of dynamic weighing of chrysotile asbestos (temperature of dehydration, 950 °C).*

(Ordinate: weight loss, percent. Abscissa: temperature.)

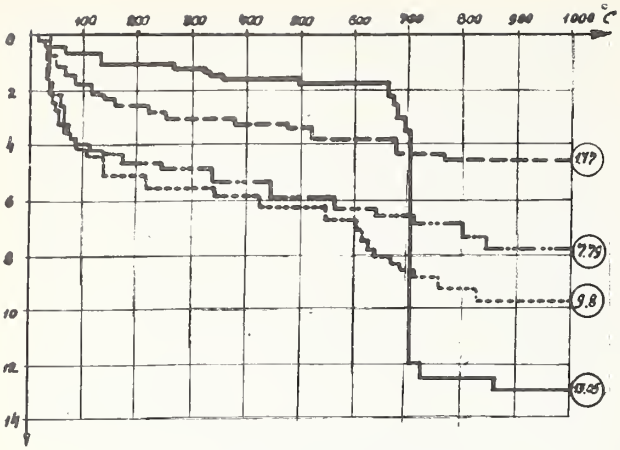

FIGURE 9. *Curves of dynamic weighing of chrysotile asbestos (temperature of dehydration, 800 °C).*
(Ordinate: weight loss, percent. Abscissa: temperature.)

The high mechanical strengths of dehydrated magnesium silicates, obtained on autoclaving, table 9, made it feasible to investigate their applicability as building materials.

Under laboratory conditions a new autoclaved material somewhat like asbestos cement was obtained wherein portland cement was entirely replaced by thermally cured (at 700 to 900 °C) nonclassified wastes of asbestos factories (Bozhenov and Salnikova—1958). Technical properties of the slabs obtained are given in table 10. A valuable property of the new material is its stability in aggressive environments and at high temperatures, which is of practical interest for special constructions.

TABLE 9. *Compressive strength of water-mineral pastes*

No.	Cementing material	Temp. of dehydration	Compressive strength at 9 days			
			Normal hardening	Autoclaved at		
				8 atm	15 atm	100 atm
		°C	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1	Serpentine olivine	800	0	154	147	239
2	Chrysotile asbestos.	800	29	108	86	154
3	Chrysotile asbestos.	950	23	208	238	287

TABLE 10. *Technical qualities of pressed slabs after autoclaving at 8 atm*

Material	Composition of mixture	Binding strength		Density	Water absorption
		1 day	1 year		
		kg/cm²	*kg/cm²*		*Percent*
1. Asbestos-magnesium slabs.[a]	85% of cementing material of fired wastes+15% of asbestos 1V c	234	310	1.69	16-24
2. Asbestos-cement slabs.[b]	85% of portland cement +15% of asbestos 1V c	305	310	1.96	16-24

[a] The slabs obtained on the basis of fired wastes with aggregate of asbestos are called "asbestos-magnesium."

[b] Asbestos-cement slabs were produced simultaneously with asbestos-magnesium slabs and under the same conditions.

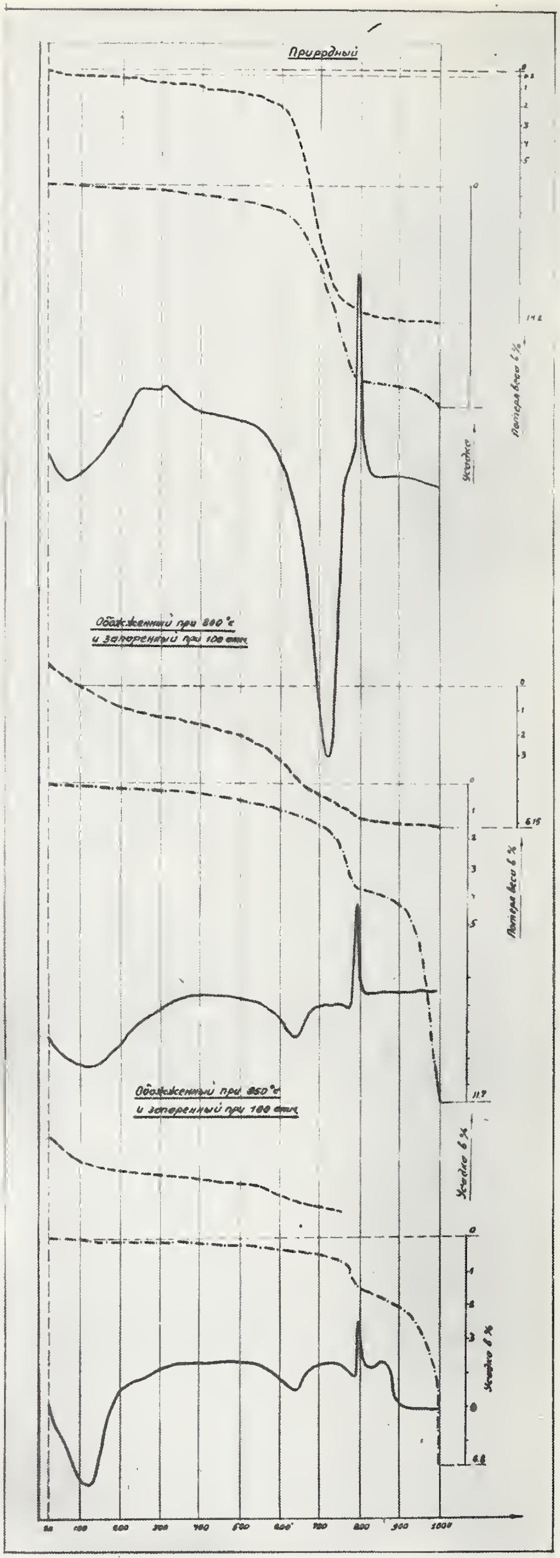

FIGURE 10. *Curves of complex thermal analysis of chrysotile asbestos.*

Abscissa: temperature, °C. Upper set of curves: untreated sample. Middle set: dehydrated at 800 °C and steam cured at 100 atm. Lower set: dehydrated at 960 °C and steam cured at 100 atm. Dashed curves, weight loss, percent; dot-and-dash curves, shrinkage, percent; solid curves, thermal effects.

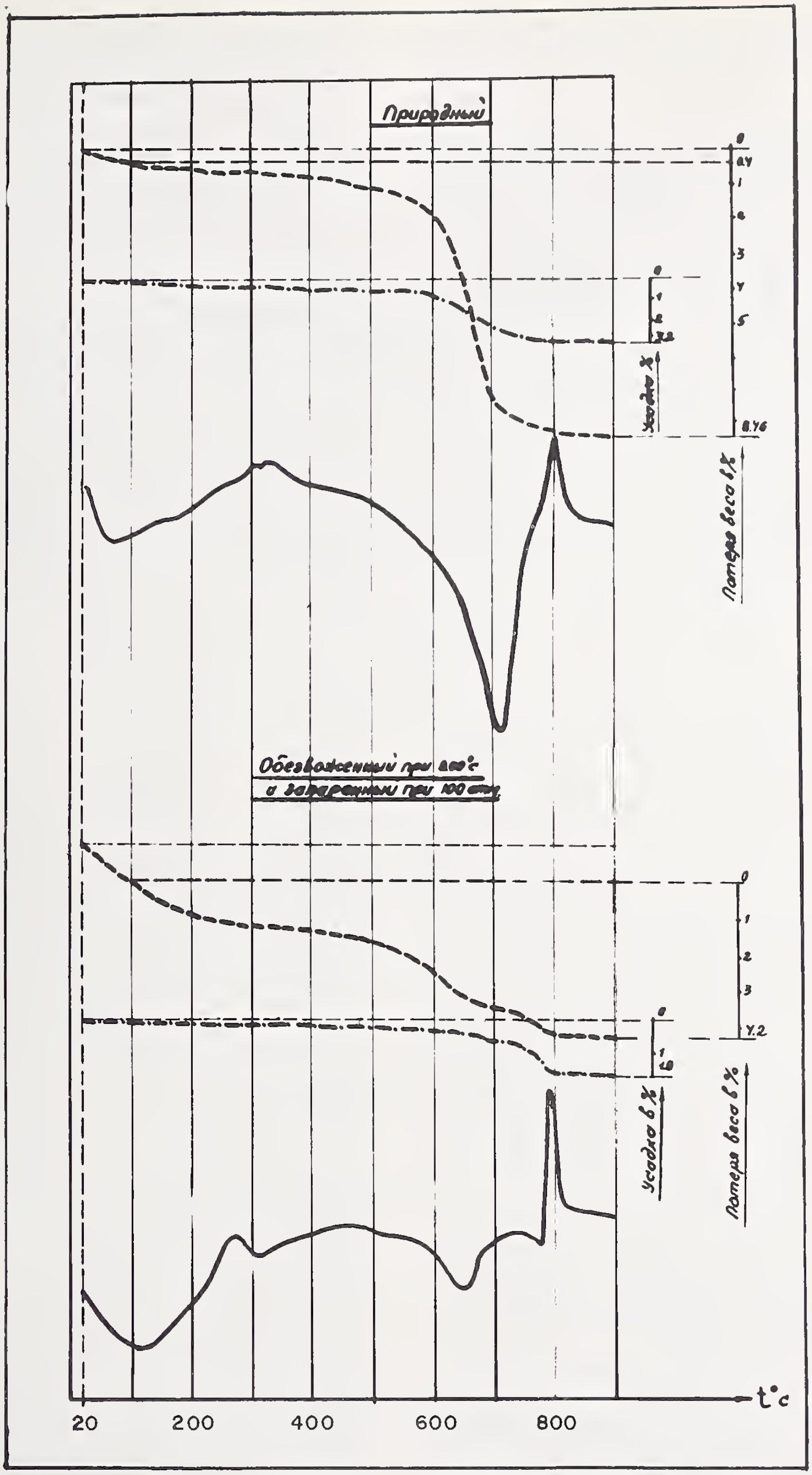

FIGURE 11. *Curves of complex thermal analysis of serpentine olivine.*

Abscissa: temperature, °C. Upper set of curves: untreated sample. Lower set: dehydrated at 800 °C and steam cured at 100 atm. Dashed curves, weight loss, percent; dot-and-dash curves, shrinkage, percent; solid curves, thermal effects.

Tests of specimens autoclaved at steam pressure of 200 atm (Rakitskaya—1959) showed compressive strengths increasing nearly 4 times as compared with the strengths of the specimens autoclaved at 10 atm.

In specimens produced from portland cement with 15 percent asbestos aggregate we observe strength decrease under conditions of pressure increase.

From the results of laboratory and pilot-plant investigations we can say that autoclaved materials of varied utility can be obtained, based on magnesium silicates.

Martin slags contain about 20 minerals: calcium silicates, magnesium silicates, periclase, and some other compounds. It was established that Martin slags can be used as cementing material in the production of autoclaved building products of dense and cellular structure.

The study of a great number of Martin slags showed that all of them were able to hydrate. Hydrothermal curing has great influence on slag hardening. Under normal conditions, hardening of slags proceeds slowly; upon autoclave treatment the strength of specimens increases 50 to 60 times.

For example, specimens tested after autoclaving at 8 atm attained strengths as follows:

in paste —270 kg/cm^2
in 1:1 mortar—575 kg/cm^2
in 1:3 mortar—340 kg/cm^2 in compression and
75 kg/cm^2 in bending.

The strength of some slags reached 700 kg/cm^2 in one year.

Side by side with high cementing properties of slags, some slags were found to have the capability of bloating and cracking in the process of autoclave treatment. This behavior is probably connected with the presence of periclase, MgO.

The results of work carried out over several years allows us to state that the use of high-pressure steam makes it possible to obtain building materials with interesting qualities, on the basis of new raw materials. Great prospects are open for the efficient use of natural resources and the complete use of raw minerals.

Autoclave Curing of Cementing Materials with High-Pressure Steam (8 to 200 atm)

The study of the chemical processes of hardening of portland cement clinker under normal and hydrothermal conditions enabled us to conclude that at high temperature and pressure the reactions of minerals and water occur more intensively than under mormal conditions of temperature and humidity, and that the products of autoclave hardening have their own specific character.

Experimental work and theoretical considerations in the field of hydrothermal curing of cement, concrete, and lime-sand mixtures led to the suggestion that since autoclave treatment of the cited materials accelerates the hardening processes by as much as 30 times even at 8 atm (174 °C), more intensive curing at high steam pressure might be even more effective. Unfortunately, before 1950 this question had undergone neither experimental nor plant-scale study, and there were no pertinent data in the literature.

The theoretical foundations for physicochemical processes taking place under hydrothermal conditions were only partly studied, and dealt with natural calcium hydro-compounds and the products of hydrosilicate synthesis in the system CaO-SiO_2-H_2O.

It is impossible not to mark the fact that with the use of the method of artificial hydrothermal synthesis of hydrated minerals the development of experimental mineralogy and petrography, and the science of crystallochemistry of silicates as well, have considerably outstripped the practical application of hydrothermal curing.

For the first time, in 1950, we began an investigation (P. I. Bozhenov and G. F. Suvorova, 1955) of the influence of high-pressure steam (from 8 to 200 atm, in the temperature range from 174 to 364 °C) on cements of different mineralogical compositions.

The aim of the investigation was the study of the dynamics of reaction of cement and its physicochemical properties, and investigation of new formations of hydrated cements under a wide range of pressures which would make it possible to learn more profoundly the technology of building products fabricated by autoclaving.

Before describing the results of the work, it is necessary to remark that during 1950 to 1960 great improvements were achieved in theoretical work and in the practical perfection of the technological production of autoclaved building materials.

All said above leads to the conclusion that autoclave curing of building materials is one of the most effective and progressive technological methods in the building materials industry, as is generally recognized.

The first experiments had for their object the establishment of the general requirements for autoclave hardening of cements at high pressures and temperatures. It was also desired to investigate the composition and structure of the new formations in the products of cement hardening, after autoclave curing.

Cement specimens of different mineralogical composition were exposed to autoclaving. Their compositions are given in table 11.

For providing the necessary pressure, a laboratory autoclave-bomb was made, with capacity of 500 cm^3 and for a working pressure of 300 atm. Specimens 3 × 3 × 3 cm were prepared of neat cement paste of plastic consistency and of 1:3 plastic mortars.

Table 11. *The influence of autoclaving on the strength of cement paste and mortars of different mineralogical composition*

	Cement No.	A C		5 C		4 C		3 C		2 C		B C		C	
Minerological composition of cement in %.	C_3S	59		57		47.6		47.2		33.3		28		20.5	
	C_2S	18		18		26.0		29.4		37.7		46		54.7	
	C_3A	4		7.6		10.7		6.9		12.7		5		15.1	
	C_4AF	15		14.2		10.9		15.2		14		17		1.2	
Regime of hardening		*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%
		Cement paste (1:0)													
Normal hardening during 28 days		965	100	1450	100	1165	100	1175	100	1260	100	845	100	835	100
Autoclaving at	8 atm	520	54	1060	73	760	65	530	45	620	49	520	73	440	53
	15 atm	510	53	680	47	560	48	570	49	580	46	770	91	232	28
	25 atm	190	19	210	14	205	18	126	11	190	15	480	57	156	19
	50 atm	180	18	140	9	87	7.5	75	6	106	8	300	35	80	9
	100 atm	105	11	143	10	77	7	53	5	120	10	105	12	83	10
	200 atm	70	7	80	6	41	3	43	4	45	4	65	8	67	8
		Cement mortar (1:3)													
Normal hardening during 28 days		348	100	192	100	140	100	111	100	370	100	230	100	166	100
Autoclaving at	8 atm	313	90	236	123	175	125	225	203	380	103	425	185	235	142
	15 atm	430	124	315	164	185	132	240	216	396	107	460	200	290	175
	25 atm	600	172	312	162	226	162	220	198	430	116	365	159	227	137
	50 atm	330	95	175	91	120	86	132	119	242	66	220	96	205	123
	100 atm	165	48	135	70	113	81	134	121	214	58	193	84	179	118
	200 atm	175	22	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	145	88

Autoclave curing of the specimens was carried out at the following pressures and temperatures:

8 atm—174 °C
15 atm—200 °C
25 atm—225 °C
50 atm—365 °C
100 atm—310 °C
200 atm—364 °C.

The rate of temperature increase and decrease in the autoclave corresponded to 1.2 degrees per minute. Upon reaching the chosen value, the pressure was kept constant for 6 hr. The compressive strength of the specimens was determined just after autoclaving, and after rather long times of normal storage (up to 1 year) as well.

The results of tests of the compressive strength of specimens autoclaved at pressures of 8 to 200 atm are given in table 11.

In the investigated range of pressures, the strength of the specimens achieved its maximum for cement paste at pressures of 8 to 15 atm and for cement mortars at pressures of 15 to 25 atm. On intensification of hydrothermal curing (to 200 atm) a tendency toward reduction of strength was observed.

Hydration of cements with high contents of active minerals (C_3S and C_3A) occurs rather rapidly even when autoclaving at the lower pressures (8 to 10 atm), but cementing materials with high contents of slowly hardening components such as C_2S require more intensive autoclaving (up to 15 atm).[2]

High-pressure steam has greater influence on cement mortar (1:3).

The use of steam at the pressure of 15 to 20 atm for all the cements increased the compressive strength of specimens by 2 to 3 times as compared with the strength of the specimens at the age of 28 days under conditions of normal hardening, and by 30 to 50 percent in comparison with autoclaving at 8 atm. Belite cement, particularly, was greatly affected by autoclaving.

On autoclave treatment, silica sand as an aggregate plays an active part in the development of physicochemical properties, depending on autoclaving conditions.

The latest investigations showed that the long regime adopted for the first experiments was apparently inexpedient, particularly when using high-pressure steam.

Numerous experiments with different initial materials showed that when using high-pressure steam it is necessary to reduce the general technological cycle of hydrothermal curing from the 12 to 14 hr regime at 8 atm to a 4 to 8 hr regime at 16 to 25 atm (fig. 12).

On the basis of a great number of experiments, it appeared possible to use a new technological method of treatment—autoclaving of materials at high pressure without curing. This was called "peak regime" (increasing+decreasing).

Figure 13 presents the results of one of the experimental series on the determination of peak regime influence on the hardening of cement mortar of the composition 1:3, of plastic consistency.

The analysis of the given material confirms the great advantage of using high-pressure steam (16 to 20 atm) in comparison with autoclaving at 8 atm, because of the possibility of reducing the duration of the general technological cycle of curing of building materials by one-half while simultaneously increasing the qualitative indices.

The experiments show that the relative effect of autoclaving is higher for belite cements than

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[2] The autoclaving of neat cement paste (1:0) is considered here.

for cements with high contents of C_3S and C_3A (see table 11). This conclusion was proved with nepheline cement, as its mineralogical composition consists mainly of $2CaO \cdot SiO_2$ (80 to 85 percent) (see fig. 14).

Proved possibilities (on the basis of tests with portland cement) of sharp reduction of the autoclaving regime by increase of pressure to 15 to 25 atm became a basis for conducting investigations on the behavior of lime-sand mortar, using high-pressure steam.

In figure 15 are presented the results of tests obtained by Petrenko (1952 to 1956) during his study of the influence of steam pressure on the strength of lime-sand mortars prepared with sands of different grain fineness. From figure 15 it is clear that the maximum strength corresponds to a pressure of 15 to 25 atm. Increase of the total surface of the quartz sand grains increases the strength. In order to learn the influence of lime, special tests were carried out. Their results are given in table 12.

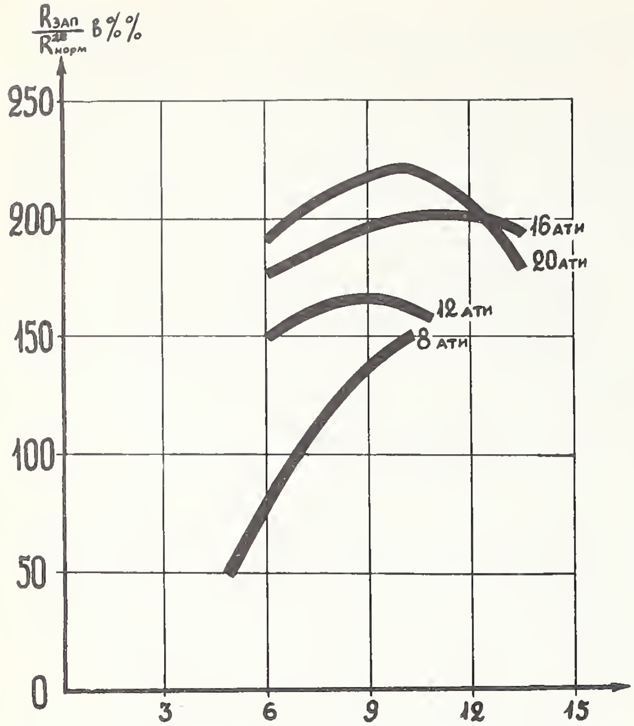
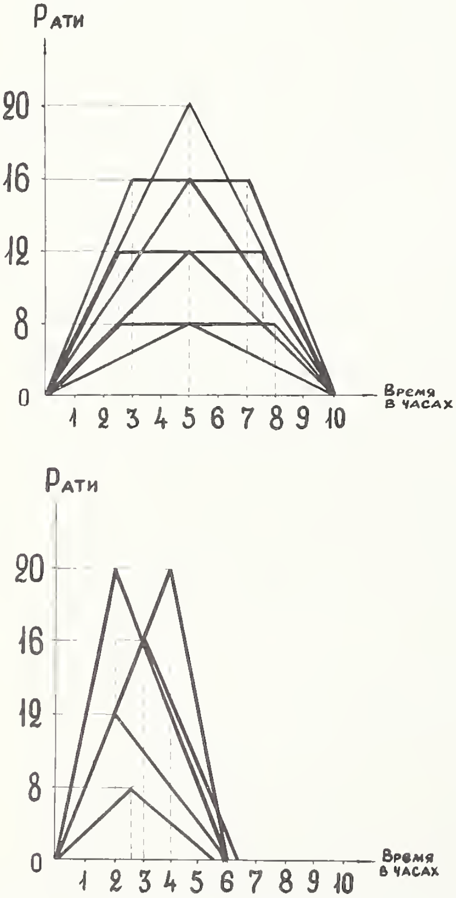


FIGURE 12. *Strength dependence of cement mortars and concrete on time of autoclaving.*

(Ordinate: ratio of compressive strength of steam-cured to normally hardened specimens, percent.)

(Abscissa: autoclaving period, hours. Pressures indicated in atm.)



P	Pressure Regime				Compressive Strength	
	Increase	Hold	Decrease	Total		
	hr	*hr*	*hr*	*hr*	*kg/cm²*	%[a]
8	2.5 5	2.5 0	2 5	10	286 274	159 152
12	2.5 5	5 0	2.5 5	10	296 284	165 158
16	3 5	4 0	3 5	10	360 358	200 200
20	5	0	5	10	403	216

[a] Relative to 28-day strength of 180 kg/cm².

P	Pressure Regime				Compressive Strength	
	Increase	Hold	Decrease	Total		
	hr	*hr*	*hr*	*hr*	*kg/cm²*	%[a]
8	2.5	0	3	5.5	110	60
12	2	0	4	6	274	152
16	3	0	3.5	6.5	319	178
20	2	0	4	6	337	187
	4	0	2	6	359	200

[a] Relative to 28-day strength of 180 kg/cm².

FIGURE 13. *"Peak-regime" influence on hardening of cement mortar of the composition 1:3 of plastic consistency.*

(Ordinate: steam pressure, atm. Abscissa: autoclaving period, hr.)

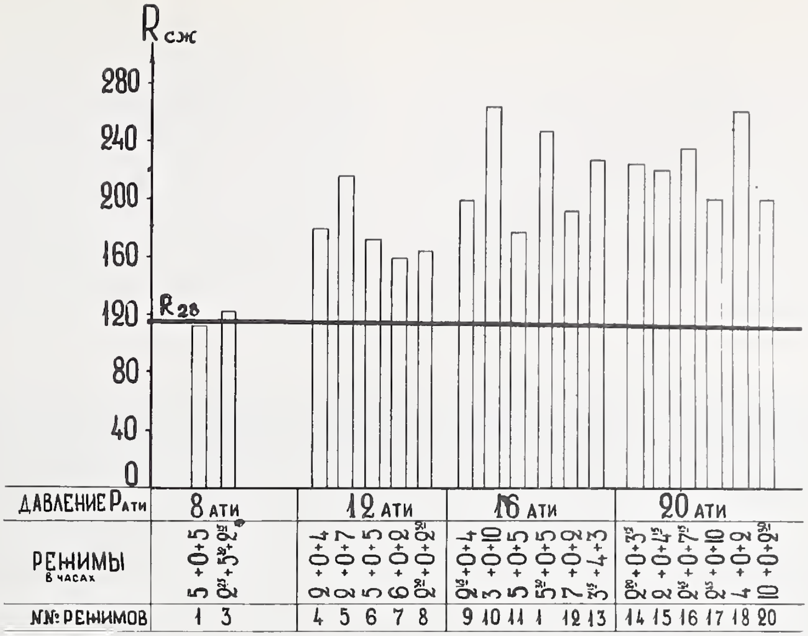


FIGURE 14. *Influence of different regimes of autoclaving on strength of nepheline-cement mortars.*

(Ordinate: compressive strength, kg/cm². Data below graph indicate pressure in atm, regime in hr, and number of regime, respectively.)

TABLE 12. *The influence of high-pressure steam curing on the strength of lime-sand mixes*

Composition of mixture lime-sand, %	Compressive strength in kg/cm², pressure at (atm)									
	8	10	12	14	16	19	22	25	40	100
10:90	350	355	**368**	364	360	363	331	268	214	175
15:85	321	339	323	**366**	327	321	298	305	286	154
25:75	459	656	580	691	750	828	730	750	698	493
30:70	320	491	519	780	713	807	850	**934**	885	531

From table 12 it is clear that the optimum pressure value changes, depending on the mixture composition.

With increase of the lime content in mixtures, the maximum value of strength moves in the direction of higher pressures, up to 25 atm inclusive. Tests carried out confirmed that for lime-sand mixtures, too, it is necessary to reduce the duration of autoclaving with increase of the steam pressure in the autoclave.

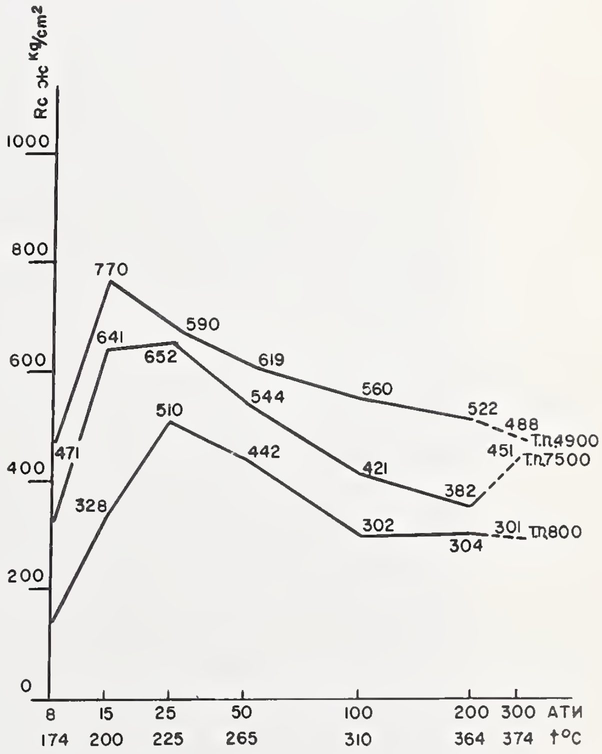


FIGURE 15. *Influence of steam pressure on the strength of lime-sand mortars.*

(Ordinate: compressive strength, kg/cm². Abscissa: steam pressure, atm, and temperature. Specific surface of sand, cm²/g, is indicated at right of curves.)

Regularities, proved during the investigations, in the change of the compressive strength of cement and lime-sand materials depending on the autoclaving regime, led the authors to study the dynamics of new formations in dependence on the mineralogical composition of the initial materials and the autoclaving regime by means of differential thermal analysis, the method of dynamic weighing, petrography, X-ray analysis, and some other methods of investigation.

The thermographs of cements hydrated at different pressures are given in figures 16 and 17.

Comparative analysis of thermal effects indicated by the heating curves showed that during autoclave curing new products of hydration are developed, quite different from the products of normal hardening in composition and structure.

Endothermic effects observed in the intervals of 100 to 140 °C, 200 to 250 °C, 400 to 450 °C are characteristic of the loss of free water and the

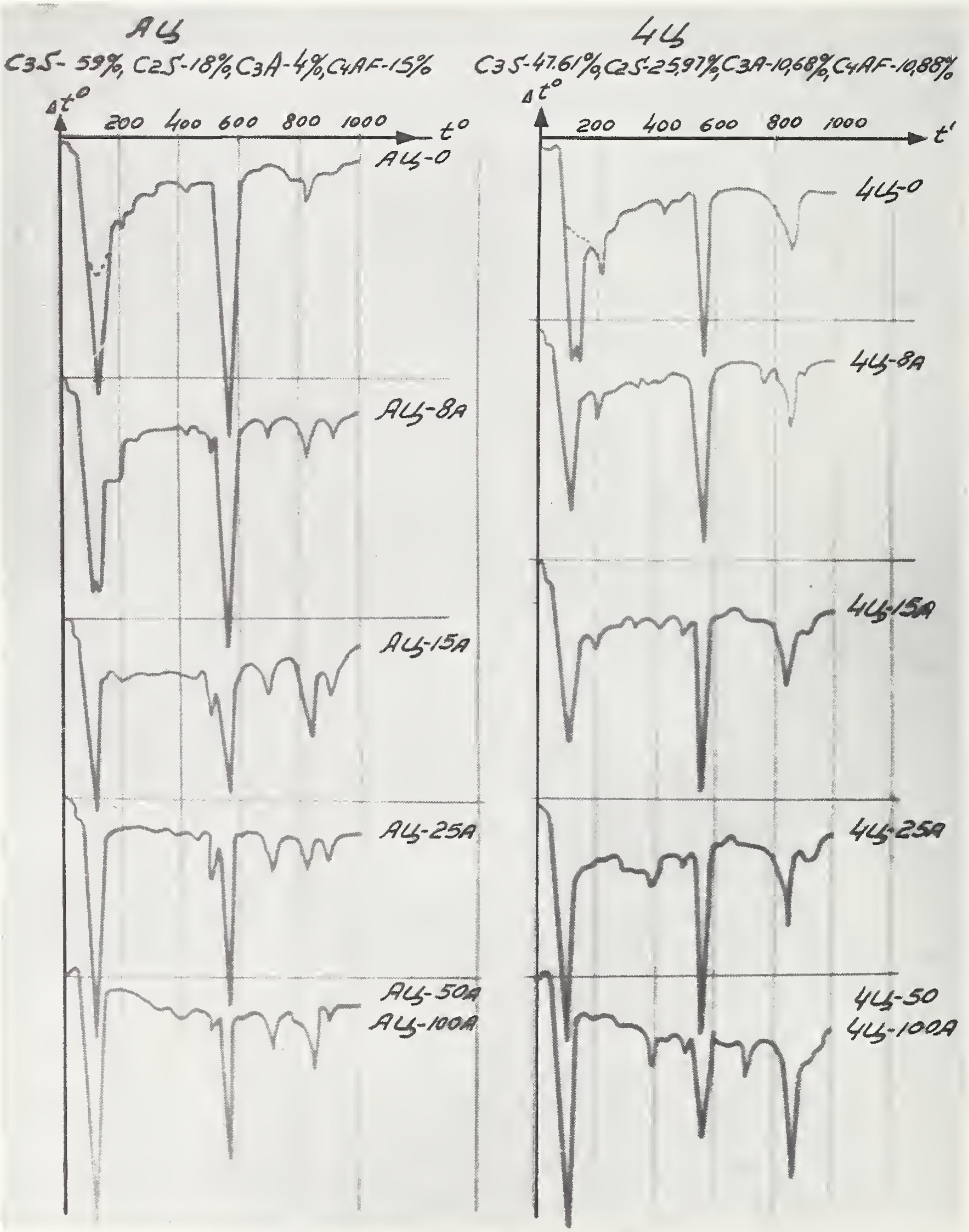


FIGURE 16. *DTA curves of cement paste (1:0) after autoclaving at 8 to 100 atm.*

Left column: cement AC; right column: cement 4C. Top curves: cement hardened under normal conditions; other curves: after autoclaving at pressures indicated.

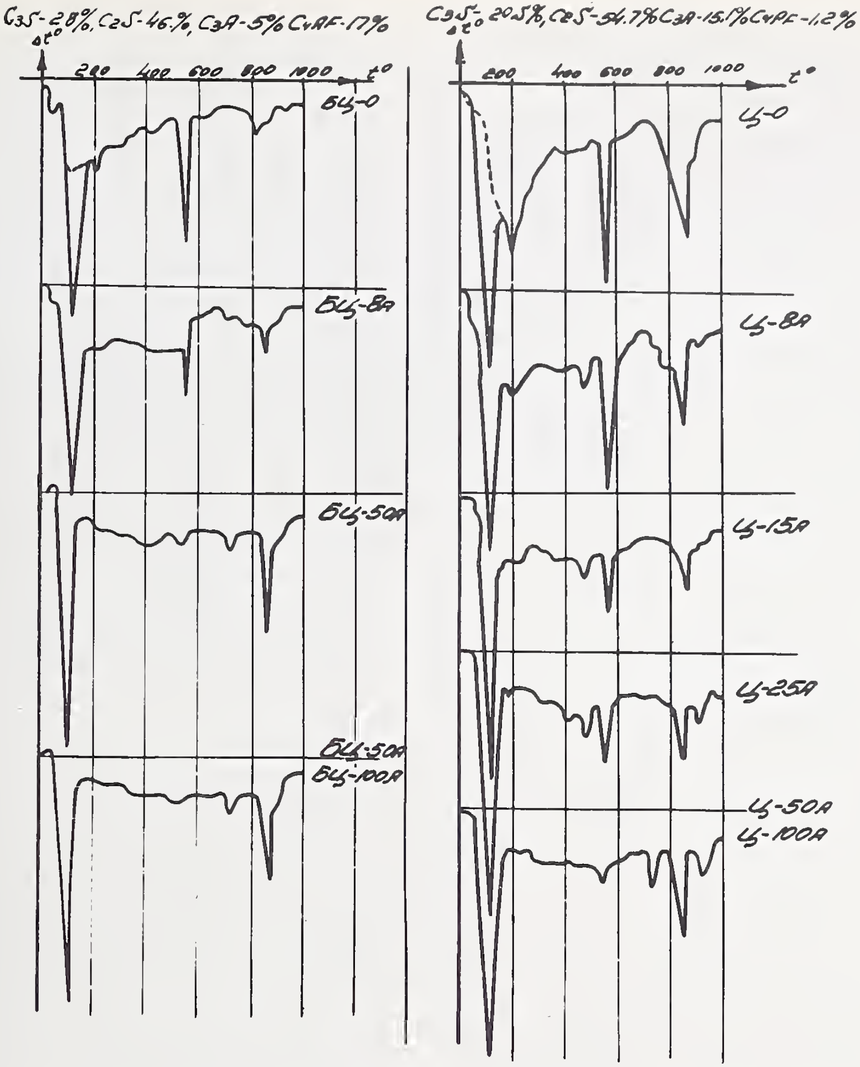


FIGURE 17. *DTA curves of cement paste (1:0) after autoclaving at 8 to 100 atm.*

Left column: cement BC; right column: cement C. Top curves: cement hardened under normal conditions; other curves: after autoclaving at pressures indicated.

evaporation of capillary moisture which exists in gel products of cement hardening.

In all the cases of pressure increase, gradual decrease and even disappearance of the endothermic effect at 550 to 580 °C, characteristic of the decomposition of $Ca(OH)_2$, was observed, showing the combination of lime in new products of hydration.

Clearly expressed endothermic drops in the intervals of 620 to 740 °C and 800 to 900 °C characterize crystalline structures of calcium hydrosilicates of varied composition appearing under conditions of high pressure and temperature on one hand and decarbonation of $CaCO_3$ (second effect) on the other hand.

The investigation of the products of cement hydration by the method of dynamic weighing in the process of heating up to 1,000 °C confirmed that with pressure increase in autoclave treatment new products of hydration are formed (fig. 18).

With pressure increase, gradual decrease of free and weakly-bound water was observed, as characterized by the loss of moisture in the interval 100 to 400 ° C. Gradual diminishing of the content of $Ca(OH)_2$ was confirmed also, as by the DTA curves.

Increase of the hydrated products which lose water in the narrow temperature interval 640 to 720 °C was observed.

Comparing the dehydration curves of the investigated cements with those for nepheline slurry, hydrated for a year, and for a sand-lime mixture autoclaved at 15 atm, one can see that in these cases new formations have similar composition not depending on the initial materials.

Petrographic investigation of specimens of normal and autoclave hardening confirmed the increase of the degree of hydration and cement crystallization with increase of pressure. So we can confirm that densification of the gel products

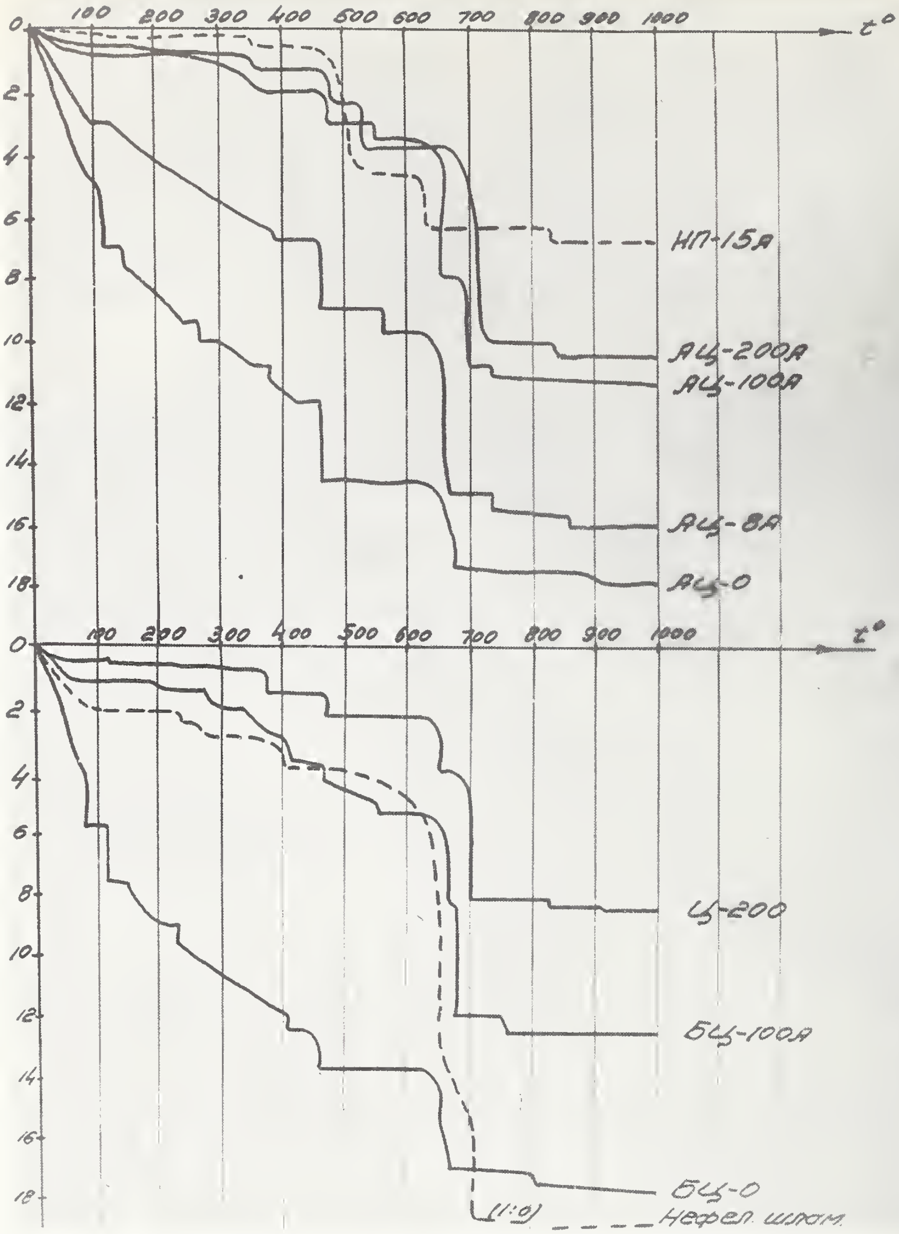


FIGURE 18. *Curves of dynamic weighing of cement-paste (AC, BC, C).*
(Ordinate: weight loss, percent. Abscissa, temperature, °C.) Curves, top to bottom:
lime-sand mixture, 15 atm.

AC, 200 atm.
AC, 100 atm.
AC, 8 atm.
AC, hardened under normal conditions
C, 200 atm.
BC, 100 atm.
BC, hardened under normal conditions
nepheline slurry

of hardening provides firmer binding, that, on the contrary, increased crystallization at high pressure promotes a decrease of the compressive strength of hardened cement paste owing to the formation of a coarsely crystalline modification, of fragile structure.

The results obtained permit the assumption (according to Sheykin—1944) that in hardening cement, the most rational proportions of gel and crystalline components are those that give the optimum value of mechanical strength. Predominance of one phase over the other reduces the physicochemical properties of the hardened cement paste. Therefore, the optimum regime and intensity of hydrothermal curing depend on the mineralogical composition of the cement, which in its turn is connected with the different rates of hydration of different clinker minerals.

Thermographic investigations carried out provide some material for explaining the process of interaction of CaO and SiO_2 in commercial lime-sand mortars. In figure 19 is given the thermogram (curve I) ($CaO:SiO_2=1:1$) of the mortar. Before the test, quick lime was hydrated to lime hydrate. The thermogram shows the existence of three main substances in the composition of the initial mortar: $Ca(OH)_2$, by the endothermal effect of dehydration at 500 to 550 °C; SiO_2, by the polymorphous conversion of α-quartz at 573 °C; and $CaCO_3$, for which dissociation begins at 780 °C and ends at 920 °C.

On treatment of mortars having the ratios $CaO:SiO_2=1:10$, 1:3, and 1:1 (curves II, III, IV) in the autoclave at a pressure of 16 atm for 8 hr, one observes the following changes of thermal effects (fig. 19):

1. Increase of the products of hardening within the temperature interval of dehydration at 120 to 400 °C. The gel structural component, formed by submicroscopical new formation, loses so-called "zeolitic water," over this range of temperature.
2. Increased endothermic effect at 450 C°, which in this case refers to the dehydration of $Mg(OH)_2$.
3. The endothermic effect representing the polymorphous conversion of α-quartz (573 °C) decreases with increase of basicity of the composition because of the fact that in lime-rich mortar a great amount of SiO_2 interacts with lime (in fig. 19, compare curves I and IV).
4. In the temperature interval 680 to 750 °C, the endothermic effect is interpreted as dehydration of calcium hydrosilicate, possibly of crystalline structure. Recrystallization of these dewatered hydrates is followed by sharp exothermic reaction in the range of 800 to 850 °C, which is so pronounced that it covers completely the endothermic effect of $CaCO_3$ dissociation, occurring at the same temperature interval, and possibly accelerates the latter process.

On the thermograms one notices the increase of the area representing recrystallization with the increase of new formations.

The following series of curves (fig. 20) reflects the influence of the intensity of hydrothermal curing on lime-sand mortars. Up to 25 atm (225 °C) one notes a considerable gel phase which on the curves is characterized by a wide area of endothermic effect at 100 to 400 °C.

If the autoclave treatment is carried out at temperatures higher than 225 °C, this effect on the heating curves is absent, implying the absence of a gel phase.

As in the preceding series of tests, the endothermic effect at 573 °C shows the phase conversion of α-quartz.

At the temperature of 620 °C, the removal of bound water from calcium hydrosilicates begins.

The dehydration reaction is completed at 680 to 740 °C. As shown, not only the quantity but also the composition of new formations depend on the autoclave curing regime.

The endothermic effect of calcium hydrosilicate dehydration is, in all cases, followed by an intense exothermic reaction beginning at 800 °C and ending at 840 to 850 °C. This effect may be explained by phase conversion of the dehydrated part of the calcium hydrosilicate.

One can judge the irreversibility of this reaction by the repeated thermogram (fig. 21), which showed no effects except the polymorphous conversion of quartz.

The results of thermal analysis of lime-sand mortars, prepared with sands of different specific surfaces showed no essential qualitative differences in new formations.

On hydrothermal curing, the processes of hydrosilicate formation are of complicated character,

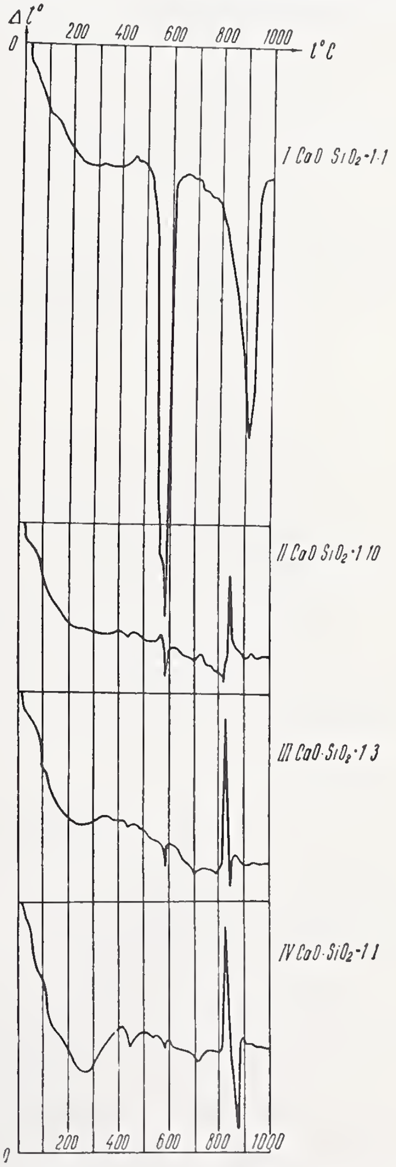


FIGURE 19. *DTA curves of lime-sand mortars autoclaved at 16 atm. for 8 hours. (Curve I, before autoclaving)*

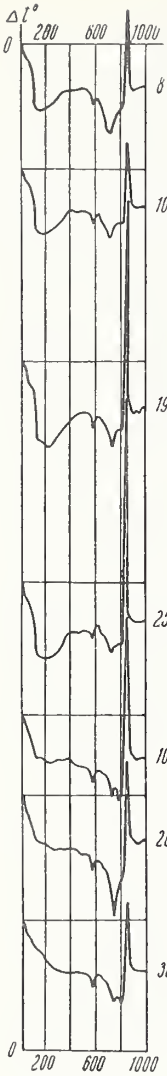


FIGURE 20. *DTA curves of lime-sand mortars autoclaved at 8 to 300 atm.*
(Figures at right give pressure in atm. and time in hr.)

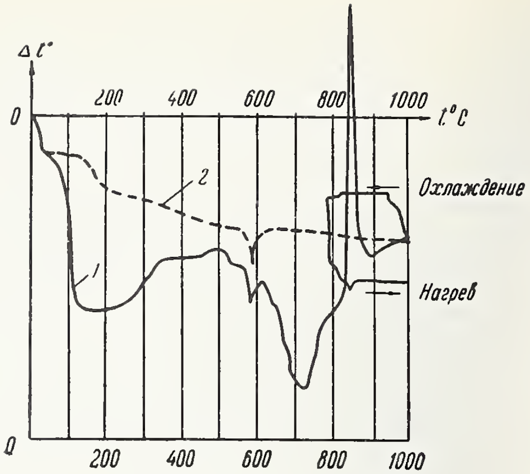


FIGURE 21. *No. 1—The first thermogram.*
No. 2—The second thermogram.

and combinations formed with increase of curing time or temperature are able to change the basicity and the quantity of structurally-bound water.

The results of chemical analysis given in table 13, show that with increase of steam pressure the quantity of bound CaO is nearly constant, and the content of soluble SiO_2 increases considerably, i.e., the quantity of less-basic hydrosilicates increases owing to interaction of previously formed new formations with silica.

Summarizing the investigations carried out we can draw the following conclusions:

1. In the investigated range of autoclaved lime-sand mortars (8 to 300 atm), complete binding of lime with the silica of the sand occurs. The absence of the endothermic effect of $Ca(OH)_2$ dehydration at 550 °C points to this conclusion.
2. New formations—hydrosilicates of different composition—interact with quartz, forming less-basic hydrosilicates when the pressure increases or the autoclave curing lengthens.
3. The strength of lime-sand brick depends on the structure and quantity of new formations and the interrelation of the gel and crystalline phases. Low-temperature curing (10 atm) leads to predominantly gel-like hydrosilicates, while curing at

TABLE 13. *Data of chemical analysis of autoclave-cured samples*

Composition of mortar, lime: sand	Fineness of mortar grinding, cm²/g	Pressure-time atm–hr	Free CaO	CaO found	Insoluble SiO_2	Soluble SiO_2	Soluble silica relative to dried mortar	Hygroscopic moisture	Bound H_2O+CO_2
				%	%	%	%	%	%
1:3	7500	8–8	None	16.46	50.97	15.90	20.80	1.68	6.62
		10–3	None	17.52	56.01	14.16	17.65	2.62	7.05
		19–3	None	17.52	51.48	19.06	23.60	1.48	6.75
		25–3	None	17.38	51.05	18.93	23.60	2.52	5.90
		100–0	None	17.86	49.74	23.61	28.15	1.12	3.79
		200–0	None	18.30	51.16	19.90	24.80	0.21	6.02
		300–0	None	18.24	50.29	22.86	27.40	none	4.13
1:3	5200	8–8	None	18.13	51.32	15.95	20.45	1.65	8.25
		12–3	None	17.93	50.34	17.16	21.86	1.83	7.08
		12–6	None	17.66	48.82	17.70	22.20	2.54	7.10
		12–24	None	17.04	49.16	20.45	25.35	2.58	6.04

50 to 200 atm leads predominantly to hydrosilicates with crystalline structure. The maximum strength requires rational proportions of both phases.

4. The data obtained confirm the assumption that by choosing the optimum regime of autoclaving it is possible to obtain products with high strength, i.e., there is a possibility of controlling the process of mineral formation.

5. On the basis of the investigations carried out it may be proved that use of high-pressure steam in the manufacture of silicate products allows one to shorten the autoclaving cycle considerably. Consequently, the autoclave turnover will increase, and the production of plants making building products and units will increase, together with simultaneous improvement of the quality of the product.

General Conclusions

1. Autoclave treatment, by means of high-pressure steam, of products based on various cementing materials is one of the most effective technological methods for considerably accelerating the hardening.

2. The optimum steam pressure in the autoclave depends on the mineralogical composition of the cementing materials. Cements with high contents of active components (C_3S, C_3A) autoclaved at the pressure of 16 atm require a sharp reduction of the curing regime, because at this pressure the process of hardening of such cementing materials achieves the stable state more rapidly.

Cementing materials with high contents of C_2S and C_4AF, and lime-sand mortar, need more intensive autoclaving in the range of 16 to 25 atm, with reduced regime of curing.

3. In all cases of production of building products at high pressure (15 to 25 atm), it is necessary to reduce the duration of the general cycle of autoclave curing at 8 atm from the 12 to 14 hr employed to 4 to 8 hr.

4. The analysis of products of autoclave hardening of cementing materials shows that for low-temperature curing (8 to 12 atm) the gel structure prevails in the end-product; for high-temperature curing (25 to 200 atm), hydrocompounds of crystalline structure prevail.

5. For obtaining materials with optimum qualities it is necessary to achieve the most rational proportion between the gel and crystalline phases in the end product.

6. By changing the regime of autoclaving it is possible to control the process of the formation of minerals, and thus to obtain products with the necessary structural properties.

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Paper III–S13. Concerning the Hydration Products of C_3S and β–C_2S*

H. G. Kurczyk and H. E. Schwiete

Synopsis

The calcium silicates $3CaO{\cdot}SiO_2$ and β-$2CaO{\cdot}SiO_2$ undergo set, when mixed with small quantities of water (w/c—0.1 to 0.5), in a manner similar to portland cement. This stiffening process is accompanied by the formation of a hydrous calcium silicate. This product of hydrolysis and hydration has a variable chemical composition, and was earlier designated in cement literature as "gel" or as "the gel phase." Electron microscope studies have shown conclusively that this calcium hydrosilicate is crystalline. It crystallizes in the form of needles. The crystallites have an average length of 5000 A. Dynamic differential calorimetry and quantitative X-ray analysis have permitted the determination of the composition or $CaO{:}SiO_2$ ratio of this phase as 1.8 to 1.9.

Electron diffraction diagrams show that the hydration product of $3CaO{\cdot}SiO_2$ and β-$2CaO{\cdot}SiO_2$ is morphologically and structurally similar to the mineral tobermorite, $Ca_5Si_6O_{18}H_2{\cdot}4H_2O$. It is therefore designated as the "tobermorite-like phase." Further fine structure studies by means of electron beams and X-rays have yielded the elementary cell of the tobermorite-like phase.

The lattice constants are: $a_0=11.2\pm0.3$ A
$b_0=7.32\pm0.07$ A
$c_0=27$–28 A
$\alpha=\beta=\gamma=90°$

The crystalline lattice is strongly distorted. The tobermorite-like phase has the same structural elements as tobermorite. It differs from the latter only in that between the layer packets of tobermorite additional Ca^{++}- and OH^--ions are deposited. The exact positions of these ions could not be determined. However, with the results of the investigation as a basis, a hypothetical structure formula could be set up for the tobermorite-like phase:

$$Ca^x[Ca_4Si_6O_{16}(OH)_2][Ca^x(OH)_2]_n$$

$n=5$–7. The calcium atoms with unknown lattice coordination are designated by x.

Résumé

Les silicates de calcium, $3CaO{\cdot}SiO_2$ et β-$2CaO{\cdot}SiO_2$, subissent le phénomène de prise quand on les mélange à de petites quantités d'eau (e/c–0.1 à 0.5), d'une façon comparable au ciment portland. Cette réaction de durcissement s'accompagne de la formation d'un silicate de calcium hydraté. Ce produit d'hydrolyse et d'hydratation a une composition chimique variable, et on le trouve désigné précédemment dans la littérature du ciment sous le nom de "gel" ou "phase de gel". Des études au microscope électronique ont révélé d'une manière concluante que cet hydro-silicate de calcium est cristallin. Il se cristallise sous forme d'aiguilles. Les cristaux sont de 5000 A de long en moyenne. La calorimétrie dynamique différentielle et l'analyse quantitative des rayons X ont permis de déterminer que la composition ou le rapport $CaO{:}SiO_2$ de cette phase est de 1.8 à 1.9.

Les diagrammes de diffraction électronique indiquent que le produit d'hydratation de $3CaO{\cdot}SiO_2$ et β-$2CaO{\cdot}SiO_2$ est par sa morphologie et sa structure semblable au tobermorite minéral $Ca_5Si_6O_{18}H_2{\cdot}4H_2O$. On le désigne par conséquent sous le nom de "phase semblable au tobermorite". Des études supplémentaires de fine structure au moyen de rayons électroniques et de rayons X ont donné la cellule élémentaire de la phase semblable au tobermorite.

Les constantes du réseau sont: $a_0=11.2\ \pm0.3$ A
$b_0=7.32\ \pm0.07$ A
$c_0=27$–28 A
$\alpha=\beta=\gamma=90°$

Le réseau cristallin est fortement déformé. La phase semblable au tobermorite a les mêmes éléments de structure que le tobermorite. La seule différence d'avec ce dernier réside dans le fait que des ions supplémentaires de Ca^{++} et OH^- sont déposés entre les paquets de couche de tobermorite. Les positions exactes de ces ions n'ont pas pu être déterminées. Cependant, sur la base des résultats de la recherche, on a pu établir une formule hypothétique de structure pour la phase semblable au tobermorite:

$$Ca^x[Ca_4Si_6O_{16}(OH)_2]\ [Ca^x(OH)_2]_n$$

$n=5$–7. Les atomes de calcium avec coordination de réseau inconnue sont désignés par x.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Institut für Gesteinshüttenkunde, Rhein. Westf. Technische Hochschule Aachen, Germany.

Zusammenfassung

Die Calciumsilikate 3 $CaO \cdot SiO_2$ und β-$2CaO \cdot SiO_2$ erstarren nach dem Ansetzen mit kleinen Wassermengen (W/Z=0,1 bis 0,5) ähnlich wie der Portlandzement. Dieser Erstarrungsvorgang ist mit der Bildung eines wasserhaltigen Calciumsilikates verbunden. Dieses Hydrolysen- und Hydratationsprodukt hat eine wechselnde chemische Zusammensetzung und wurde früher in der Zement-Literatur als "Gel" oder als "Gelphase" bezeichnet. Elektronenmikroskopische Untersuchungen ergaben eindeutig, daß dieses Calciumhydrosilikat kristallin ist. Es kristallisiert nadelförmig. Die Kristallite haben eine mittlere Länge von 5000 Å. Mit Hilfe der dynamischen Differenzkalorimetrie und der quantitativen Röntgenanalyse konnte die Zusammensetzung bzw. das $CaOS:iO_2$-Verhältnis dieser Phase mit 1,8–1,9 ermittelt werden.

Elektronenbeugungsdiagramme zeigen, daß das Hydratationsprodukt von $3CaO \cdot SiO_2$ und β-2 $CaO \cdot SiO_2$ dem Mineral Tobermorit $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$ morphologisch und strukturell sehr ähnlich ist. Es wird daher mit dem Namen "tobermoritähnliche Phase" bezeichnet. Weitere Feinstrukturuntersuchungen mit Elektronenstrahlen und Röntgenstrahlen ergaben die Elementarzelle der tobermoritähnlichen Phase:

Die Gitterkonstanten betragen:

$$a_0 = 11{,}2 \pm 0{,}30 \text{ Å}$$
$$b_0 = 7{,}32 \pm 0{,}07 \text{ Å}$$
$$c = 27 - 28 \text{ Å}$$
$$\alpha = \beta = \gamma = 90^\circ$$

Das Kristallgitter ist stark fehlgeordnet. Die tobermoritähnliche Phase enthält die gleichen Strukturelemente wie der Tobermorit. Sie unterscheidet sich vom letzteren dadurch, daß zwischen den Schichtpaketen des Tobermorits zusätzlich Ca^{++} und OH^--Ionen eingelagert sind. Die genaue Lage dieser Ionen konnte nicht ermittelt werden. Basierend auf den Untersuchungsergebnisse konnte eine hypothetische Strukturformel der tobermoritähnlichen Phase aufgestellt werden:

$$Ca^x[Ca_4Si_6O_{16}(OH)_2]\,[Ca^x(OH)_2]_n$$

$n=5$–7. Die Calciumatome mit unbekannten Gitterkoordinaten sind mit x bezeichnet.

Introduction

The calcium silicates β-Ca_2SiO_4 and $Ca_3(SiO_4)O$ are the principal components of portland cement clinker.

The hydration products of these components play a decisive role in the hardening process of portland cement. A final explanation of the course of hydrolysis and hydration of calcium silicates would constitute an important contribution to the theory of hardening of hydraulic cementing materials.

It has been known for a long time that the calcium silicates C_3S and β-C_2S, like cement itself, take a set when mixed with a "small" quantity of water and yield a product which is relatively strong in compression. This setting process is associated with the formation of a hydrous calcium silicate. This product of hydrolysis and hydration has a varying chemical composition and was formerly designated in cement literature as "gel" or as the "gel phase".

H. F. W. Taylor [1][1] established that this gel phase is identical with a synthetically obtained calcium silicate hydrate, which he designated as CSH(I). It is characteristic of this phase that its composition can vary over a wide range (CaO:SiO_2=0.8–1.5) without loss of its fundamental structure. Furthermore, it is characteristic that no stoichiometric relation of lime to silica and water could be established for this compound.

C. F. Claringbull and M. H. Hey [2] found that Taylor's CSH(I) was structurally very similar to the natural mineral "tobermorite"—$5CaO \cdot 6SiO_2 \cdot 5H_2O$. X-ray diagrams of tobermorite and CSH(I) show good agreement in d-values and intensities. Because of this agreement, all phases having a tobermorite-like X-ray diagram have been denoted in German literature as "tobermorite-like" phases.

Experimental Analysis of the Hydration Products in the Systems: C_3S-H_2O and β-C_2S-H_2O

Favorable conditions for analytical investigation of the calcium silicate hydrates that are formed exist only if the reaction involved in their formation has been completed, i.e., if the hydration products are no longer interspersed with remnants of unreacted initial substances. This condition is satisfied in tests in which the initial substances are shaken with water or lime water. This test method, however, does not reproduce conditions

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[1] Figures in brackets indicate the literature references at the end of this paper.

existing in a mortar layer, since the decisive concentration conditions are quite different here. For this reason, we hydrated the calcium silicates C_3S and β-C_2S with small quantities of water (w/c—0.5), and believe that our test conditions successfully reproduced conditions of practice. This test method is naturally beset with some difficulties, as the pastes never reach the stage of completed reaction. X-ray determination of the nonhydrated initial substances permitted us to overcome this difficulty.

The initial substances, C_3S and β-C_2S, were synthesized through solid-state reactions. The β-C_2S lattice was successfully stabilized by an admixture of 0.5 percent of B_2O_3.

The alkali content of the synthetic calcium silicates was as follows:

	C_3S	β-C_2S
Na_2O+K_2O	0.019%	0.019%

The ground samples of C_3S and β-C_2S (4000 Blaine) were mixed with water (w/c=0.5) and hydrated in plastic tubes in a thermostat at 30 °C. The hydrated samples were investigated by means of dynamic differential calorimetry (DDC), roentgenographically, and with the electron microscope after 1, 2, and 3 months.

Test Methods

An important aid in determining the course of the reaction is the determination of free lime hydrate in the hydration products. In this determination we used B. Franke's [3] acetic acid ester-isobutyl alcohol method. We found, however, that the solvents used attacked the finely crystalline calcium silicate hydrates, especially after several hours of boiling. A suitable method of determining free $Ca(OH)_2$ was found in dynamic differential calorimetry.

Dynamic Differential Calorimetry (DDC)

In comparison with differential thermal analysis (DTA) DDC permits a quantitative determination of the thermal effects. Like DTA, the DDC method is based on the familiar differential method. The significant innovation in DDC lies in the fact that the temperature measurements are not taken at the center of the specimens (fig. 1b), but on metal accessories (platinum cups) (fig. 1a), from which the total heat requirement of the samples is established. The advantage of this method over DTA consists also in that the sample under study can be weighed following every peak.

A detailed report on "Fundamental Principles and Scope of Application of the Dynamic Differential Calorimeter" was published by H. E. Schwiete and G. Ziegler in *Reports of the German Ceramic Society* (*Ber. der DKG*), V. 35, 1958, pp. 193–204.

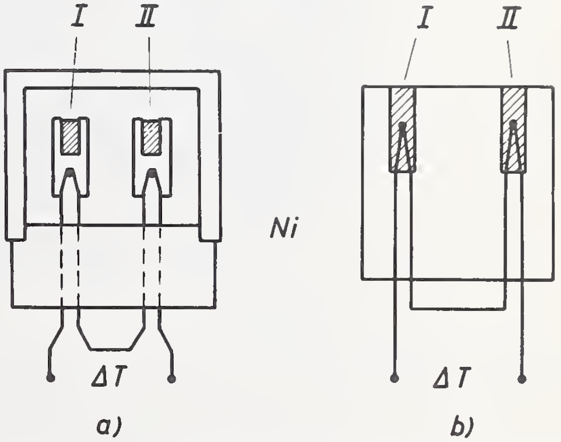

FIGURE 1. *Arrangement for (a) dynamic differential calorimetry and (b) DTA.*

Determination of the Quantity of Liberated $Ca(OH)_2$ by Means of DDC

The reaction:

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

is associated with an endothermic effect which is proportional to a corresponding peak area on the DDC diagram (fig. 2). This area (F) was determined by means of a planimeter. With the aid of the final weight of the sample (E_2) and a calibration value (K), the quantity of liberated CaO can be determined from the following equations:

$$\frac{\text{moles CaO}}{\text{moles } \beta\text{-}C_2S} = \frac{0.757(F/K)}{E_2} \cdot 3.08 \cdot \frac{100}{H}$$

$$\frac{\text{moles CaO}}{\text{moles } C_3S} = \frac{0.757(F/K)}{E_2} \cdot 4.04 \cdot \frac{100}{H}$$

where:

E_2(g) = final weight of the sample after heating to 1000 °C (in a DDC determination)

F(cm^2) = area of the $Ca(OH)_2$ decomposition peak

K(cm^2/g) = calibration value for the determination of $Ca(OH)_2$

0.757; 3.08; 4.04 = conversion factors

H = percent of hydrated C_3S or β-C_2S (resp.) obtained by X-ray diffraction (counter tube).

The values obtained for the quantities of CaO liberated during hydration served for the computation of the CaO: SiO_2 ratio in the calcium silicate hydrate phase formed in the systems C_3S–H_2O and β-C_2S–H_2O.

$CaO:SiO_2$-ratio of the calcium silicate hydrate phase in the C_3S–H_2O system; w/c=0.5; hydration temperature 30°C:

After 1 month	*After 2 months*	*After 3 months*
1.88	1.87	1.92

$CaO:SiO_2$-ratio of the calcium silicate hydrate phase in the β-C_2S-H_2O system; w/c=0.5; hydration temperature 30 °C:

After 1 month	*After 2 months*	*After 3 months*
1.86	1.80	1.85

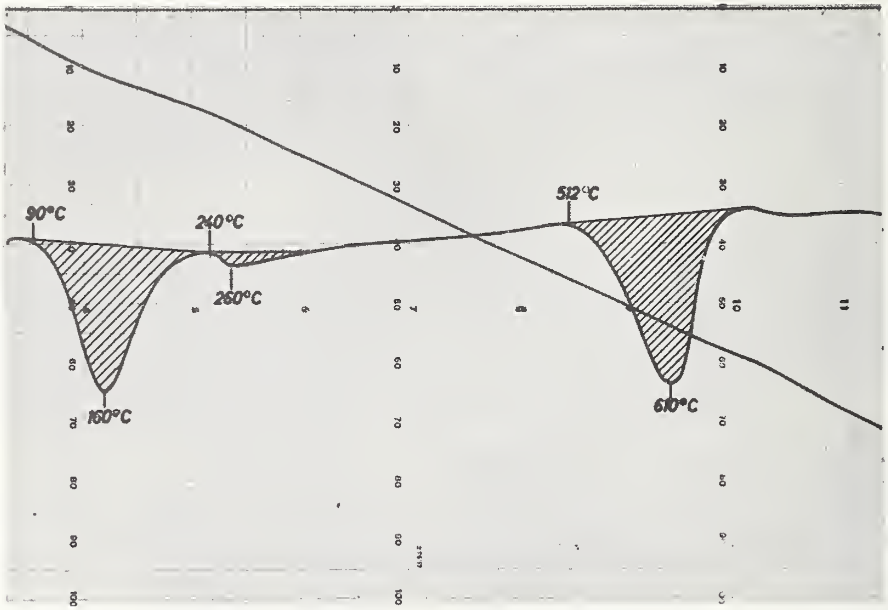

FIGURE 2. *DDC-plot of hydrated* C_3S *(30 °C; w/c=0.5; duration of hydration—1 month).*
512 °C—dehydration of $Ca(OH)_2$.

Electron Microscope Studies

First we followed the hydration process of tricalcium silicate in its initial stage. Figure 3 shows two electron micrographs of single C_3S particles hydrated on the object holder with a drop of water. After every examination the samples were stored in a moist atmosphere. After

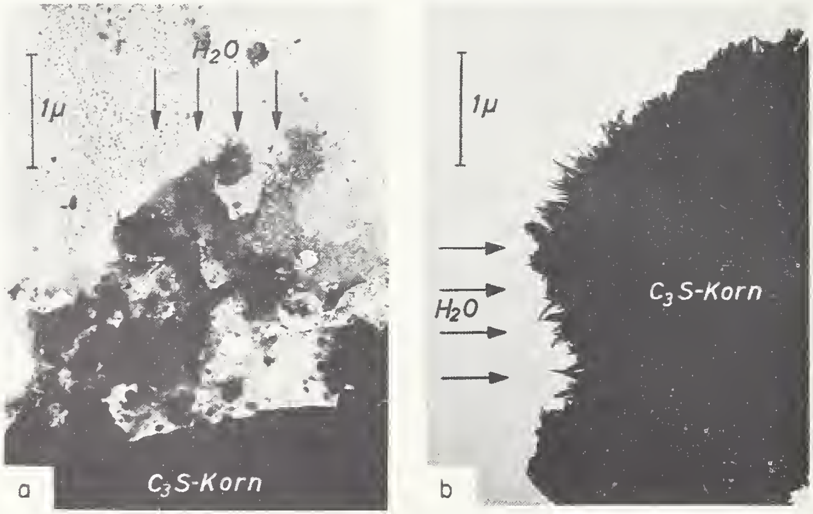

FIGURE 3. *Electron micrograph of hydrated* C_3S.
(a) hydrated 1 hour; (b) hydrated 5 days.

5 days the crystallization nuclei of the calcium silicate hydrate phase can already be detected. This study was followed by studies of C_3S and β-C_2S pastes. The micrographs (figs. 4 and 5) reveal needle-shaped hydration products. Electron diffraction is needed to identify these crystallites. Figure 6 shows a small area diffraction micrograph taken from the first series of the investigation. Table 1 presents the computed d_{hkl}-values of the entire investigated series.

The d_{hkl}-values obtained above are not sufficient to compute the lattice constants of the hydration products. For this reason we tried to obtain the hydrosilicate phase in a pure state so as to permit a larger area to be diffracted. We hoped that such multiple crystal diffraction would yield a diagram with more rings. We produced the hydrosilicate phase in anhydrous insobutyl alcohol in which C_3S with particle size less than 1 μ was reacted with water (w/c=1). The hydrosilicate phase thus obtained appears in figures 7 and 8.

The electron micrographs (figs. 9 and 10) were irradiated at a low electron beam intensity. The dotted rings are produced by the β-C_2S hydration

TABLE 1

No.	I	d_{hkl}	Selected area
		A	
1	s	3.1–2.8	CSH—needle-shaped from C_3S pastes.
	w	1.79–2.8	
2	s	3.0–2.8	Do.
	w	1.80	
3	s	3.0–2.8	Do.
	w	1.80	
4	s	3.1–2.8	CSH—needle-shaped from β-C_2S pastes.
	w	-----------	
5	s	3.0–2.8	Do.
	w	1.82	

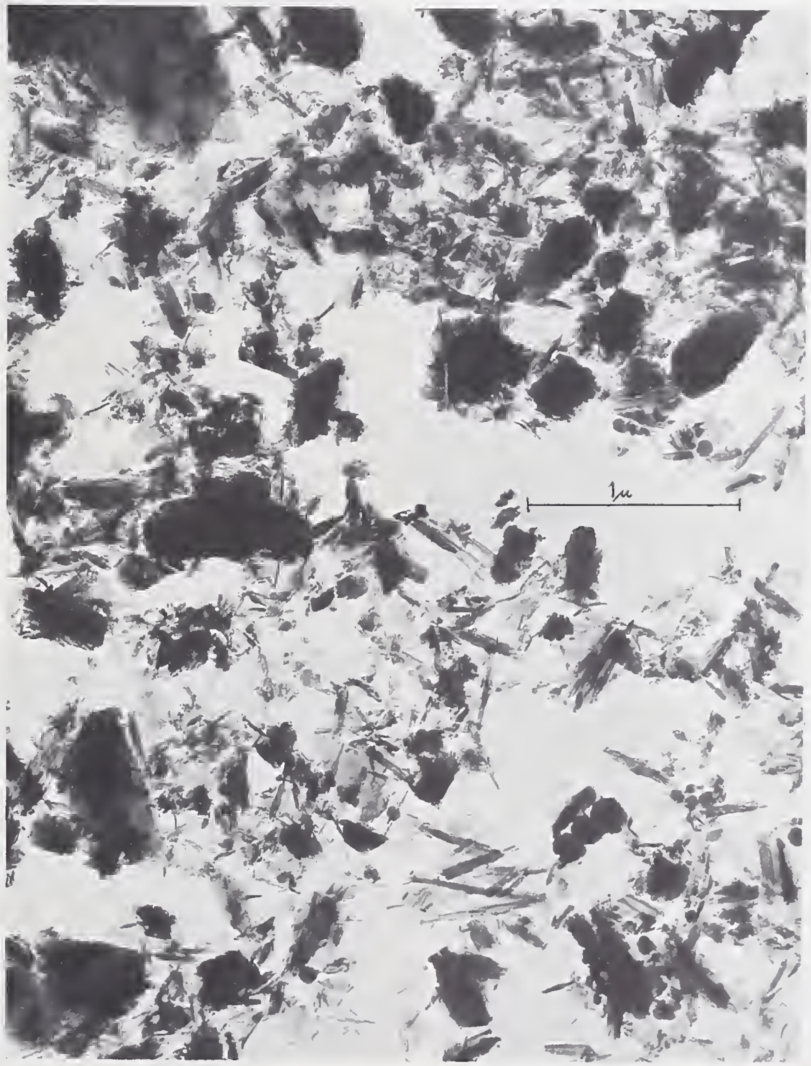

FIGURE 4. *Electron micrograph of hydrated* C_3S, *w/c=0.5; duration of hydration, 1 month; hydration temperature, 30 °C; average length of calcium silicate hydrate crystals, 5,000A.*

product (w/c=0.5), the sharp bright rings by the gold calibration preparation.

A comparison of the *d*-values of C_3S and β-C_2S hydration products shows that C_3S and β-C_2S at low w/c ratio yield identical hydration products. A comparison of these values with *d*-values of Taylor's CSH(I) phase also shows good agreement. Deviations occur only in intensities, a fact evidently attributable to the difference in the effects of electron beams and X-ray beams on the crystalline lattice.

We mentioned in the introduction that Taylor's CSH(I) phase is structurally similar to the naturally occurring mineral tobermorite. As our hydration products conformed to the CSH(I) phase (differences were recorded only in the basa

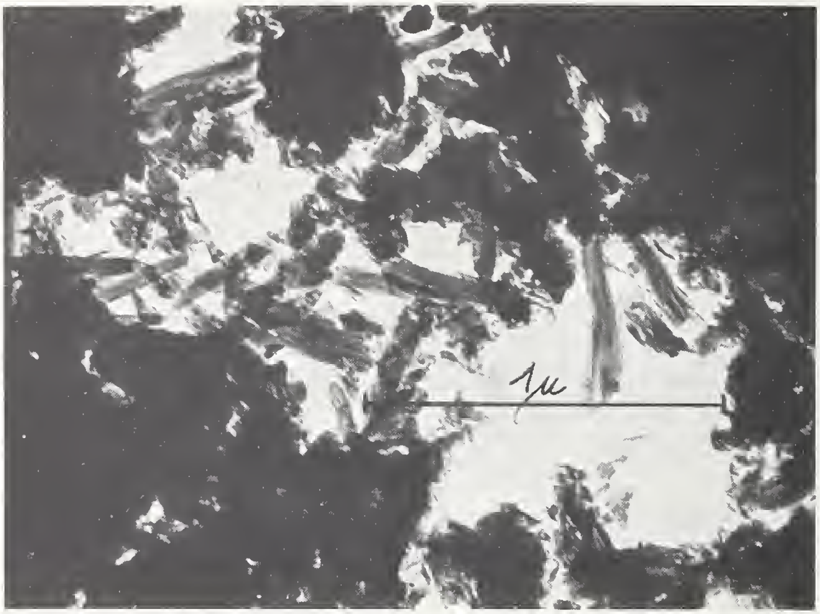

FIGURE 5. *Electron micrograph of hydrated β-C_2S; w/c=0.5; duration of hydration, 1 month; hydration temperature, 30 °C.*

Prepared in isobutyl alcohol with ultrasonic pulse (10 min). Average length of the calcium silicate hydrate crystals: 5,000A.

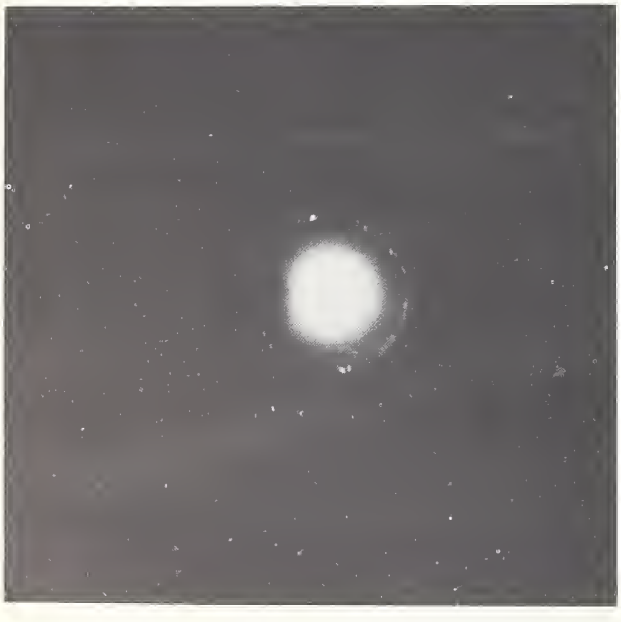

FIGURE 6. *Diffraction diagram of the C_3S hydration product (crystal bundles).*

FIGURE 7. *Electron micrograph of CSH, the hydration product of C_3S; w/c=1.0; hydration temperature, 30 °C.*

Figure 8. *Diffraction diagram for figure 7.*

Calibration value: λ·L=52.2 Amm.

d_{hkl}-values computed from diffraction diagram

Ring radius, *r*	*I*	d_{hkl}
mm		*A*
17.1	vs	3.06
18.7	vs	2.80
24.1	w	2.17
28.6	s	1.83
30.3	w	1.73
32.3	s	1.62
35.0	s	1.495
38.1	w	1.371
41.2	w	1.270
44.7	w	1.169

diffraction) they must also bear a structural likeness to tobermorite. Surprisingly, this similarity does not apply when the chemical composition of tobermorite is compared to that of our hydration products. Natural tobermorite, $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$, has a CaO:SiO$_2$ ratio of 0.83, while our DDC studies yielded for C_3S and β-C_2S hydration products a CaO:SiO$_2$ ratio from 1.8 to 1.9. This remarkable feature of the tobermorite-like phase must be related to the character of the tobermorite lattice. Some data on the structure of tobermorite are already available in the literature [4]. Its final structure has not yet been defined.

Figure 9. *Electron micrograph of hydrated β-C_2S.*
Duration of hydration: 3 months; Hydration temperature: 30 °C.

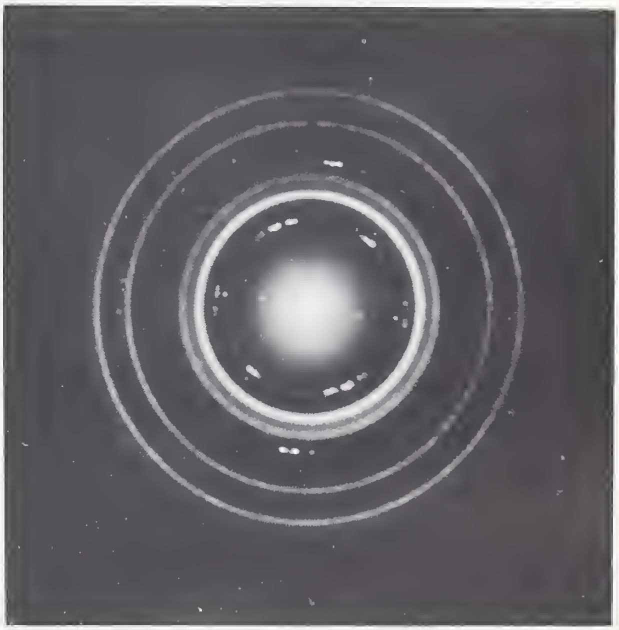

Figure 10. *Small-area diffraction diagram for zone A (fig. 9)*

Calibration value: λ·L=52.7 Amm.

d_{hkl}-values computed from diffraction diagram

Ring radius, *r*	*I*	d_{hkl}
mm		*A*
17.30	s	3.05
19.00	s	2.78
28.75	s	1.83
32.40	w	1.77
38.50	w	1.37

Electron Microscope Studies of Single Tobermorite Crystals

Single tobermorite crystals (figs. 11 and 12) were isolated by means of selective screening and their diffraction patterns examined. Figures 13, 14, 15, and 16 show electron diffraction pictures of such single crystals. We present two diagrams side by side, figure 17, in which the left diffraction diagram represents the b^*-c^* zone of the reciprocal lattice, while the right diagram is that of the a^*-b^* zone. The position of the point interferences shows that the crystals lie at (100) and (001). No (010) points could be established.

FIGURE 11. *Electron micrograph of synthetic tobermorite—* $5CaO \cdot 6SiO_2 \cdot 5H_2O$.

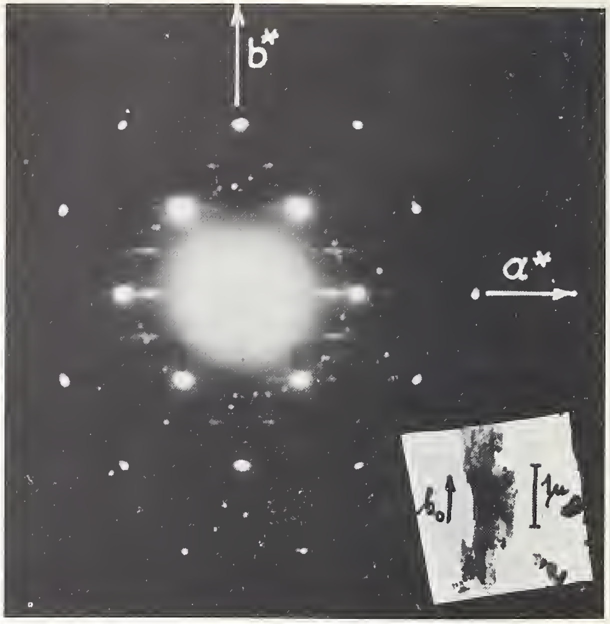

FIGURE 14. *Tobermorite single-crystal diffraction diagram; (001) normal to electron beam; irradiated in the* c_0 *direction.*

FIGURE 12. *Electron micrograph of synthetic tobermorite—* $5CaO \cdot 6SiO_2 \cdot 5H_2O$.

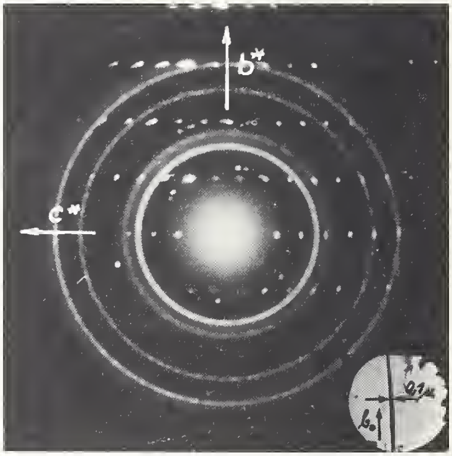

FIGURE 15. *Tobermorite single-crystal diffraction diagram; (100) normal to electron beam; irradiated in the* a_0 *direction.*
Ring pattern: gold calibration substance.

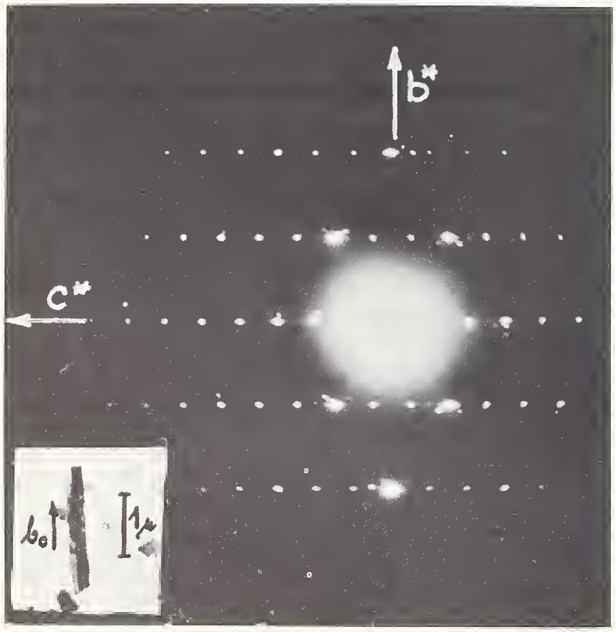

FIGURE 13. *Tobermorite single-crystal diffraction diagram; (100) normal to electron beam; irradiated in the* a_0 *direction.*

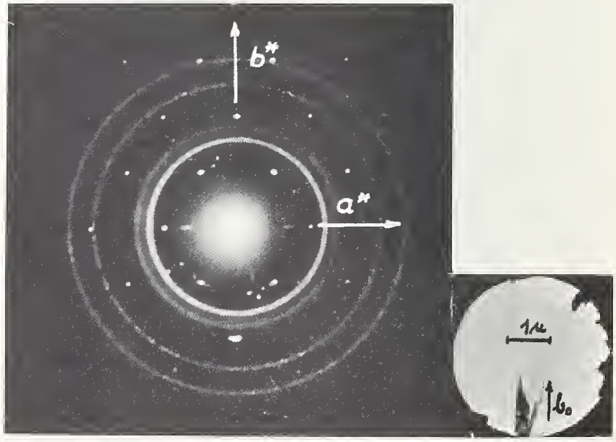

FIGURE 16. *Tobermorite single-crystal diffraction diagram; (001) normal to electron beam; irradiated in the* c_0 *direction.*
Ring pattern: gold calibration substance.

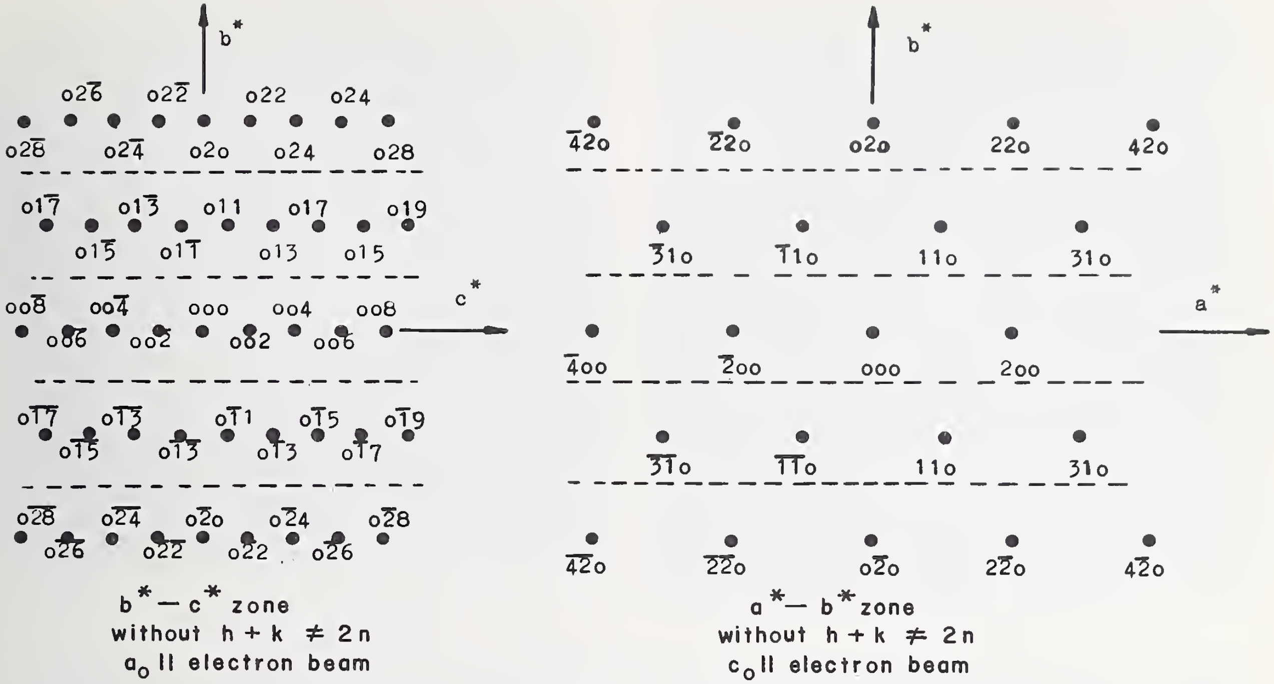

FIGURE 17. *Indexing of electron diffraction diagrams of tobermorite single crystals.*

Results

The following lattice constants were determined on the basis of electron diffraction diagrams:

Tobermorite	*Tobermorite-like phase*
$a_0 = 10.9 \pm 0.30$ A	$a_0 = 11.2 \pm 0.30$ A
$b_0 = 7.32 \pm 0.07$ A	$b_0 = 7.32 \pm 0.07$ A
$c_0 = 17.15 \pm 0.09$ A	$\gamma = 90°$.
$\alpha = \beta = \gamma = 90°$	

From X-ray diffraction, we have:

Tobermorite	*Tobermorite-like phase*
$a_0 = 10.9 \pm 0.30$ A	$a_0 = 11.2 \pm 0.30$ A
$b_0 = 7.32 \pm 0.07$ A	$b_0 = 7.32 \pm 0.07$ A
c_0(El.)$= 17.15 \pm 0.09$ A	----------------
c_0(X-ray)$= 22.4 \pm 0.05$ A	c_0(X-ray)$= 27.0$–28.0 ± 0.05 A

We can see that there is a difference of 5.2 A between c_0 values of tobermorite obtained with the electron microscope and with X-ray diffraction. This difference is related to the interlayer water in tobermorite. Tobermorite contains 4 moles of H_2O per formula unit. This water is lodged between the stable elements of the structure as in montmorillonite. It is driven off by the strong electron bombardment and the individual structural packets become superimposed. The electron beams thus produce a one-dimensional contraction of the elementary cell in the direction of the c-axis from 22.4 to 17.15 A. The superimposed stable structural elements of tobermorite are probably not oriented ideally, as parallel to c^* there appear streak-shaped reflections which point to a disturbance in the lattice with respect to the c-axis.

Structure of the Tobermorite-Like Phase

Electron-microscope studies have shown that the hydration products of tricalcium silicate and β-dicalcium silicate are morphologically and structurally very similar to the mineral tobermorite, $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$. The lattice constants a_0 and b_0 of tobermorite and of the tobermorite-like phase are identical (figs. 18 and 19). This justifies the assumption that these two phases consist of identical structural elements. According to Megaw and Kelsey [4] tobermorite is a layered mineral, a view confirmed by our diffraction patterns. The tobermorite packets consist of two layers of a combination of 4CaO with SiO_4 three-link chains ("dreierketten") on (001) surfaces which run parallel to b. These layered packets are so packed one on the other that the SiO_4 chains are superimposed. The tubular voids between the SiO_4 chains accommodate the remaining Ca and O atoms, whose exact positions are not fixed. The water lodged in the packet (1 H_2O per formula unit) is present in all probability in the form of OH groups connected with the Si ions. Interlayer water is present between the packets. The packet contains four formula units, $Ca_5[Si_6O_{16}(OH)_2]$.

In the tobermorite-like phase we have a CaO:SiO_2 ratio of 1.8 to 1.9. It must therefore be assumed that the excess CaO is built in between the packets. This arrangement is indicated by the magnitude of the c_0 spacing of the tobermorite-like phase, $c_0 = 27$–28 A. In between the individual packets we thus have a space of 10 to 11 A.

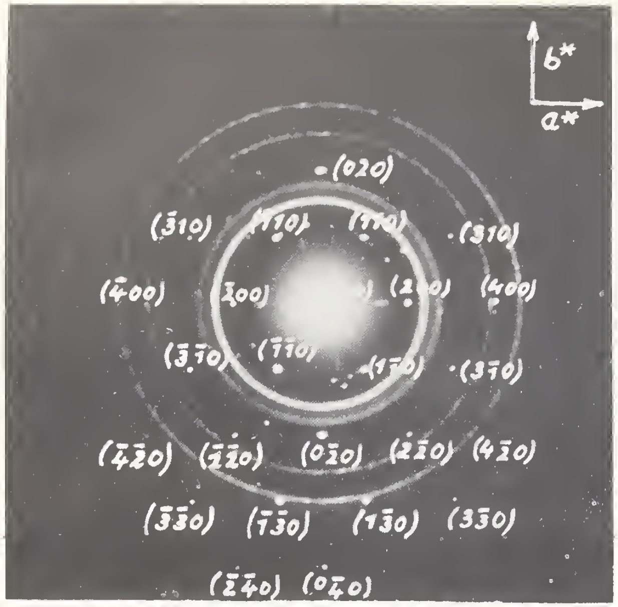

FIGURE 18. *Tobermorite single-crystal diffraction diagram a^*-b^* zone; $a_0=10.9\pm0.3$ A; $b_0=7.32\pm0.07$ A.*

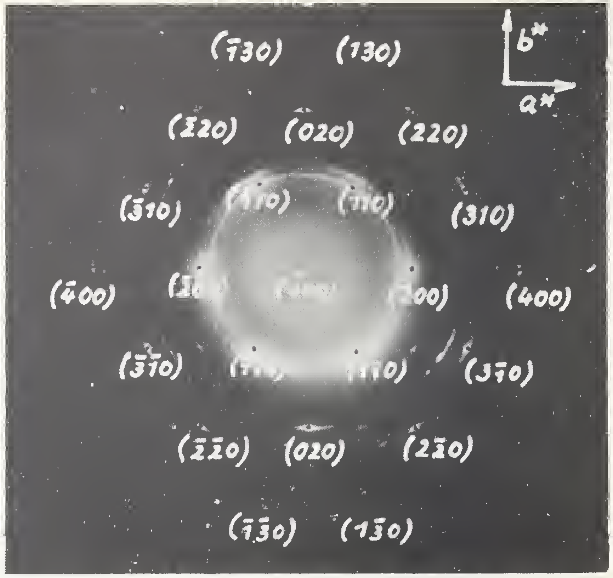

FIGURE 19. *Multiple-crystal diffraction diagram of the tobermorite-like phase.*

1.8–$1.9CaO\cdot SiO_2\cdot nH_2O$. $a_0=11.2\pm0.3$ A; $b_0=7.32\pm0.07$ A

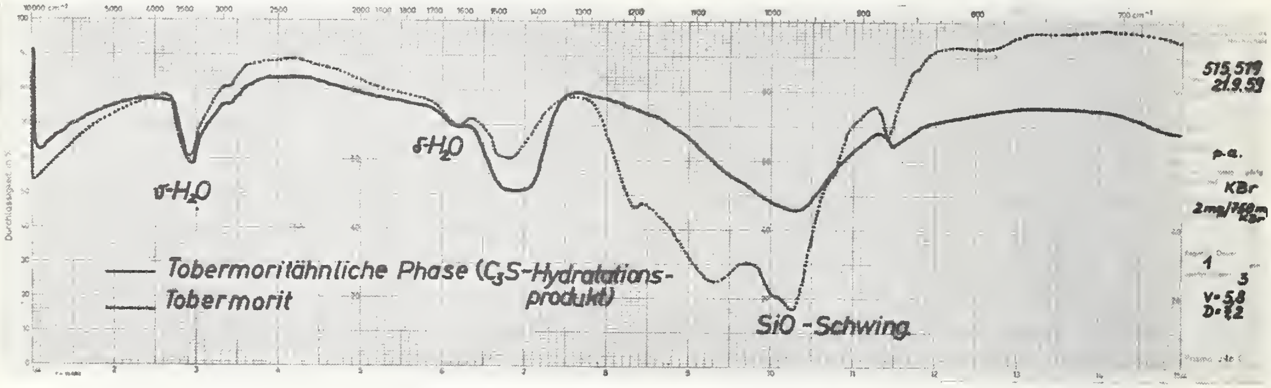

FIGURE 20. *Infrared absorption spectra.*

Solid line, tobermorite-like phase (C_3S hydration product); dotted line, tobermorite.

One can imagine that this space is filled with hydrated or solvated Ca ions. However, the Ca-OH groups must be present without orientation as no additional *hkl* diffraction lines could be observed for the tobermorite-like phase. Such phenomena are also encountered with certain expansive clays.

On the basis of the above we have evolved a hypothetical structural formula for the tobermorite-like phase. The formula includes the composition of the stable packets, according to Megaw and Kelsey, and the $Ca(OH)_2$ groups packed between the layers. The Ca atoms with unknown lattice constants are denoted by *x:*

$$Ca^x[Ca_4Si_6O_{16}(OH)_2]\ [Ca^x(OH)_2]_n$$

$n=5$–7.

Infrared (IR) absorption studies confirm the similarity between the hydration products and tobermorite (fig. 20).

In conclusion we must state that our views on the structure of the tobermorite-like phase are based on an idealized picture. A final answer to the question of how the additional Ca and OH ions are inserted or entrapped can be given only when it is possible to take pictures of single crystals of tobermorite-like crystals, which is very difficult in view of the small dimensions of the crystals.

However, it can be accepted with certainty that the hydration products of C_3S and β-C_2S are crystalline. The continuous change of the concentration relations in a mortar layer permits the formation of only highly disoriented crystallites which is clearly revealed by the electron-diffraction patterns.

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SESSION IV. CHEMISTRY OF HYDRATION OF PORTLAND CEMENT

Paper IV–1. Early Hydration Reactions of Portland Cement*

Kenneth T. Greene

Synopsis

The literature dealing with the early hydration reactions of portland cement at ordinary temperature, published since the Third International Symposium in London in 1952, is reviewed. Considerable research has been reported on various aspects of the hydration of the individual compounds of cement. Our knowledge of the hydration of portland cement itself is less extensive.

The general course of the early chemical reactions of hydration is traced, and the nature and composition of the products of hydration of the alumina-bearing phases are discussed. The reactions of the aluminates and ferrites predominate at very early ages, those of the silicates from about the time of initial set onward.

The solution-precipitation and solid-phase reaction theories, two possible mechanisms of cement hydration, are considered in the light of published data. It is concluded that both types of process may be involved, with solution and precipitation probably prevailing immediately after water contact, while the solid-phase type of reaction may typify the later hydration. The later hydration rate is probably controlled, in most cements, by diffusion of water through the layers of gelatinous hydration products.

The chemical and physical nature of the cement gel is discussed in relation to the development of structure in the paste. The evidence indicates that setting and hardening are intimately connected with the development of a very high surface area in the gel, and that both physical and chemical forces are involved.

Résumé

L'exposé passe en revue la littérature qui traite des réactions du début d'hydratation du ciment portland à température ordinaire, littérature publiée depuis le Troisième Symposium International de Londres en 1952. Les résultats d'études considérables sur les différents aspects de l'hydratation des composés individuels du ciment ont été rapportés. Notre connaissance de l'hydratation du ciment portland proprement dit est moins extensive.

Le cours général des premières réactions chimiques de l'hydratation est retracé et la nature et la composition des produits d'hydratation des phases contenant de l'alumine sont discutées. Les réactions des aluminates et des ferrites prédominent au tout début, celles des silicates environ dès le moment de la prise initiale, et de là continuent.

Les théories sur la réaction de la solution-précipitation et la réaction de la phase solide, deux mécanismes possibles de l'hydratation du ciment, sont examinées à la lumière des résultats publiés. On en conclut que les deux types de réaction peuvent se présenter l'un et l'autre, la solution et précipitation l'emportant probablement sitôt après le contact avec l'eau, tandis que le type de réaction de la phase solide est caractéristique de l'hydratation ultérieure. La vitesse d'hydration ultérieure est probablement contrôlée, dans la plupart des ciments, par la diffusion de l'eau à travers les couches de produits d'hydratation gélatineaux.

La nature chimique et physique du gel de ciment est discutée en fonction du développement de la structure dans la pâte. Il est démontré que la prise et le durcissement sont intimement liés au développement dans le gel d'une large surface spécifique et que des forces physiques aussi bien que chimiques interviennent.

Zusammenfassung

Die Literatur des ersten Hydratationsreaktionen des Portlandzements bei Zimmertemperatur, die nach dem Dritten Internationalen Symposium des Jahres 1952 in London veröffentlicht wurde, wird besprochen. Viele Arbeiten über die verschiedenen Hydratationsstufen einzelner Verbindungen des Zementes sind erschienen, aber unsere Kenntnisse der Hydratation des Portlandzements selber sind nicht so vollständig.

Die allgemeine Tendenz der ersten chemischen Hydratationsreaktionen wird besprochen, und die Natur und Zusammensetzung der Hydratationsprodukte der tonerdehaltigen Phasen werden beschrieben. Die Reaktionen der Aluminate und der Ferrite sind bei frischen Zementpasten die maßgebenden; mit der ersten Verfestigung ungefähr machen sich die Silikatreaktionen stärker bemerkbar.

Zwei Mechanismen der Zementhydratation sind möglich, nämlich die Niederschlagbildung aus Lösungen, und Reaktionen in fester Phase; beide Möglichkeiten werden an Hand der Veröffentlichungen besprochen. Es wird der Schluß gezogen, daß beide Arten Prozesse vorkommen können, wahrscheinlich in der Weise, daß Auflösung und Niederschlagbildung sofort nach Berührung mit Wasser einsetzt, und daß Reaktionen in fester Phase sich während der späteren Hydratation ereignen. Diese spätere Hydratation wird vermutlich bei den meisten Zementen durch die Wasserdiffusion durch die gelatinierten Hydratationsproduktslagen hindurch kontrolliert.

Die chemische and physikalische Natur des Zementgels wird in ihrer Beziehung zur Ausbildung der Pastenstruktur besprochen. Es sieht so aus, als ob die Erstarrung und das Erhärten mit der Ausbildung einer sehr großen Oberfläche des Gels in engster Beziehung stehen, und daß sowohl physikalische als auch chemische Kräfte ins Spiel kommen.

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Introduction

The chemical reactions involved in the hydration of portland cement have been studied with increasing intensity in recent years. It can be truthfully said that much progress has been made in the understanding of these reactions, although it will be admitted by all that there is still much more to learn.

At the Third International Symposium on the Chemistry of Cement held in London in 1952, the current state of knowledge of the chemical reactions of portland cement at ordinary temperature was ably reviewed by Steinour [1].[1] The present paper is an attempt to survey the more significant advances made in this same field since the Third Symposium, giving particular regard to the early reactions, by which the author means those which take place from the time the cement and water first come into contact, through the stage generally described as final set, up to the age of perhaps 2 or 3 days.

As pointed out by Steinour, early research dealt largely with phase equilibria in the simpler systems, $CaO-SiO_2-H_2O$, $CaO-Al_2O_3-H_2O$ and $CaO-Al_2O_3-CaSO_4-H_2O$, and with the hydration of the so-called pure cement compounds. For the most part only limited studies were made on mixtures of cement compounds or on commercial portland cement because of the difficulties of interpretation. Even when hydration studies were made on cement, a large excess of water was frequently used. The results of such experiments, although yielding valuable data, could not be related directly to pastes of ordinary consistency.

It must still be said that the direct study of the chemistry of hydrating cement paste, having water-cement ratios in the practical range, is very difficult, although new and improved methods are gradually increasing our knowledge. The more promising of these include new developments in the study of the liquid phase of hydrating paste and refined techniques for the analysis of the solid hydration products at early ages using X-ray diffraction, differential thermal analysis (DTA), thermogravimetric analysis, and infrared absorption and nuclear magnetic resonance methods.

The present discussion will be limited as much as possible to the hydration of portland cement, since the hydration of the calcium silicates and aluminates is being covered by other contributors to this symposium. However, it will be necessary to refer frequently to the literature on the pure calcium silicates and aluminates because of their intimate relationship with the hydration of cement. It will be necessary to deal in considerable detail with the normal hydration reactions involving gypsum. It is not the purpose of this paper, however, to discuss the problem of abnormal reactions, such as false set, except as it has a bearing upon the hydration of a normally retarded cement.

A survey of the published work on cement hydration since the Third Symposium reveals an extensive literature with regard to the hydration products formed when C_3S, C_2S, C_3A, C_4AF, etc. react with water. On the contrary, there appears to be relatively little new information available on the very early reactions in actual portland cement paste, particularly the reactions taking place within the first few minutes of water contact. While it is realized that research on the pure compounds is essential, and to a considerable extent must precede that upon cement paste, nevertheless the present writer believes that the time has come for more concerted attempts to correlate the results of the two lines of investigation.

There are undoubtedly numerous unpublished data bearing upon the problem of the very early hydration reactions of cement which, if made available, could contribute significantly to an understanding of this complex question. Some information of this nature has been obtained in the laboratories of the Ideal Cement Company and will be reported later in the present paper.

General Course of Early Chemical Reactions

Composition of Liquid Phase

Ordinary portland cement containing gypsum for control of setting time, usually about 4 or 5 percent, begins to react extremely rapidly when mixed with water. In fact the reaction is so rapid as to be properly termed immediate and is, consequently, very difficult to measure. It is known that lime, sulfate, and alkalies enter the solution swiftly in a paste having a water-cement ratio in the range of 0.4 or 0.5. The $Ca(OH)_2$ concentration soon reaches saturation, and lime continues to dissolve to give a supersaturated solution.

If the calcium sulfate is essentially in the form of the dihydrate, the solution will generally rapidly become saturated, but not supersaturated to any great degree, with $CaSO_4$. If calcium sulfate hemihydrate or other dehydrated forms of gypsum are present in the cement, it is well known that the solution may become supersaturated with $CaSO_4$ also. However, since we are here assuming that the gypsum is in its fully hydrated form, this situation will not be considered.

Various investigators have studied the chemical composition of extracts from cement pastes taken at various times after mixing. One of the most extensive of such studies was that of Kalousek, Jumper, and Tregoning [2]. Their results showed appreciable amounts of alkalies, lime, sulfate, and

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[1] Figures in brackets indicate the literature references at the end of this paper.

hydroxide at periods of time as short as 7 min, while the concentrations of alumina, iron, and silica were very low. Recent work by Strelkov [3] also indicated low values for silica in solution and also for alumina at periods of time as short as 2 min after mixing. Steinherz and Welcman [4] obtained similar results with solutions separated 1 min after mixing cements with 60 percent of water. Hansen [5, 6, 7] obtained information which led him to believe that the concentrations of silica and alumina are very low, even as early as 1 min after mixing. However, data for times less than 1 min are generally lacking, and Steinour [8] in his discussion of Hansen's most recent paper [7] points out that it is not proven that the concentrations of alumina and silica do not reach high values immediately upon mixing, followed by a decline to the values which have been determined at 1 min and longer. In fact, it seems very likely that this is the case. At any rate, it can be said that after a relatively short period of time the solution becomes essentially one of Na^+, K^+, Ca^{++}, SO_4^{--}, and OH^- ions.

If equilibrium prevailed during the first few moments after water contact, it would be a relatively simple matter to infer the concentration of lime and sulfate, if the concentrations of the alkalies were known, because the solubilities of calcium hydroxide and calcium sulfate are determined by the concentration of alkalies in this system. These relationships were shown by the work of Hansen and Pressler [9]. However, the solution is in a state of very rapid change for some time after mixing, and thus equilibrium criteria cannot be applied during this period.

Identity of Calcium Sulfoaluminate

Although there is considerable uncertainty concerning the exact state of affairs in these first moments, a few things are known with a reasonable amount of assurance. First, it is obvious that the lime-bearing constituents of the clinker begin to hydrolyze immediately with release of calcium hydroxide into the solution. The principal source of this calcium hydroxide is probably the C_3S, although the C_3A and calcium aluminoferrite phase may also contribute a part.

At the same time Al_2O_3 from the alumina-bearing phases is reacting rapidly with the sulfate made available by the solution of the gypsum, and the ample amount of calcium hydroxide now present in the liquid phase. The product of this reaction is fundamentally a calcium aluminate sulfate, commonly called calcium sulfoaluminate, the identity of which has been the subject of some controversy.

The question has been whether the calcium sulfoaluminate produced initially is the high-sulfate form represented by the formula $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$, known also by the mineral name ettringite, or the so-called monosulfate or low-sulfate form, $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$. The work of Jones [10], of D'Ans and Eick [11], and Eitel [12] showed that the compound stable under equilibrium conditions is the high-sulfate form. However, due to the fact that we do not have equilibrium conditions or anything approaching them in the first few moments, some investigators have been of the opinion that the low-sulfate form might be produced first as a metastable phase, later converting to the high-sulfate form.

Steinour [13] suggested that the product formed might be different, depending on whether or not the solution is already saturated with $Ca(OH)_2$ and $CaSO_4$ when the aluminates begin to react. He believed that saturation with $Ca(OH)_2$ and $CaSO_4$ should favor the low-sulfate form.

Previous to the Third Symposium, Kalousek, Davis, and Schmertz [14] had applied the method of differential thermal analysis (DTA) to hydrating cement paste and interpreted their results to mean that the high-sulfate sulfoaluminate is the initial product formed. More recently Taylor [15], using X-ray diffraction, detected the high-sulfate form at the age of 1 day.

Manabe and Kawada [16], using solutions containing radioactive sulfur-35, reported that in fresh cements the formation of calcium sulfoaluminate occurs immediately after mixing with water. These authors do not specify which calcium sulfoaluminate is meant, but presumably it is the high-sulfate form.

Indications of Differential Thermal Analysis

It may be appropriate at this point to introduce data obtained by the writer in the laboratory of the Ideal Cement Company which pertain directly to this problem. The method of differential thermal analysis has been used in our laboratories for nearly 5 years in the study of cement hydration. The equipment which we use is available commercially and is illustrated in figure 1. Four samples can be analyzed simultaneously, with the curves being recorded automatically. Various heating rates are available, but the rate most commonly used in our studies has been 10 °C per minute. The temperature limit of this apparatus is about 1,100 °C.

With regard to the DTA method it should be emphasized that variables, such as heating rate, particle size and weight of the sample, and configuration of the furnace, affect the shape and features of the curves produced. This variability must be borne in mind when comparing results obtained in different laboratories or on equipment of different design. The results are generally only qualitative, or at best, semiquantitative, but are quite useful when properly interpreted.

It should be stated also that the method of drying is very critical in the differential thermal analysis of hydrated cements. Too severe drying must be avoided because some of the less stable hydration products will be destroyed or dehydrated to the extent that some of the thermal effects will be diminished. We have found that vacuum drying at room temperature is generally satisfactory. The evacuation is carried out

Figure 1. *Apparatus for differential thermal analysis.*

at a pressure of perhaps 1 or 2 mm of mercury and usually is not prolonged beyond the point at which the free water is removed (about 2 or 3 hr for young pastes). Special techniques to stop hydration are used when the period of hydration is very short.

In connection with the data about to be presented, mention should be made of other reports on cement hydration using the DTA method, recently published by Lommatzsch [17], Rey [18], and Mchedlov-Petrosyan, Bunakow, Goworow, Latischew, Lewtschuk, and Sstrelkowa [19]. Rey, in particular, points out some of the difficulties inherent in this method, and precautions which must be taken. He emphasizes the importance of the manner of drying as it affects the shape of the DTA curves.

Figure 2 illustrates the DTA curves obtained in our laboratory on a typical cement hydrated for various periods of time up to 7 days, along with a curve for the unhydrated cement. The curve for the latter shows a typical double endothermic reaction for gypsum between about 140 and 170 °C. Slightly below 500° there is a broad endotherm which is believed to be related to calcium hydroxide formed during exposure to the air. Between 700 and 800° is a long, broad endotherm caused by calcium carbonate, also produced through exposure.

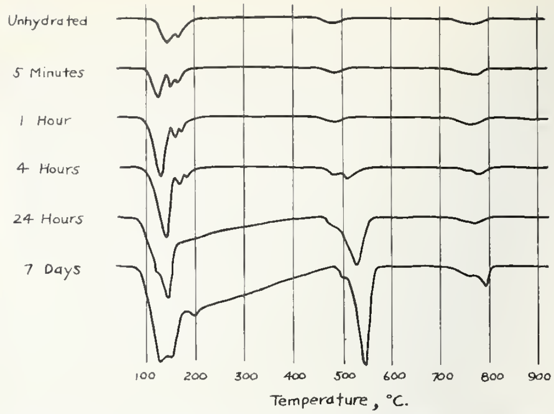

Figure 2. *DTA curves of a portland cement hydrated for various lengths of time.*

After 5 min hydration, a new, rather sharp, endothermic peak is seen at about 130°. This peak is attributed to the high-sulfate calcium sulfoaluminate ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$). The gypsum double peak is still present, but it is reduced in size. At 1 hr the calcium sulfoaluminate has increased considerably in amount, and the gypsum has decreased somewhat further. At 4 hr there has been a continuation of the reaction producing sulfoaluminate and, in addition, a small new peak has appeared just above 500°, indicating the start of formation of crystalline calcium hydroxide.

The reason for the double character of the peaks in the vicinity of 500° is not entirely clear. A possibility is that the small endotherm represents chemisorbed water held on the surface of free lime particles, while the second, larger peak is due to the more coarsely crystalline calcium hydroxide formed by crystallization from solution. In another set of experiments it was found that the presence and size of the small peak correlated fairly well with the free-lime content of the cements studied.

At 24 hr a marked increase in calcium hydroxide is recorded, but the chief interest now focuses on the low-temperature dehydrations. The double peak of gypsum is now seen to be absent, and a distinct shoulder is visible on the low-temperature flank of the sulfoaluminate peak. At 7 days this shoulder has grown so as to become a peak exceeding that of the sulfoaluminate. Experiments run on clinker without added gypsum, to be described later, indicate that this peak is due to calcium silicate hydrate. The peak is particularly sensitive to the manner of drying and can be almost eliminated from the thermograms by prolonged vacuum drying at a low pressure.

A new endotherm at about 200° is seen in the curve for the 7-day sample. This peak is attributed to the low-sulfate calcium sulfoaluminate ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$) or possibly to a solid solution of this compound with tetracalcium aluminate hydrate ($4CaO{\cdot}Al_2O_3{\cdot}13H_2O$). The question of the composition of this phase will be discussed in more detail further on. Other experiments not illustrated indicate that this phase ordinarily makes its first appearance at some time between 24 and 48 hr.

One additional feature should be mentioned in connection with the 7-day curve. The rather definite upward slope of the line between 200 and 500° suggests that some water is being lost gradually from the paste in this temperature range. This effect is noticeable but less pronounced at 24 hr. It undoubtedly correlates with the work of other investigators [20, 21, 22, 23], using thermogravimetric methods, which shows that water is lost over quite an extended temperature range from hydrated calcium silicates and hydrated cement paste. Of interest also are the growth of the calcium hydroxide peak between 24 hr and 7 days, and the increase in the size of the calcium carbonate endotherm between 700 and 800°.

Returning to the question of the identity of the calcium sulfoaluminate first formed during hydration of a cement, these curves and many others similar to them, which have been obtained in our laboratory, have convinced the writer that under ordinary circumstances the high-sulfate form is always the first to form. Experiments in which the hydration is topped after 2 min give similar results, although the quantity of this phase is less than at later periods.

When the quantity of gypsum is sufficient, which is the case with most cements, the high-sulfate sulfoaluminate always forms initially, followed by the appearance of the low-sulfate form, or a closely related phase, after the gypsum has been used up. We have attempted to confirm these indications by means of X-ray diffraction, but the results have not been too successful thus far. It is believed that a heavy-liquid concentration technique, similar to that employed by Taylor [15], would indicate the presence of the high-sulfate form even at very early ages.

An indirect confirmation of the above conclusions was found in experiments made with clinker without gypsum added, or with insufficient gypsum for normal retardation. DTA curves illustrating these results are given in figures 3 and 4. The curve for clinker hydrated for 5 min (fig. 3) shows no sign of the typical endothermic peak associated with the high-sulfate sulfoaluminate, but instead shows an endotherm in the neighborhood of 200 °C.

A peak in this location has been correlated by other investigators, as well as ourselves, with the hexagonal tetracalcium aluminate hydrate ($4CaO \cdot Al_2O_3 \cdot 13H_2O$) or a related solid solution [14, 18]. It will be noted that this endotherm persists up to the age of 7 days. Figure 4 shows the results at 4 hours' hydration with the same clinker, to which was added 1 percent, 2 percent, and 4 percent of gypsum.

It appears that 1 percent of gypsum was not sufficient to prevent the formation of the $4CaO \cdot Al_2O_3 \cdot 13H_2O$ for this period of hydration, since this form, as well as the high-sulfate sulfoaluminate, is present in small amount in this sample. Two percent of gypsum has resulted in a fairly large amount of high-sulfate sulfoaluminate and has effectively prevented the formation of $4CaO \cdot Al_2O_3 \cdot 13H_2O$. The sample with 4 percent of gypsum shows the high-sulfate sulfoaluminate and an excess of unreacted gypsum.

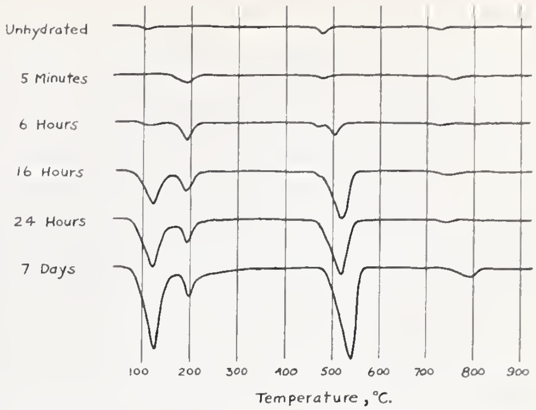

Figure 3. *DTA curves of a portland cement clinker hydrated without gypsum for various lengths of time.*

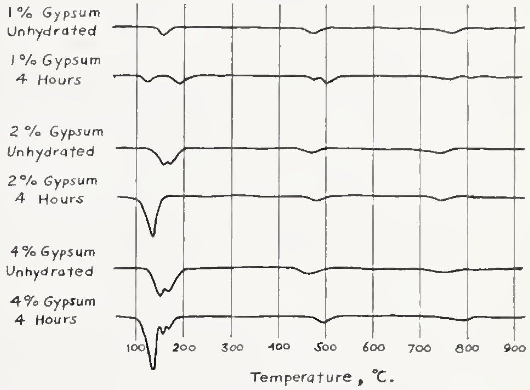

Figure 4. *DTA curves of a portland cement clinker hydrated with various amounts of added gypsum.*

The suggestion of Steinour, previously mentioned, that formation of the low-sulfate sulfoaluminate may be favored initially when hydration takes place in a solution already saturated with $Ca(OH)_2$ and $CaSO_4$, was investigated using the same cement as in the experiments of figure 2. The cement was hydrated for 2 min at a water-cement ratio of 0.4, both with distilled water and saturated $Ca(OH)_2$-$CaSO_4$ solution. Hydration was stopped by stirring the paste into an excess of acetone, filtering, and drying in vacuum for 1 hr.

The DTA curves obtained are shown in figure 5. It will be noted that the endotherm for the high-sulfate sulfoaluminate is present in the upper curve (at about 120 °C) but is almost completely suppressed in the lower curve. However, it is significant that there is no indication (at about 200 °C) of the presence of the low-sulfate or solid-solution phase in either curve.

Perhaps a word should be said here in explanation of the prominent endotherms between 100

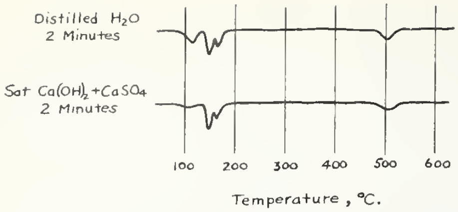

FIGURE 5. *DTA curves of a portland cement hydrated for two minutes with distilled water and with a solution saturated with* $Ca(OH)_2$ *and* $CaSO_4$.

and 150° in several of the curves of figure 3. These endotherms could be attributed mistakenly to the high-sulfate sulfoaluminate were it not for the fact that they were obtained on samples of clinker to which no gypsum had been added. The percentage of SO_3 in the clinker itself is too small to produce any such quantity of sulfoaluminate.

There is considerable reason for believing that these endotherms are due to calcium silicate hydrate, as mentioned previously. It will be noted that the size of the endotherms associated with this phase, when dried similarly, increases with time at a rate roughly proportional to the quantity of calcium hydroxide, strongly suggesting that they are related to the hydration of the calcium silicates.

Simplified Summary of Reactions

Based on the foregoing considerations, the writer would like to suggest the following as a simplified statement of the course of the early hydration reactions at ordinary temperature: An ordinary portland cement, when mixed with water to form a paste of a water-cement ratio in the range of 0.4 or 0.5, and cured in a moist atmosphere, begins to react immediately. The gypsum and alumina-containing phases of the clinker immediately start to react to form the high-sulfate calcium sulfoaluminate. Tricalcium silicate also starts to hydrolyze at a very early stage, and the solution soon becomes supersaturated with calcium hydroxide.

The calcium sulfoaluminate gradually increases in amount, and the gypsum is gradually used up by reaction with the aluminates. The gypsum has generally disappeared after about 24-hr hydration. Sometime later, depending upon the amount of gypsum present and the characteristics of the particular cement, the low-sulfate calcium sulfoaluminate, or a solid solution of this compound with hexagonal tetracalcium aluminate hydrate, begins to make its appearance as a solid phase.

Concurrently with the sulfate-aluminate reactions, the C_3S is hydrating, and as evidence of this, crystalline calcium hydroxide begins to form. This compound can sometimes be detected by DTA after 2 or 3 hr. It continues to increase in amount with time, and is a rough indicator of the development of the calcium silicate hydrate phase. Dicalcium silicate hydrates also, but at a much slower rate than the C_3S, and contributes its share to the total calcium silicate hydrate.

The minor clinker constitutents, such as the alkalies, may alter the rate of hydration of a cement, but the present evidence seems to indicate that the chemical nature of the hydration products is not radically altered by the percentages of these minor constituents normally present. The role of the iron-containing phases in the early hydration reactions is uncertain at the present time. Some investigators believe that compounds analogous to the calcium sulfoaluminates are formed, or perhaps solid-solution compounds containing both iron oxide and alumina. More will be said of this subject later.

Nature and Composition of Alumina-Bearing Phases

Absence of $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$

It is perhaps appropriate at this point to explain the absence of the cubic tricalcium aluminate hexahydrate ($3CaO{\cdot}Al_2O_3{\cdot}6H_2O$) from the above picture of the early hydration reactions. Previously cited phase equilibria studies [10, 11, 12] have shown that this compound is the stable phase in equilibrium with calcium hydroxide and high-sulfate sulfoaluminate in the system $CaO–Al_2O_3–CaSO_4–H_2O$. These studies also showed that the hexahydrate, although stable, is greatly retarded in its crystallization, and the low-sulfate double salt forms instead.

Kalousek, Davis, and Schmertz [14] found no evidence of the hexahydrate in hydrating cement, although they did find evidence of its presence in clinkers hydrated for 28 days and longer. Their conclusion was that only very small amounts of SO_4^{--} are required to inhibit the formation of the hexahydrate and that this SO_4^{--} stabilizes the hexagonal structure of the low-sulfate double salt or solid solution. Later work appears to confirm this explanation.

Experiments conducted in our laboratories have suggested another factor which does not seem to have been mentioned by other investigators. This is the effect of the calcium silicates on the hydration of the tricalcium aluminate. It is well known that tricalcium aluminate when mixed alone with water hydrates very rapidly, producing mainly hexahydrate along with some tetracalcium aluminate hydrate and dicalcium aluminate hydrate ($2CaO{\cdot}Al_2O_3{\cdot}8H_2O$). It hydrates somewhat less rapidly when mixed with saturated calcium hydroxide solution, but still produces considerable $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$.

In our experiments we found that when C_3A was mixed with C_3S, or a mixture of C_3S and C_2S, and hydrated, the hexahydrate was prevented from forming, and only the hexagonal calcium aluminate hydrate was produced. We have not found evidence of the hexahydrate by DTA in either clinkers or cements at ages up to 7 days. However, this is not to say that this compound may not form after longer periods of hydration.

The retarding action of calcium hydroxide is also frequently mentioned in the literature, particularly as it applies to the hydration of the calcium aluminates. Thus, it would seem that the hydration of the C_3A in a cement, particularly at early ages, is controlled by the combined effect of the calcium sulfate, the calcium hydroxide, and the calcium silicates present.

New Data on Hydrated Calcium Aluminates and Sulfoaluminates

The actual composition of the hexagonal solid-solution phase at various stages of hydration is a problem which requires further elucidation. It appears to have been generally accepted by most investigators that the low-sulfate calcium sulfoaluminate and the tetracalcium aluminate hydrate form a solid-solution series. However, it has not been possible up to this time, so far as the writer is aware, to determine the position in this series of the hexagonal phase present in a hydrating cement at any particular time. Unfortunately, the DTA curves of the two end members of the series are very similar, particularly the curves arising from the small amounts present in hydrating cement. The published X-ray diffraction patterns [24] also are similar, but possibly differ enough so that with refined techniques the X-ray method might be used to indicate the composition of the solid solution.

Considerable material is found in the recent literature on the calcium aluminate hydrates and the calcium sulfoaluminate compounds. Nicol [20] studied the reactions of the pure calcium aluminates with a limited amount of water, using the methods of thermogravimetric analysis and X-ray diffraction.

Roberts [25] studied the calcium aluminate hydrates and reported several hexagonal forms which had not been described previously. At 25 °C a hydrate with the formula, $4CaO \cdot Al_2O_3 \cdot 19H_2O$, was found which Roberts believed to be the stable form in contact with solution. It appears from this work that $4CaO \cdot Al_2O_3 \cdot 13H_2O$ is actually a dehydrated form of this more highly hydrated compound. Roberts found two forms of the $13H_2O$ hydrate and also two other tetracalcium aluminate hydrates having water contents of $11H_2O$ and $7H_2O$. Thus, the situation appears to be quite complex, and much additional work will be required to correlate these compounds with those which may be present in actual hydrating cements.

Astreeva and Lopatnikova [26] have recently studied the composition and properties of the hydrated calcium sulfoaluminates. They state that the composition and structure of the sulfoaluminates arising from the various alumina-bearing cement clinker compounds differ, basing their conclusion on microscopic, chemical, electron-diffraction, and electron-microscope determinations. Two of the conclusions of these authors are of particular interest. They state that during the hydration of the aluminates and aluminoferrites in the presence of gypsum, the high-sulfate sulfoaluminate always forms independently of the quantity of gypsum, and that if insufficient gypsum is present to react with all of the calcium aluminate to form the high-sulfate sulfoaluminate, the remainder forms the hexagonal hydrated calcium aluminate ($4CaO \cdot Al_2O_3 \cdot 13H_2O$). They further state that the calcium monosulfoaluminate or low-sulfate form is not produced.

These conclusions are presumably based on differences in the measured properties of the phases. Astreeva and Lopatnikova also observed that part of the water of crystallization can be driven off from crystals of the hydrated calcium sulfoaluminates without breaking down the original crystal form, but that further removal of water leads to destruction of the crystals.

Turriziani and Schippa [27] have made a detailed study of the system $CaO–Al_2O_3–CaSO_4–H_2O$ by X-ray and DTA methods. They concluded that the DTA method is capable of semiquantitative results in the identification of the various sulfoaluminate phases occurring in this system. According to them, it is possible under favorable conditions to determine with good approximation the range of molar ratios, $CaSO_4:Al_2O_3$, of the solids. These investigators believed that they had observed a new hexagonal phase similar to the low-sulfate sulfoaluminate but possessing a different X-ray diffraction pattern. Further work indicated that the differences in X-ray spacings were related to the humidity conditions under which the samples were dried.

One highly important observation of Turriziani and Schippa relates to the X-ray diffraction patterns and optical properties of solids with a molar ratio, $CaSO_4:Al_2O_3$, of less than unity. The optical properties were found to vary with this ratio, as would be expected in the case of a true solid-solution series. However, the X-ray diffraction patterns of all materials with a molar ratio less than unity showed the lines of tetracalcium aluminate hydrate, as well as those of the low-sulfate sulfoaluminate, irrespective of the $CaSO_4$ content. The intensity of the $4CaO \cdot Al_2O_3 \cdot 13H_2O$ lines increased with decreasing calcium sulfate content, while that of the $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ lines decreased. These authors conclude that it is possible that the two compounds may intercrystallize into a solid composed of alternating layers of both compounds. Further work is needed to clarify this situation. If Turriziani and Schippa's observations are confirmed, then the earlier work of Kalousek [28] and Jones [10] must be revised.

Other Complex Hydration Products

Calcium sulfoferrites. It was mentioned previously that compounds analogous to the sulfoaluminates but containing iron oxide in addition to alumina are possibly formed in hydrating cement paste. There is good evidence for the formation of these compounds in the pure oxide systems, but in the cement-water system the evidence is largely circumstantial. In their discussion of Steinour's paper at the Third Symposium [1], Malquori and Cirilli [29] presented data confirming the existence of calcium sulfoferrites analogous to the high-sulfate and low-sulfate sulfoaluminates.

Relatively little can be found in the literature of the intervening years relative to these interesting compounds. Budnikov and Gorshkov [30] have investigated the reactions of calcium aluminates and calcium aluminoferrites with gypsum. Their X-ray diffraction patterns showed the presence of the high-sulfate calcium sulfoaluminate, in mixtures of gypsum with synthetic $6CaO{\cdot}2Al_2O_3{\cdot}Fe_2O_3$, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, and $6CaO{\cdot}Al_2O_3{\cdot}2Fe_2O_3$. Reactions of dicalcium ferrite ($2CaO{\cdot}Fe_2O_3$) with gypsum gave lines corresponding to the high-sulfate calcium sulfoferrite. Their original paper was not available to the writer, but the abstract makes no mention of solid solution between the alumina and iron compounds. Malquori and Cirilli [29] believed that such solid solutions were possible.

Contrary to the results cited above, Watanabe and Iwai [31], using electron microscopy, X-ray diffraction, and DTA, observed no compound corresponding to the composition $3CaO{\cdot}Fe_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$ in the hydration products of dicalcium ferrite and calcium sulfate. Schippa [32] recently studied the system $CaO\text{-}Fe_2O_3\text{-}CaSO_4\text{-}H_2O$ and reported the existence of both high-sulfate and low-sulfate analogs. The low-sulfate compound was found to exist in two different hydrated forms, depending on the relative humidity of the medium.

The above investigations were made on systems of pure compounds and, thus, are not directly applicable to cement hydration. The following statement of Steinour in his Third Symposium paper [1] still appears to stand today: "The role of iron oxide in the reactions of cement hydration is still an obscure matter on which much more work must be done."

Calcium silicoaluminates. The possibility of complex phases containing other constituents should not be overlooked. References to various calcium silicoaluminates have appeared frequently in the literature. Thus, we have the phase known as Strätling's compound (also called "gehlenite hydrate") with the formula $2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}XH_2O$ [33, 34].

Turriziani and coworkers [35, 36, 37] have confirmed the existence of this compound and have identified it in the reaction products of dehydrated kaolin and calcium hydroxide at ordinary temperature. Benton [38] also identified Strätling's compound in the reaction products of calcined kaolin and calcium hydroxide, and of calcined kaolin and portland cement, at 38 °C (100 °F).

Another calcium silicoaluminate is a compound analogous to the high-sulfate calcium sulfoaluminate. This compound was prepared by Flint and Wells [39], who also were able to obtain a phase corresponding to the low-sulfate sulfoaluminate, with the formula $3CaO{\cdot}Al_2O_3{\cdot}CaSiO_3{\cdot}12H_2O$. Mohri [40] has recently reported the formation of one of these phases in the hydration products of preparations in the system $CaO\text{–}Al_2O_3\text{–}SiO_2$ and gives an X-ray diffraction pattern and an electron micrograph.

The hydrogarnet solid solutions should also be mentioned, although their relation to the hydration of cement at ordinary temperature is not at all clear. These compounds can be readily prepared under hydrothermal conditions, but although tricalcium aluminate hexahydrate ($3CaO{\cdot}Al_2O_3{\cdot}6H_2O$) is considered to be one end member of this series, the mixed hydrogarnets have not, to the writer's knowledge, been reported as having been formed at room temperature. However, zur Strassen [41] apparently believes that both hydrogarnets and Strätling's compound (gehlenite hydrate) may be produced during hydration at ordinary temperature. He states that there may be formed, besides calcium silicate, aluminate, and ferrite hydrates, complex hydrates which simultaneously contain lime, alumina, and silica or alternatively lime, alumina, iron oxide, and silica. In experiments described by him there were found only "gehlenite hydrate" and members of the hydrogarnet solid-solution series.

Calcium carboaluminates. Other complex compounds of possible significance are the calcium carboaluminates. At least two forms have been reported, corresponding respectively to the high- and low-sulfate forms of calcium sulfoaluminate. These compounds are important in the present discussion, not only because they may be formed by reaction of a moist hydrating cement paste with carbon dioxide in the air, but also because most cements contain small quantities of alkali carbonates, which may possibly react to produce carboaluminates when the cement is mixed with water.

Bessey [42] prepared both high- and low-carbonate forms with the formulas, $3CaO{\cdot}Al_2O_3{\cdot}3CaCO_3{\cdot}XH_2O$ and $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}XH_2O$. Although there has been some speculation concerning the possible occurrence of such compounds in hydrating portland cement, evidence for such occurrence has been lacking, and it has been assumed quite generally that calcium carbonate is the only product of the reaction of portland cement with carbon dioxide, as well as with alkali carbonates in cement.

Recently, however, Turriziani and Schippa [43] have identified the low-carbonate form in a film formed on the surface of the water contained in a vessel in which cubes of alumina cement paste had been curing for a period of about 2 years. These authors also prepared this compound in the laboratory, and their identification is based upon the agreement of the X-ray patterns. Carlson [44] in a study of the system $CaO–Al_2O_3–H_2O$ at 1 °C believed that he had obtained a carboaluminate, probably having the formula, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$, as the result of CO_2 picked up during storage of his reaction mixtures. Budnikov and Azelitskaya [45], in a very recent article on the effect of added electrolytes on the hardening process of C_3A, state that in the presence of 0.5 percent of calcium carbonate, large amounts of gel-like $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 18H_2O$ are formed. Until recently, however, there has been no suggestion that a calcium carboaluminate might be formed in a hydrating portland cement paste.

Some experiments in our laboratories, using the DTA method, may be of interest in this connection. A cement was hydrated for 24 hr at room temperature at a water-cement ratio of 0.35, both with and without 2 percent of sodium carbonate by weight of the cement. The DTA curves are shown in figure 6. Curve No. 2, which represents the cement to which the sodium carbonate had been added, bears a marked resemblance to the curve for the monocarboaluminate given by Turriziani and Schippa [43] in their paper. These data are only suggestive, and it is hoped that it may be possible to confirm the presence of carboaluminate by X-ray diffraction methods.

In spite of considerable evidence indicating the possibility of the formation of various complex alumina-bearing compounds during the early stages of portland cement hydration, it is obvious that our knowledge of the precise state of affairs is very limited. We believe there is good evidence of a compound closely akin to the high-sulfate calcium sulfoaluminate or ettringite which forms at very early ages, and likewise, there is rather convincing evidence of a hexagonal phase related to the low-sulfate sulfoaluminate, which makes its first appearance at a somewhat later time. We do not know, however, to what extent these phases are solid solutions containing appreciable amounts of iron, silica, and carbonates. The solution of this problem is one of great difficulty, and we must expect that progress will be slow.

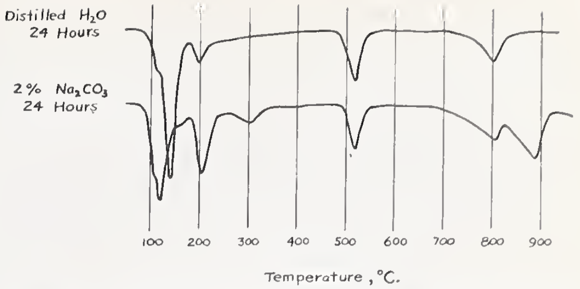

FIGURE 6. *DTA curves of a portland cement hydrated for 24 hr with distilled water and with a solution containing 2 percent of* Na_2CO_3 *by weight of cement.*

An example of the type of question which comes to mind is as follows: Is the hexagonal phase, which appears after the gypsum is depleted, similar to the one which forms almost instantaneously when a clinker without gypsum is mixed with water, or are there significant differences in composition? The phase represented in early hydration of clinker, for example, may be essentially pure tetracalcium aluminate hydrate, whereas the phase appearing later in hydrating cement may possibly represent a more complex solid solution or interlayered compound, containing any or all of the substances mentioned above. It will be necessary first to resolve some of the contradictions in the literature and then, as new methods and techniques make it possible, to correlate the well-established facts on the chemical systems involved with results obtained with the cement-water system.

Reactions of Calcium Silicate Phases

Except for the very rapid hydrolysis reaction of C_3S, whereby the solution quickly becomes supersaturated with calcium hydroxide, the observable reactions of the calcium silicates of cement are much slower than those of the calcium aluminates and aluminoferrites. Thus, definite crystalline compounds cannot usually be identified until calcium hydroxide begins to crystallize after several hours of hydration.

Until recent years it was not possible to distinguish or to conclusively prove the existence of crystalline calcium silicate hydrates in cement paste, and consequently, the calcium silicate hydrates were considered to be essentially amorphous. It is now well-established that the so-called "cement gel" is composed essentially of calcium silicate hydrate crystals but of such a small particle size as to be colloidal in behavior. The "crystallization" theory of Le Chatelier and the "colloidal" theory of Michaelis, long considered to be in opposition to each other, are, thus, now recognized as both being partially correct.

Since the calcium silicate hydrate occurring in portland cement paste is poorly crystallized, even after rather long periods of hydration, it is studied with great difficulty at very early ages. Thus, while we know that the calcium silicates of clinker are entering into hydration reactions from the very moment of water contact, we find that the conventional methods of study do not provide much information concerning the nature of the hydration product initially formed. Nevertheless, it is frequently possible to gain considerable insight into the early chemical reactions by indirect methods.

The literature records a great deal of research on the hydration products of the calcium silicates. However, these studies have of necessity been made on products obtained only after days or weeks of hydration, since the materials obtained at early ages do not give recognizable X-ray patterns (other than that of $Ca(OH)_2$). Consequently, these studies indicate the character of the ultimate hydration products but do not tell us much concerning the nature of these materials during their early stages of formation.

This work, like that relating to the calcium aluminates and ferrites, is properly the subject of another paper being given at this symposium and will not be considered in detail in the present discussion. Suffice it to say here that the hydration product of both C_3S and C_2S at ordinary temperature is generally considered to be a poorly crystallized, extremely fine-grained material resembling the mineral tobermorite. It is essentially the material designated as CSH(I) by Taylor [46] and as CSH(B) by Bogue [47], perhaps mixed also with CSH(II) (Taylor) or C_2SH_2 (Bogue). There is evidence that this tobermorite-like calcium silicate hydrate is also produced in hydrating portland cement paste [15].

It has been mentioned previously in connection with the hydration of the calcium aluminates and aluminoferrites that portland cement reacts very rapidly with water when mixed to form a paste. The same is true for C_3S, but the reaction of C_2S is much slower. The concentration of lime quickly reaches saturation and continues to increase to give a metastable supersaturated solution. This calcium hydroxide probably comes mainly from the C_3S, since pure C_3S behaves similarly. However, the silica in solution is very low at 1 min, which is about the earliest time after mixing at which it has been possible to make measurements. Since the rapid release of calcium hydroxide into the solution is evidence of a considerable early reaction, the question naturally arises as to the form of the silica or calcium silicate which is formed.

It was mentioned previously in connection with the hydration of the alumina-bearing compounds, that although the concentrations of alumina and silica are always found to be very low at 1 min and longer after mixing, there is some reason to believe that they may reach much higher values within the first minute. Whether the silica concentration is initially high would seem to be of great importance, not only with respect to the nature of the very early hydration products of the calcium silicates but also as it relates to the mechanism of hydration. By the latter is meant the more or less traditional dissolution and precipitation theory, versus the topochemical or solid-state reaction theory of hydration. I should like to discuss these questions in some further detail.

Nature of Early Calcium Silicate Hydrate

The similarity between the hydration of pure C_3S and of fully retarded portland cements strongly suggests that the setting phenomenon in cement is produced mainly by the products of the hydration of the C_3S. This has been well stated by Steinour [13]. However, while there is evidence of almost instantaneous reaction of C_3S with water with formation of a supersaturated solution of calcium hydroxide, yet no structure begins to develop until the time of initial set.

These facts strengthen the view that the calcium silicate hydrate is in a colloidal form during this period. This concept would seem to be confirmed by the results of Smirnova, Zaitseva, and Rehbinder [48], indicating that the surface area increases on the order of tenfold during the first 30 to 45 min of hydration. Without here going into the relative merits of the solution-precipitation theory as against the solid-state reaction theory, it would be expected, in any case, that the formation of hydration products on or near the cement grains would rapidly choke or quench the initial rapid reaction. This behavior appears to be the case, although the data on heat liberation obtained by Forbrich [49] and Lerch [50] show that this period of reduced rate of reaction is followed by a period of accelerated reaction prior to initial set. The reason for this delayed acceleration is not clear but must be related in some way to the fundamental mechanism of hydration.

Solid-State Reactions

Cement chemists have proposed from time to time that hydration is fundamentally a group of solid-phase reactions. This mechanism was suggested by Hansen [5] in his discussion of Steinour's paper at the Third Symposium. Hansen has recently developed his hypothesis in greater detail [7]. Jeffery [51] also discusses the question of possible hydration by solid-state reaction. Hansen's argument is based largely on the fact that although C_3A and C_3S appear to react very rapidly with water and with soluble constituents such as chlorides and sulfates in solution, only very small amounts of alumina and silica are found in the extracts as early as 1 min after mixing.

Steinour [8] shows that there is reason to believe that the alumina and silica concentrations may have been much higher during the critical first minute. If this condition were to be demonstrated conclusively, then it seems that the solid-state reaction theory would be rather effectively refuted for this very early age. This statement is particularly true of Hansen's hypothesis, since he assumes diffusion into the solid crystals of the clinker phases but very little outward diffusion of dissolved constituents into the solution.

In connection with the question of solid-state or, strictly, in this case, solid-liquid reactions, it should be noted that Strelkov [3] favors this type of mechanism. Strelkov, however, visualizes the formation of reaction products on the surfaces of the grains that are highly soluble because of their poorly ordered structure. These highly soluble products then dissolve and form supersaturated solutions from which the stable hydration products of lower solubility precipitate.

Of interest, also, is Strelkov's observation that when the liquid was extracted under constant pressure, the concentration of dissolved constituents increased with time, and also that the concentration increased with pressure for a given time of extraction. This behavior led him to conclude that the liquid phase is more concentrated in the vicinity of the surface of the hydrating grains than in the interstices between them. Steinherz and Welcman [4] also believe that the hydration processes are topochemical or solid-state reactions or else take place in the very close proximity of the clinker grains. They noted that the chemical composition of the liquid extracted at one minute was not influenced significantly by the fineness of the cement.

Van Bemst [22] concluded, from studies of the hydration of the pure calcium silicates at ordinary temperatures, that the hydration of C_3S first results in CSH(I) by a process of solution and precipitation, before the solution becomes saturated with $Ca(OH)_2$. As the concentration of $Ca(OH)_2$ increases so as to reach saturation or supersaturation, the higher-lime hydrate CSH(II) forms directly on the surfaces of the hydrous silicate grains by an unknown mechanism. This latter behavior certainly resembles a solid-state reaction. Van Bemst believes that the hydration of β-C_2S results in CSH(I), and that the mechanism is qualitatively the same as that for the formation of CSH(I) from C_3S.

Funk [52] found that water vapor alone at 100 °C can act on β-C_2S to produce a high-lime tobermorite phase as loose acicular crystals, but without strength development. An aqueous solution phase was necessary for hardening to take place. From this observation he concluded that some mechanism other than solution and precipitation may be at work during the reaction of water and β-C_2S.

A satisfactory decision on the relative importance of solid-phase reactions in the hydration of cement must await further research. It may well turn out that both solution-precipitation, and topochemical reactions are involved, with the solution-precipitation phenomena predominating at the very early ages, while the later reaction is governed primarily by the solid-state type of mechanism, as suggested by Lea [21, p. 223]. It appears that the evidence is pointing in this direction.

Protective Coatings

One thing is certain; namely, that adsorption and surface effects play a major role in the early reaction process. It seems nearly as certain that part, at least, of the early formed hydration product is deposited on or very near the surfaces of the clinker grains. In the case of grains of C_3A and aluminoferrite, this coating is undoubtedly a phase similar in composition to the high-sulfate calcium sulfoaluminate, based on evidence previously cited. In the case of C_3S grains, the coating is probably a very poorly crystallized calcium silicate hydrate of colloidal particle size. It seems likely that these phases are fairly distinct and "pure" when they originally form, but that as hydration progresses they become more and more intermingled.

It is possible that the coating of calcium sulfoaluminate which forms on the surfaces of the alumina phases, as well as the calcium silicate hydrate which forms on the anhydrous silicate particles, is initially of a colloidal nature and acts as a protective film, slowing down the original very rapid reaction. The concept of protective coatings is, of course, not at all new, but is found in the early cement literature. In the case of C_3A and the calcium aluminoferrite, the coating does not prevent reaction but simply controls it, preventing a rapid hydration of these compounds as long as gypsum is available to maintain it.

The action of the coating on the C_3S grains needs further study. As previously mentioned, it appears that the hydration of C_3S is initially rapid, declining subsequently to a relatively low rate, after which it accelerates again at about the time of initial set. This behavior suggests that for some unknown reason the retarding ability of the coating loses its effectiveness at about this time.

Fractional Rate Hypothesis

Several years ago research workers at the Portland Cement Association reported data which appeared to indicate rather conclusively that the compounds or phases of cement do not hydrate independently or at the same rate as they do when hydrated individually [53, 54, 55]. From the results of three different lines of investigation, these researchers concluded that the cement compounds hydrated at equal fractional rates—that is, when one compound was one-half hydrated, each of the other compounds was also one-half hydrated. Thus, the quantity of any particular compound which had hydrated at a given time was believed to be dependent upon the percentage of that compound present in the cement. This conclusion was rather surprising, since C_3A and C_2S, for example, have greatly differing hydration rates when hydrated individually.

The experimental results which led the P.C.A. investigators to formulate the hypothesis of equal fractional rates were those indicating a constant ratio between the heat of hydration and the nonevaporable or combined water, a constant ratio between surface area and combined water, and equal fractional rates of disappearance of the unhydrated clinker phases as determined by X-ray diffraction.

Before proceeding further, it should be stated that the hypothesis was never suggested as applying to all types of cement, but only to the United States of America Types I and III and not to these in the very early stages of hydration. The hypothesis thus is perhaps not directly pertinent to the subject of this paper, since we are interested here mainly in the early reactions. Yet it is of interest as it illustrates how various approaches can be used to bear upon a particular problem of cement chemistry.

The determination of the rates of hydration of the cement compounds by X-ray diffraction is a direct method and, granting that sufficient accuracy is possible, it should give valid results. The constancy of the ratios between the heat of hydration or specific surface on the one hand, and the nonevaporable water on the other hand, constitutes less direct evidence. Although equal fractional rates of hydration should give constant ratios of heat of hydration and surface area to combined water, it appears that the fractional rates need not be equal to lead to this result.

Thus, we may have fractional rates of hydration for the different phases which differ markedly from one another, yet if these fractional rates bear a constant ratio to one another during hydration, the gel produced will tend to have a constant composition, and constant ratios of heat of hydration and surface area to combined water will be observed. This relationship would hold until one of the phases had completely reacted.

While more precise results may prove the fractional rate hypothesis to apply only imperfectly to the hydration of cement, still the data indicate that once a fairly steady state is developed, the average composition of the reaction products being formed does not change greatly with time. In other words, hydration seems to produce, in general, more and more of the same kind of gel. This average composition would not be expected to hold in the very early stages of hydration, and indeed the data indicate that it does not. The reactions involving the alumina phases and gypsum, which are initially very rapid and later much retarded, appear to be relatively independent of the others.

Diffusion as a Controlling Process

The tendency toward equal or constant fractional rates of hydration of the cement minerals suggests that some mechanism is operating which is able to overcome, to a considerable extent, the characteristic individual hydration rates. This hypothesis is compatible with the idea that, following the initial very rapid reactions, the hydration of cement is controlled by diffusion through the film or coating of hydration products on the cement grains. A very interesting discussion of this matter by zur Strassen has recently been published [56]. He concludes that as an approximation, the hydration of tricalcium silicate is diffusion-controlled, following a square-root law, while that of dicalcium silicate is linear. In C_3S the reaction takes place so rapidly that the supply of water is limited. The reaction therefore follows the law of diffusion, according to which the rate of reaction is inversely proportional to the thickness of the reacting layer. According to zur Strassen, the retarding effect of the gel film applies to C_3A and C_4AF also, but the hydration of C_2S is already so slow that it remains linear for a considerable length of time, and the controlling effect of diffusion comes into play only with a greater thickness of the gel layer.

Taking the experimental data, together with theoretical considerations, we arrive at a picture somewhat as follows: The initial reactions are dominated by the hydration of the aluminate and ferrite phases and their reactions with gypsum. The hydration reactions of the clinker minerals are never truly independent but approach closer to this situation at the beginning of hydration. As coatings of reaction products form, there is a slowing down of the most rapid reactions and a tendency toward equalization of rates or at least the establishment of fairly constant fractional rate ratios between the hydration reactions of the different clinker phases. The overall average hydration rate is controlled largely by diffusion of water through the gelatinous hydration products already formed. With cements unusually high in C_2S, the later hydration is controlled by the very slow intrinsic hydration rate of this compound rather than by the diffusion mechanism.

Chemical Nature of Cement Gel

Related to the problem of relative hydration rates and whether the cement compounds hydrate, to an appreciable degree, sequentially rather than simultaneously, is the question of the chemical constitution of the resulting gelatinous hydration product. As pointed out by Brunauer [54], the gel comes from all the constituents of the cement. Is the gel a very fine-grained physical mixture of chemically different hydration products, or is it fairly homogeneous, even down to molecular dimensions, so that the ultimate gel particles may be thought of as being copolymers of the hydrates?

Hydration studies at early ages favor the concept of chemically distinct hydrates, with DTA curves illustrated earlier in this paper being examples of such evidence. On the other hand, the DTA data of Kalousek, Davis, and Schmertz [14], obtained on older pastes, indicate a merging of the thermal effects of the different hydrates into one large composite peak suggestive of a single homogeneous substance.

The fact that properties such as heat of hydration, surface area, and combined-water content can be calculated as though they were additive with respect to the different cement compounds has been used as an argument in favor of a mixture of distinct hydration products. Brunauer [54] points out, however, that even if the gel is a copolymer of compounds, some additivity would not be surprising. Thus, we may say that the gel probably becomes progressively more homogeneous with time of hydration but that the scale of dimension of this homogeneity is uncertain. Electron microscopy and electron diffraction can be expected to throw additional light on the physical and chemical nature of the ultimate gel particles.

Development of Structure

The physical mechanism of the development of structure in a cement paste, corresponding to setting, has been the subject of much debate. The transition from a mobile or plastic paste to a semirigid mass without plasticity is gradual, but is obvious to any observer. The physical cause of this stiffening or setting is not so obvious.

A paste of normally retarded cement immediately after mixing is a suspension of discrete cement particles in water. Powers [57] and Steinour [58] showed that normally this suspension soon begins to act as one continuous flocculated mass. Their bleeding studies showed that in spite of the rapid chemical reactions which take place on mixing, the bleeding rate is remarkably constant for a considerable time, indicating no radical change in the physical state of the cement suspension.

They interpreted this constancy to mean that the degree of subdivision of the cement was not altering significantly during this period. However, this conclusion is at variance with the results of Smirnova, Zaitseva, and Rehbinder [48], who reported that the surface area may increase tenfold, reaching a maximum value during the first 30 to 45 min. It is difficult to reconcile such a large increase in surface area with a constant bleeding rate.

Most writers seem to view the stiffening of a cement paste as being caused by the increasing volume of hydration products, with a corresponding decrease in distance between particles, until finally plastic flow is greatly restricted, and cohesive forces begin to operate as more and more of the particles are drawn into contact with one another. This mechanism is essentially the picture outlined by Lea [21, p. 223] and, in somewhat more detail, by Jeffery [51]. Hardening then would be due to an increase in the number of "welds" between gel particles as hydration proceeds.

A rather different mechanism of cement setting has been proposed by the Russian school of investigators. This theory, which is based on an earlier one of A. A. Baikov, is developed, with some variations, in papers by a number of authors, including Okorokov [59], Segalova, Rehbinder, and Luk'yanova [60], Rehbinder [61], Sivertsev [62], and Strelkov [3]. The process is thought of as consisting of three distinct phases, which, however, may overlap in time.

The first is a self-induced dispersion or "colloidization" of the cement particles, particularly of the C_3A. This dispersion is followed by the formation of a coagulated thixotropic structure from the dispersion of cement particles and hydration products, and finally by the development of a crystalline structure of new hydrated compounds through crystallization out of a supersaturated solution. The formation of the coagulated structure corresponds to setting, and the strengthening of the structure through formation of crystalline hydrates brings about the later hardening.

Adsorption plays a prominent part in this theory, and the effect of hydrophilic retarders such as calcium lignosulfonate is explained on this basis. These retarders promote the self-dispersion of the cement grains, by which is meant a breaking down into particles of colloidal dimensions and the stabilization of the resultant suspension, thus delaying the coagulation phase. The process is considered to affect the C_3A to the greatest degree, with C_3S affected less strongly. It is believed to operate also in ordinary gypsum-retarded cements without admixtures. The Russian theory combines features of both the earlier crystallization and colloidal theories of cement setting and hardening, placing the colloidal phase at an earlier point in the hydration process than the crystallization phase. Certain aspects of the theory harmonize well with the results of other recent investigations. In particular should be mentioned the prominent place given to adsorption and colloidal phenomena. On the other hand, it contains features which are difficult to reconcile with other data.

One of these apparent conflicts is the evidence for a large increase in surface area of the cement particles during the early stages of hydration, as determined by the rate of adsorption of radioactive calcium-45 [48], and the results of the bleeding studies of Powers [57] and Steinour [58], which indicated that the particle size of the cement did not change significantly.

Also, the Russian theory pictures the setting as being caused primarily by coagulation of the dispersed aluminate phases, whereas there is much other evidence indicating that in the absence of the abnormal "flash" set or "false" set, the C_3S is mainly responsible for the setting. As mentioned previously, pure C_3S sets in a manner very similar to a cement retarded by a sufficient amount of gypsum. According to Rehbinder [61], the hydration processes of the silicate components contribute to the later hardening and strength development, but relatively little to the setting. Additional work is clearly indicated to help resolve these difficulties.

There is no question that the surface area of a cement paste increases tremendously by the time it has set and hardened. The anomaly pertains only to the initial period prior to the attainment of set. To state the question in other words, "Does the surface area of the hydration products increase rapidly soon after mixing, as the work of the Russian investigators indicates, or does it remain relatively unchanged for a considerable length of time, as the bleeding data of Powers and Steinour imply?" In this connection it should be noted that there may be some loss of plasticity in a normal cement paste in the period preceding what is ordinarily called initial set.

Published information on the viscosity or consistency of cement pastes during the early period of hydration is scanty, however, and somewhat lacking in agreement, doubtless due to differences in cements and conditions of test. Dorsch [63] performed experiments which indicated a rapid increase in viscosity of cement pastes for the first hour after mixing, followed by a shorter period during which it remained unchanged. The viscosity then increased again as setting occurred until no flow could be obtained.

Kozlowski [64], in a recent discussion, shows a consistency-time curve for portland cements which indicates a constant low consistency up to 2 hr, followed by a rather sudden and rapid stiffening, with a leveling off at about 4 hr. The original low value was restored by vigorous stirring, after which the paste again stiffened, attaining initial set at about the seventh hour. In these tests the consistency was measured with a penetration rod.

Tests made in our laboratories, using an adaptation of the Halliburton Thickening-Time Tester for oil-well cements, showed no significant thickening up to 2 hr after mixing for pastes of gypsum-retarded cements at a water-cement ratio of about 0.40 and a temperature of 80 °F (27 °C). These results are in agreement with Kozlowski's insofar as they indicate no appreciable structure formation in the first 2 hr. However, it must be emphasized that the test methods were quite different. Our pastes were continuously agitated during this period, while Kozlowski's were not. It is probable, too, that more sensitive methods of measurement would detect changes in consistency at this early age. Further research on this aspect of early hydration should prove fruitful.

A widely held view concerning the development of strength and rigidity in a hydrating portland cement paste is that these properties are probably due to a combination of physical forces often known as van der Waal's forces and chemical-bond forces [54, 55]. Another view emphasizes the idea that the rigidity is derived from the interlocking and intertwining of very minute fibrous crystals [65].

These two concepts are not necessarily in opposition. It is very likely that all of these factors enter into the hardening process. An experiment recently described by Czernin [66] demonstrates in an almost spectacular way the magnitude of the physical or van der Waal's forces when the surface area of a material becomes very great. Czernin ground 100 g of quartz sand to a Blaine surface area of 20,000 cm^2/g and molded this powder with 20 g of water. A specimen formed from this paste was able to support a weight of 10 kg. A nearly completely hydrated cement paste has been shown to contain about 20 percent of combined water and to have a surface area of the order of 2,000,000 cm^2/g. Consequently the high strength obtained by cement in time is not at all surprising.

Hayden [67] presents data which indicate that no more than 0.5 percent of water of hydration may be required to bring about final set. Czernin points out that even 0.5 percent of fixed water may be equivalent to 50,000 cm^2/g of surface area when one considers that 20 percent of combined water produces 2,000,000 cm^2/g of surface area. From this it appears that physical forces related to surface area may contribute significantly to the setting phenomenon.

Conclusion

In summary, we conclude that our knowledge of the hydrated calcium aluminates and ferrites and of the calcium silicates has been materially increased in the last 8 years but that there are still many unanswered questions regarding the details of the hydration of actual portland cement at ordinary temperature. We find the evidence indicating that the initial reactions of hydration are extremely rapid and are dominated by the hydration of the aluminate and ferrite phases and their reactions with gypsum. The C_3S reacts rapidly with water also, and although there is a strong suggestion that the initial setting or development of structure is due primarily to the C_3S, this phenomenon normally does not begin for several hours.

We find considerable evidence that the clinker minerals exert a significant influence on one another during their hydration. They never hydrate in a truly independent manner but approach closely to this situation at the very beginning of hydration. Early reaction products probably form coatings on the cement grains, thereby slowing down the most rapid reactions and tending to produce an equalization of rates or the establishment of relatively constant fractional rate ratios between the hydration reactions of the different clinker phases. It appears that the overall average hydration rate is controlled largely by diffusion of water through the gelatinous hydration products already formed.

The evidence is conflicting as to whether the early hydration reactions are basically the result of solution and precipitation or whether they are more properly described as topochemical or solid-state reactions. It appears likely that the very earliest reactions take place by solution and precipitation, while the later hydration is diffusion-controlled and approaches the solid-phase type of process.

Most researchers agree that the setting or development of structure in a hydrating cement paste is intimately connected with adsorption and the operation of surface forces. The relative importance of physical and chemical forces is not yet clear. There is also some difference of opinion regarding the details of the chemical and physical changes involved in the process of setting. In the author's opinion the setting process is a field where we may expect to see some of the most significant developments in the future.

Research on cement hydration in the next few years will undoubtedly give us the answers to many of the questions now facing us, and some of the differences of opinion will be resolved. As our knowledge progresses we may expect new questions to arise and new differences to develop, but after all is said and done, is not this inevitable and even to be desired if our progress is to be real?

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Discussion

W. C. Hansen

The author refers to the work of Czernin with quartz powder with a surface area of 20,000 cm^2/g as demonstrating the manner in which physical forces might contribute to the strengths of hardened cement pastes. In light of recent work on freshly formed surfaces of silica, there may be some question as to whether or not the strength obtained from a specimen of powdered quartz and water is primarily the result of physical forces.

Benson and Castle,[1] in a review of the literature and from their own work, show that freshly formed surfaces of silica undergo chemical reactions with various materials. Van Lier, de

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Bruyn, and Overbeek [2] studied the solubility in water and solutions of NaOH of powdered quartz before and after treatment with a solution of HF. The untreated powder had an erratic and much higher rate of solution than did the treated powder. They concluded that the surfaces of the particles of the former probably had a combination of cracks, dislocations, and protruding edges that gave this powder an abnormally high rate of solution. The depth of this disturbed layer on the surfaces of the particles was estimated to be approximately 300 A. The acid-treated quartz had a solubility at 25 °C of 1.8×10^{-4} moles/kg.

This work with silica and other powders suggests that disturbed surfaces on particles of portland cement might have pronounced effects during the early reactions of cement with water. It seems that this might be a profitable area for research by those working on cement.

Discussion

Elmer T. Carlson

Dr. Greene made mention of certain complex hydrated compounds generally referred to as silicoaluminates. In the following, I shall not comment on the compound C_2ASH_8, often called Strätling's compound or hydrated gehlenite, the existence of which is now well established. My remarks will be confined to the two silicoaluminates, C_4ASH_{12} and $C_6AS_3H_{30-32}$, reported by Flint and Wells [1],[3] which were considered to be analogous to the well-known sulfoaluminates. These have already been briefly commented on by zur Strassen and Schmitt [2] in their discussion of an earlier paper in this symposium. It was pointed out in the latter discussion that Dörr [3] at one time believed that he had successfully prepared C_4ASH_{12}, but that his later experiments failed to confirm this conclusion. The other compound, $C_6AS_3H_{30-32}$, recently has been reported by Mohri [4] but from his petrographic and X-ray data it appears unlikely that he actually had the same compound as that described by Flint and Wells.

Over a period of several years, numerous attempts have been made in our laboratories to repeat the preparation of C_4ASH_{12}, both by closely following the procedures of Flint and Wells and by systematically varying the proportions of the reactants over a wide range. In all cases, confirmation has been lacking. Data relative to a few typical experiments are given in table 1.

It may be seen that in each case, after storage of the reaction mixtures at room temperature for 2 months, the predominant phase was C_2ASH_8 ("gehlenite hydrate") with lesser amounts of C_4AH_{13} and other phases. Identification was based on X-ray diffraction patterns. The experiments listed in the table are comparable to three of the experiments tabulated by Flint and Wells [1] in their report of the preparation of C_4ASH_{12}.

A large number of similar reaction mixtures have been prepared and studied. It is significant that in most of the experiments, the precipitate was seen, by microscopic examination, to consist of two types of material; one apparently a gel (similar to CSH), the other consisting of platy crystals. Occasionally, after some weeks, C_3AH_6 was also observed. Products that appeared to be homogeneous were obtained only if the initial concentration of Al_2O_3 was less than a rather low, not precisely determined value. In such cases, the precipitate was of the gel type.

In view of this failure to duplicate the preparation of C_4ASH_{12}, it was decided to reexamine the data of Flint and Wells, to see whether they might permit a different interpretation from that given by the authors. The proposed formula for the silicoaluminate was based on chemical analysis, which was undoubtedly accurate, but necessarily based on the assumption of a homogeneous precipitate. The assumption of homogeneity was based on microscopic evidence, which is subject to some uncertainty because of the extreme minuteness of the crystals and their tendency to agglomerate. The refractive indices reported for the proposed silicoaluminate, 1.538 and 1.523, are well within the range of values reported for C_4AH_{13} by various

Table 1. *Precipitation from aqueous* CaO-Al_2O_3-SiO_2 *mixtures during two months storage at room temperature*

Experiment number		1	2	3
Initial volume, ml		460	350	300
Weight of oxides present	CaO, g	0. 813	0. 460	0. 661
	Al_2O_3, g	. 165	. 082	. 070
	SiO_2, g	. 080	. 080	. 068
Final concentration of solution	CaO, g/l	1. 082	. 740	1. 126
	Al_2O_3, g/	0. 004	. 007	0. 004
	SiO_2, g/	. 001	. 001	. 002
Molar ratio in ppt, C:A:S		3. 0:1:1. 0	3 9:1:2. 0	6. 9:1:1. 8
Solid phases present (from X-ray patterns)		C_2ASH_8 C_4AH_{13} C_3AH_6 (little)	C_2ASH_8 C_4AH_{13} CSH (probable)	C_2ASH_8 C_4AH_{13} CH CSH (probable)

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[3] Figures in brackets indicate the literature references at the end of this paper.

investigators. Flint and Wells stated that the X-ray diffraction pattern of the silicoaluminate was very similar to that of C_4AH_{13}. In this connection it should be borne in mind that the X-ray equipment and techniques in use at that time were less advanced than those of the present day. In particular, the patterns failed to register the low-angle reflections which later have been found most useful in distinguishing between various calcium aluminate hydrates. Unfortunately, the X-ray films for the specific preparations for which data were published by Flint and Wells apparently have been lost. Others made during the same period by the same authors, and believed to be essentially duplicates, are, however, still on file. On reexamination, it is found that all the lines may reasonably be ascribed either to C_2ASH_8, to C_4AH_{13}, or to calcium hydroxide. Thus, the evidence for the presence of C_4ASH_{12} appears rather doubtful, and its existence remains unconfirmed. This is in full agreement with the recent conclusions of Dörr, as reported here by zur Strassen and Schmitt [2].

The other silicoaluminate reported by Flint and Wells, $C_6AS_3H_{30-32}$, is a different matter. A few of the original reaction mixtures are still in existence, and the needle-shaped crystals of the supposed silicoaluminate, closely resembling ettringite, are conspicuously present. Unfortunately, they have not yet been successfully separated from the mass of gel-like material with which they are entangled. Inasmuch as this compound was discussed in a recent paper by Carlson and Berman [5], it is unnecessary to go into the details at this time. It may be noted, however, that large amounts of combined carbon dioxide were shown to be present in the precipitates, leading to the conclusion that the supposed $C_6AS_3H_{30-32}$ probably contains CO_2 in partial substitution for SiO_2.

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Discussion

T. C. Powers

Referring to Dr. Greene's excellent review, I should like to comment on the apparent conflict between conclusions drawn from some of our studies and the conclusions of Professor Rehbinder and his collaborators, mentioned in Dr. Greene's paper. Reference was made to the fact that our studies of the rate of bleeding (rate of sedimentation in a thick suspension) indicated that the size, shape, and number of cement particles are not altered appreciably by the reactions occurring within the first hour or so after contact with water. In connection with this conclusion, Dr. Greene pointed out that Professor Rehbinder and his collaborators reported that the surface area may increase tenfold before and during the period while bleeding is going on, and that this observation formed a part of the basis of the theory of cement hydration put forward by scientists in the Soviet Union.

In my opinion, there is no conflict between the large increase in specific surface area reported by the Soviet scientists and the deduction from our bleeding tests that the size, shape, and number of cement particles during the first hour or so is about the same as before the initial reactions occurred. Two different methods of observation are involved, from each of which a value for surface area can be calculated, but the results pertain to different aspects of the system.

Direct observation shows that after the initial reaction with water, the cement grains have become coated with a very thin layer of gel.[1, 2] It is obvious that during the period of bleeding the water flows over the surface of the coating and not through it. Since the coating is thin, relative to the diameter of the grain, it is not surprising that the specific surface area calculated from rate of bleeding is practically the same as that calculated from the rate of sedimentation in a nonreactive fluid. Since the presence of the coating has practically no effect, the structure of the coating is likewise of no importance with respect to the results of this method of observation. The calculation of surface area is based on the magnitude of the viscous drag of the particles, and viscous drag depends on the over-all dimensions of the individual particles, including their coatings, and on the concentration of the particles.

On the other hand, the Soviet Union scientists estimated surface area from the interaction between the solid phases in the system and certain ions in the aqueous solution in contact with the solids. Such a method, or a method based on the interaction of the dry solid with individual atoms of water vapor, depends almost entirely on the composition of the coating on the cement grains. Various methods of observation, including the electron microscope, reveal that the coating is composed of particles of the same order of size as those composing the cement gel produced by later stages of the cement reaction, which means that the specific surface area of these particles is ca. 200 m^2/g. Therefore, the presence of a small amount of gel coating on the grains is revealed by a large area available to water vapor when the specimen is dry, or to ions when the specimen is in contact with an aqueous solution.

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[1] W. Czernin, A few unsolved problems of cement hydration, this Symposium, paper V–S3.

[2] L. E. Copeland and Edith G. Schulz, Discussion of The microstructure of hardened paste, this Symposium, paper V–2.

Let us consider, for example, a cement having a specific surface area of 3,000 cm^2/g as indicated by viscous drag in water. If 1 percent of the cement has become reacted in forming the coating on the grains, and if the specific surface area of the particles composing the coating is 200 m^2/g by dry weight, the specific surface area as measured by water vapor adsorption would be 24,600 cm^2/g. Thus, the measurement based on adsorption would indicate about eight times as much surface area per gram of cement as would the measurement based on viscous drag. A calculation based on ion exchange should indicate about the same ratio.

From such considerations as those above, it is not clear why our friends in the Soviet Union choose to explain the increase in surface area occurring during the initial stages of reaction by supposing that the cement grains become shattered and dispersed by the physical action of water, and that the new surface area is due to such a breakup of cement grains.

Discussion

A. J. Gaskin

The fact that early reactions in cement pastes may be strongly influenced by adsorption and surface effects is well substantiated. Selective adsorption of ions from the solution phase, and the formation of solid coatings of precipitated reaction products are typical factors determining consistency and setting time.

It may be of interest to mention the influence of another type of surface effect in this connection, i.e., the adsorption of gases by cements in the dry state.

Some of the results of CO_2 and water-vapor adsorption have been discussed in the literature on false set, but there seems to be no record of the effects of adsorption of acid gases such as sulfur dioxide.

It has been noted in the course of our work on false set that adsorption of SO_2 by cements can be very rapid and extensive, some cements taking up as much as 0.1 percent by weight of this gas in a period of a few minutes.

The results of SO_2 adsorption have been somewhat unexpected, in that the very small amounts present in relation to the total sulfate content of the cements have been very effective in retarding certain early reactions.

The least surprising effect found has been the elimination of air-setting tendencies for short periods of storage in a humid atmosphere. This was shown by compacting treated and control cements into blocks and storing these in a damp enclosure on concrete slabs at ground level. The control blocks gained considerable strength over a period of 2 weeks, but the SO_2-treated test pieces remained friable and weak.

The extension of the times for initial and final set which can be brought about by SO_2 treatment of some cements has been less understandable. With some cements, no great changes could be induced by exposure to SO_2, but with others, not greatly different in composition, the adsorption of 0.1 percent of SO_2 by weight caused great delays in setting and hardening. Final set was less affected than initial set, but even so could be extended to twice the normal time. Initial set times could be trebled when sensitive cements were treated with SO_2 especially in the presence of water vapor, when more of the gas is taken up.

Strengths at 3 days were reduced by as much as 10 percent by SO_2 treatments, but 7-day strengths were normal, and one treated cement showed an appreciable gain in strength at 28 days.

The effects of SO_2 on cements are of theoretical rather than practical interest, as it is unlikely that sufficient exposure to the gas will occur under normal manufacturing conditions to become significant. Perhaps the only source of SO_2 generally encountered would be the sulfides present in some clinkers. A little sulfide is common in rotary kiln products, and greater quantities appear in some shaft kiln clinkers. Oxidation of sulfide to SO_2 and immediate transfer of this gas to cement particle surfaces could conceivably occur during cement milling. The intergrinding of portland cement and slag products could similarly result in SO_2 production from sulfide impurities in the slags, and subsequent adsorption of the gas on the cement.

It is of interest to note that SO_2 in the adsorbed state does not persist long in a form which can be leached off the cement and estimated as sulfite. The surface components of cement particles appear to catalyze the oxidation of the gas, or any calcium sulfite produced, and only soluble sulfate can be determined after aeration of the cement. The specific effects of the SO_2 treatment still persist after aeration. Certain other acid gases have essentially similar effects, particularly SO_3 and acetic anhydride.

Acetic acid vapor has been reported to be a useful agent in promoting free flow of cement powder, and in reducing "air-setting" effects. Acetic anhydride is a particularly potent and convenient material which may be used to gain the same results. It is easy to introduce, as spray or vapor, into a cement mill, and is more evenly taken up by cement particles. Apparently it is first adsorbed in a physico-chemical sense, then fixed by cement particle surfaces capable of catalyzing the hydration of the compound and supplying the water required to give the acid, then calcium acetate.

A side-effect of acetic anhydride additions to ball mills is the intense ball-cleaning action produced. A "coated" mill may be cleaned within a very short period by introduction of about 0.05 percent–0.1 percent of the anhydride in vapor form. Continued introduction of this amount of the agent results in the production of cement with depressed 3-day strength.

Discussion

S. A. Greenberg and V. S. Mehra

Dr. Greene makes reference to the compositions of the aqueous phases in contact with portland cements. Recent work in this laboratory makes it possible to explain quantitatively the factors that control the compositions.

Le Chatelier [1] in the last century proposed that portland cement hydrated by solution reactions and precipitation of the products from solutions. A discussion of the mechanism of hydration of C_3S is given in a symposium paper by Brunauer and Greenberg [2]. Recently Budnikov and Kravchenko [3] reported an experimental investigation of the mechanism of hydration of C_3A. Similarly $CaSO_4 \cdot \frac{1}{2}H_2O$ has been shown by Ketelaar and Heijmann [4] to hydrate in two steps: (1) solution of sulfate and (2) crystallization of gypsum from solution. Steinour [5] has proposed that after portland cement comes in contact with water the silicate and aluminate products immediately precipitate so that very little silicon or aluminum remain in solution. In this discussion the solution properties of C_3S, C_3A, and calcium sulfates will be emphasized because these are the most important solution processes in the initial stages of hydration.

It is important to our knowledge of the mechanism by which portland cement hydrates to know whether the aqueous solutions in contact with portland cements are saturated, supersaturated, or unsaturated with respect to products of hydration. This information may be obtained by evaluating the activity solubility products from a knowledge of the compositions of the solutions and the Debye-Hückel [6] equations for calculating activity coefficients. The compositions of some solutions were determined experimentally in this laboratory, but most of the data were taken from the literature. It cannot be assumed that the ion products one obtains for the different species in cement solutions represent equilibrium states. The ion products in the hydrating systems, therefore, were compared with the solubility products for pure systems under equilibrium conditions. In this manner it was possible to determine the degree of saturation of each species. An overall picture of the reactions is given in table 1.

The principal active components of the clinker in the initial stages are C_3S and C_3A. Gypsum plus the hemihydrate, and the alkali sulfates, dissolve immediately. (Dehydrated forms of calcium sulfate are formed during the grinding operations.) The sulfate species react rapidly with C_3A to form sulfoaluminate. Most alkali in cement is present as alkali sulfates; however, alkali is found also to be present in solid solution in some of the phases.

In the solutions there may be found immediately after mixing cement and water the following species: Ca^{++}, OH^-, monosilicic acid H_4SiO_4 and its ions, aluminic acid H_3AlO_3 and its ions, SO_4^{--}, K^+, and Na^+.

According to recent work, the hydrated calcium silicates exhibit variable compositions [2]. Greene reports that in the early stages of hydration the high sulfate sulfoaluminate is found. According to Greene, $4CaO \cdot Al_2O_3 \cdot 13H_2O$ forms from C_3A in the absence of gypsum. Crystalline calcium hydroxide is usually present in the early stages.

Equilibrium Solubility Products

Calcium Hydroxide

The activity solubility product for calcium hydroxide, evaluated in recent work by Greenberg and Copeland [9], is

$$K_{sp_1} = a_{Ca^{++}} a^2_{OH^-} \tag{1}$$

where a refers to the activity of each species. The activity of each ion, a_i, is equal to the product of the concentration c_i in moles/liter and the activity coefficient f_i. The concentration of each species is known from solubility data. The activity coefficients were calculated by means of the Debye-Hückel equation

$$-\log f_i = \frac{AZ_i^2\mu^{\frac{1}{2}}}{1+d_iB\mu^{\frac{1}{2}}} \tag{2}$$

where A and B are constants, d_i is the diameter of the ion, Z_i is the valence of the ion, and μ is the ionic strength. It is apparent that the activity coefficient f_i may be evaluated if the ionic strength of the solution is known.

The value of K_{sp_1} for calcium hydroxide is 9.1×10^{-6} (pK 5.04, where $pK = -\log K$) at 25 °C. It is well known, however, that supersaturated solutions of calcium hydroxide will be stable for relatively long periods of time [10].

Table 1. *Reactions at early stages*

Early reactants of portland cement	Solution	Products
C_3S C_3A $CaSO_4 \cdot \frac{1}{2}H_2O, CaSO_4 \cdot 2H_2O$ Na_2SO_4, K_2SO_4 CaO, Na_2O, K_2O	Ca^{++}, OH^- $H_4SiO_4, H_3SiO_4^-, H_2SiO_4^{--}$ $H_3AlO_3, H_2AlO_3^-, HAlO_4^{--}$ SO_4^{--} K^+, Na^+	$3CaO \cdot 2SiO_2 \cdot 3H_2O$ $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ $4CaO \cdot Al_2O_3 \cdot 13H_2O$ $Ca(OH)_2$ $CaSO_4 \cdot 2H_2O$

Gypsum—$CaSO_4 \cdot 2H_2O$

The K_{sp_2} for gypsum,

$$K_{sp_2}=a_{Ca^{++}}a_{SO_4^{--}} \tag{3}$$

was found to be 4.43×10^{-5} (pK 4.35) at 25 °C from solubility data [11] (2.06 g $CaSO_4$/1000 g H_2O) and an evaluation of the activity coefficient. Latimer [12] previously estimated the value to be 2.5×10^{-5} from thermodynamic data. The first value will be used since it is based primarily on experimental data.

Hydrated Calcium Silicate

The solubility product of a hydrate prepared from calcium oxide, silica and water at temperatures below 100 °C

$$K_{sp_3}=a_{Ca^{++}}a_{H_2SiO_4^{--}} \tag{4}$$

was evaluated [2, 13] to be 10^{-7} (pK 7.0) at 25 °C. However, the K_{sp_3} in hydrating C_3S-water mixtures exhibited values of $10^{-6.8}$ (pK 6.8). It is believed that the latter value is for the quasi-equilibrium existing in these systems. It may be proposed that the C_3S-water systems are slightly supersaturated with respect to calcium silicate. Perhaps, on the other hand, the thin crystals of hydrate formed in the C_3S-water mixtures are a little more soluble than the crystals prepared from calcium oxide, silica, and water, which exhibit a lower solubility.

Hydrated Calcium Aluminates

The nature of the aluminic acid in solution is not known. Usually we assume that aluminum oxides exhibit an octahedral structure, AlO_6. For the sake of convenience in this discussion, aluminic acid is given the arbitrary formula H_3AlO_3. The ions $H_2AlO_3^-$ and $HAlO_3^{--}$ are formed from this acid. The acidity constants for aluminic acid, $pK_1=9.3$ and $pK_2=11.9$, have been evaluated in this laboratory.

Table 2 gives solubility data for hydrated calcium aluminates as obtained by Wells, Clarke, and McMurdie [14]. For both types of hydrates, the aluminum concentrations are roughly inversely proportional to the calcium ion concentrations. Instead of attempting determinations of accurate solubility products, it was decided to investigate the constancy of the following ion products suggested by the experimental relationships.

$$K_{sp_4}=a_{Ca^{++}}a_{HAlO_3^{--}} \tag{5}$$

$$K'_{sp_4}=a_{Ca^{++}}a^2_{H_2AlO_3^-} \tag{6}$$

When all the aluminum in solution is assigned to each of the two anions, these equations give the K_{sp_4} and K'_{sp_4} values shown in table 2. It will be seen that the values for pK_{sp_4} are somewhat more constant than those for pK'_{sp_4}. On the basis of the approximate constancy of K_{sp_4}, this product will be used as an empirical guide in lieu of an accurate solubility product. Owing to its simplified nature, it increases somewhat with increase in the calcium hydroxide content of the solution.

TABLE 2. *Solubilities in system* CaO-Al_2O_3-H_2O *at 21 °C*

(Wells, Clarke, McMurdie [14])

Concentrations moles/liter×10³		Solid phase in equilibrium	pK_{sp_4} [a]	pK'_{sp_4} [b]
Al_2O_3	CaO			
1.37	3.38	Stable isometric, C_3A aq	5.42	7.86
1.28	3.70	Stable isometric, C_3A aq	5.42	7.90
0.881	3.96	Stable isometric, C_3A aq	5.55	8.19
.392	4.55	Stable isometric, C_3A aq	5.87	8.86
1.43	9.65	Metastable hexagonal cal. alum.	5.12	7.52
0.94	10.4	Metastable hexagonal cal. alum.	5.29	7.87
.656	12.4	Metastable hexagonal cal. alum.	5.41	8.14
.412	13.0	Metastable hexagonal cal. alum.	5.61	8.53
.274	14.5	Metastable hexagonal cal. alum.	5.75	8.85

[a] $K_{sp_4}=a_{Ca^{++}}a_{HAlO_3^{--}}$.

[b] $K'_{sp_4}=a_{Ca^{++}}a^2_{H_2AlO_3^-}$.

Hydrated Sulfoaluminates

Because the solubility product of a complex sulfoaluminate might be difficult to determine, for the sake of convenience K_{sp_4} was used as an index of the solubility. Table 3 lists the results of studies of the solubilities of the high sulfoaluminate phases by Jones [15, 16] and Takemoto and Suzuki [17]. Table 3 gives the concentrations in moles/liter of calcium, sulfate, aluminum, alkali (K+Na), and hydroxyl ions. The solid phases coexisting with the solutions are listed next. In the final columns, pK_{sp_1}, pK_{sp_2}, and pK_{sp_4} are given.

In table 3 it may be noted that the pK_{sp_4} values are relatively constant in the presence of alkali, and average 7.37. There is an indication from the earlier work of Jones [15] (rows 1 and 2, table 3) that the K_{sp_4} values are about ten times larger in the absence of alkali. No satisfactory explanation could be found for so great a difference.

In mixtures of the high sulfoaluminate, calcium hydroxide, and gypsum, the pK_{sp_1} and pK_{sp_2} values for the latter two compounds may be seen in table 3 to satisfy approximately the equilibrium conditions. In the presence of the relatively insoluble high sulfoaluminate the compositions of the solutions are fixed only by the solubilities of the calcium hydroxide and gypsum. This could be verified by comparing the data of Takemoto and Suzuki [17] with those of Hansen and Pressler [18] whose results are discussed in the next section.

Mixtures of Gypsum, Calcium Hydroxide, and Alkali Hydroxides

A very interesting set of data on the equilibrium solubilities of these mixtures was reported by Hansen and Pressler [18]. In table 4 the experi-

Table 3. *System* $CaO–Al_2O_3–CaSO_4–H_2O$ *and alkalies* (25 °C)

Reference	Concentrations, moles/liter x 10^3					Coexisting solid phases	pK_{sp}	pK_{sp_2}	pK_{sp_4}
	CaO	SO_3	Al_2O_3	2(K+Na)	2(OH)				
15	31.6	12.3	0.06	----	19.3	$C_3A·3CaSO_4aq$ Gypsum $Ca(OH)_2$	5.03	4.28	6.29 [a]
15	1.91	0.18	.01	----	18.9	$Ca(OH)_2$ $C_3A·3CaSO_4aq$ C_3AH_6	5.09	----	6.16 [a]
16	16.45	66.0	.02	89.1	39.5	$C_3A·3CaSO_4aq$ Gypsum $Ca(OH)_2$	4.86	4.12	7.34
16	0.293	0.656	.065	89.1	91.1	$C_3A·3CaSO_4aq$ $Ca(OH)_2$ C_3AH_6	4.82	----	7.49
17	18.6	30.1	.02	42.8	28.6	Gypsum $C_3A·3CaSO_4aq$ $Ca(OH)_2$	4.97	4.24	7.12
17	18.7	36.4	.03	47.2	30.0		4.94	4.19	6.98
17	14.9	71.6	.02	94.7	39.0		4.92	4.14	7.40
17	15.2	81.4	.03	108.6	40.7		4.90	4.12	7.25
17	15.1	118	.03	146.3	45.6		4.87	4.05	7.34
17	15.1	132	.03	159.3	47.6		4.87	4.02	7.37
17	4.3	0	.05	42.1	48.2	$Ca(OH)_2$ $C_3A·3CaSO_4aq$ C_3AH_6	5.07	----	7.27
17	2.0	0	.03	97.7	96.7		4.98	----	8.06
17	1.9	0	.15	146.2	147		4.74	----	7.52

Average (excluding first two values) 7.37

[a] Values for alkali-free solution.

mental data and the pK_{sp_1} and pK_{sp_4} values for calcium hydroxide and gypsum are listed. The values may be seen to be approximately the same as the equilibrium values of 5.04 and 4.35 for calcium hydroxide and gypsum, respectively.

Table 4.—*Solubilities at 30 °C of calcium hydroxide and gypsum in dilute alkali solution.*
(Hansen and Pressler [18])

Concentrations, moles/liter				Coexisting solid phases	pK_{sp_1}	pK_{sp_2}
CaO	SO_3	OH	K_2O+Na_2O			
0.0298	0.0141	0.0419	0.0053	$CaSO_4·2H_2O$ and $Ca(OH)_2$ in each case.	4.97	4.29
.0256	.0191	.0529	.0199		4.87	4.27
.0228	.0223	.0523	.0256		4.93	4.26
.0226	.0219	.0514	.0250		4.93	4.27
.0214	.0253	.0524	.0301		4.95	4.23
.0198	.0303	.0602	.0406		4.90	4.23
.0185	.0373	.0618	.0497		4.94	4.21
.0184	.0395	.0698	.0561		4.84	4.20
.0180	.0425	.0711	.0599		4.85	4.20
.0174	.0544	.0771	.0756		4.84	4.16

Portland Cement-Water Mixtures

Many investigations [17, 19–22] have been conducted of the compositions of the aqueous phases in contact with hydrating portland cement pastes of normal w/c ratios. In order to substantiate the reported data, a few experiments were performed in this laboratory on Type I cements. Several problems exist in such study and will be briefly discussed initially.

Two methods for separating the aqueous phase from the solids have been employed: (1) centrifugation and (2) pressure filtration. For various reasons the second procedure was adopted in this laboratory.

The methods used for the analyses of calcium, silicic acid, aluminic acid, sulfate, alkalies, and *p*H have not been clearly presented in many studies reported in the literature [20]. In the study conducted in this laboratory, standard methods are being followed. Calcium is determined by titration with versene [24]. The molybdenum blue method for silicic acid [25] is suitable for small concentrations of silicic acid. For the determination of aluminum, the photometric procedure with 8-hydroxyquinoline is followed [26, 27]. The *p*H values are measured with the glass and calomel electrodes.

Tables 5–7 summarize the results of several studies of the composition of the aqueous phases in contact with portland cements. Table 5 lists the data for clinkers alone. In table 6 the results for clinkers plus calcium sulfates are given. In table 7 may be found the data for mixtures of clinkers and several additives excluding calcium sulfates. In the tables the following data are listed in order: (1) time of hydration, (2) *p*H, (3)–(8) the concentrations of hydroxyl, sulfate, calcium, sodium plus potassium, aluminum, and silicon; in the last four columns are the pK_{sp_1}, pK_{sp_2}, pK_{sp_3}, and pK_{sp_4} values.

In the sections which follow, the compositions of the aqueous phases as a function of time are discussed with respect to the equilibrium solubilities of each solid species.

Calcium Hydroxide

In most cases the pK_{sp_1} values may be seen to be less than the equilibrium 5.04 value immediately after cement is mixed with water. These solutions continue to remain supersaturated thereafter.

Aeration of the clinker alone for 24 hours before mixing it with water causes the solutions to become unsaturated with respect to calcium hydroxide (table 5). Similar results (table 6) are found on the aeration of portland cement containing gypsum. The aqueous phases in contact with ground clinker to which hemihydrate was added may be seen in table 6 to exhibit slightly unsaturated solutions.

The addition of alkali carbonates to cement [17] (table 7) does not appreciably affect the pK_{sp_1} values. It is interesting to observe that additions of small amounts of calcium chloride and sucrose to clinkers do not reduce the degree of supersaturation of the solutions compared to normal cement solutions.

The ratio of concentrations of calcium to twice the hydroxyl ion concentration, $(Ca^{++})/2(OH^{-})$, is affected by two factors. First is the amount of alkali present in the clinker and second is the addition of calcium sulfates to the clinker. Increased amounts of alkali decrease this ratio (see tables 5, 6, and 7 for data). The addition of calcium sulfates to clinker increases the above ratio appreciably. This can be best seen from the comparison of the results on the same clinkers in tables 5 and 6.

Gypsum—$CaSO_4 \cdot 2H_2O$

It may be observed in table 6 that the pK_{sp_2} values are initially less than the equilibrium value and constantly increase with time. Thus for the most of the early hydration time the solution after initial supersaturation is close to saturation. The solutions become supersaturated in the initial stages because of the presence of the calcium sulfate hemihydrate and, secondarily, alkali sulfates. Aqueous phases in contact with clinker alone exhibit unsaturated solutions, as shown in table 5 by the pK_{sp_2} values, which are much greater than the saturation value. In table 7 it can be seen that the addition of calcium chloride and sucrose to clinker produces the same results as with clinker alone.

Calcium Silicates

The pK_{sp_3} values should be about 6.8–7.0 under equilibrium conditions. It is apparent from the results that within experimental error the pK_{sp_3} values for aqueous solutions in contact with cements and clinker (tables 5–7) indicate that the solutions are essentially saturated with calcium silicate. The addition of calcium chloride or sucrose to ground clinker does not appreciably change this situation. Aeration (tables 5, 6) does not cause any noticeable difference in K_{sp_3} values.

Calcium Aluminates

The equilibrium pK_{sp_4} value of 7.37 for calcium aluminate when calcium sulfoaluminate is present was used as an indication of the equilibrium solubility. For cement aqueous solutions the values were slightly lower, showing supersaturation. Several reasons may be offered for this behavior. Perhaps supersaturation exists because C_3A dissolves more rapidly (to give a supersaturated solution) than the rate at which the sulfoaluminate precipitates from solution. Another reason may be that hydrated calcium aluminates are present which exhibit a higher solubility than the high sulfate sulfoaluminate.

TABLE 5. *Compositions of aqueous phases in contact with ground clinkers*

Time	pH	Concentrations, moles/liter×10³						pK_{sp_1}	pK_{sp_2}	pK_{sp_3}	pK_{sp_4}
		$2OH^-$	SO_4^{--}	Ca^{++}	2(Na+K)	Al_2O_3	SiO_2				
Stein [22]—Normal consistency, 18 °C											
10 min	------------	78.8	0.512	4.7	74.6	0.324	0.266	4.72	6.57	6.89	6.48
Kalousek, Jumper, and Tregoning [19]—Clinker 1, w/c=0.35, 25 °C, low alkali											
7 min	12.68	31.5	0.25	30.8	1.45	0.020	------------	4.53	5.94	------------	6.75
120 min	12.72	34.5	.38	26.2	11.0	.039	------------	4.53	5.85	------------	6.53
Kalousek, Jumper, and Tregoning—Clinker 5, w/c=0.35, 25 °C, high alkali											
7 min	13.19	106	35.1	2.14	142	0.127	0.482	4.91	5.31	7.18	7.47
120 min	13.39	164	1.63	2.67	162	.049	.250	4.44	6.56	7.38	7.78
Takemoto and Suzuki [17]—w/c=0.27, 20 °C											
30 sec	13.38	120	8.7	1.7	137.1	------------	0.26	4.87	5.97	7.50	------------
3 min	13.45	140	0.4	1.7	138.3	------------	.25	4.74	7.32	7.52	------------
8 min	13.45	140	.5	1.4	138.3	------------	.23	4.74	7.31	7.64	------------
30 min	13.45	142	.6	1.8	138.3	------------	.18	4.70	7.12	7.64	------------
[a] 60 min	13.45	141	.9	1.7	143.2	------------	.18	4.73	6.97	7.67	------------
[b] 323 min	13.45	143	.6	1.5	143.2	------------	.24	4.78	7.20	7.59	------------
Takemoto and Suzuki—w/c=0.28, 20 °C, 24 hr aeration											
30 sec	12.80	31.4	57.3	9.1	75.5	------------	0.12	5.27	4.38	7.06	------------
3 min	12.96	45.6	29.6	1.5	75.5	------------	.20	5.67	5.37	7.54	------------
[a] 7 min	13.25	88.0	1.0	1.1	86.1	------------	.17	5.22	6.96	6.73	------------
[b] 40 min	13.29	98.4	0.4	0.3	91.0	------------	.15	5.70	7.94	8.37	------------

[a] Initial set. [b] Final set.

TABLE 6. *Compositions of aqueous phases in contact with clinker plus calcium sulfates*

Time	pH	Concentrations, moles/liter×10^3						pK_{sp_1}	pK_{sp_2}	pK_{sp_3}	pK_{sp_4}
		$2OH^-$	SO_4^{--}	Ca^{++}	2(Na+K)	Al_2O_3	SiO_2				
Stein [22]—Clinker+4% gypsum, normal consistency, 18 °C											
10 min	------------	47.6	69	16.5	99.8	1.10	0.266	4.81	4.13	6.42	5.63
60 min	------------	57.4	64.9	16.4	105.9	0.628	.266	4.65	4.16	6.55	5.88
Kalousek, Jumper, and Tregoning [19]—Clinker 1+gypsum (1.75% SO_3), w/c=0.35, 25 °C, low alkali											
7 min	12.62	27	12.0	39.6	1.29	0.029	0.033	4.63	4.24	6.80	6.55
120 min	12.66	30.5	13.1	41.0	5.5	.039	.033	4.51	4.20	6.79	6.42
Kalousek, Jumper, and Tregoning [19]—Clinker 5+gypsum (1.75% SO_3), w/c=0.35, 25 °C, high alkali											
7 min	12.91	55	97	17.1	137	0.049	0.083	4.64	4.05	7.12	7.05
120 min	13.04	74	93	19.4	150	.069	.067	4.34	4.03	7.18	6.87
Takemoto and Suzuki [17]—Commercial cement A (1.08% SO_3), w/c=0.24, 20 °C											
30 sec	12.73	27.1	149	27.5	141.1	------------	------------	4.88	3.73	------------	------------
3 min	12.88	38.0	115	25.4	142.1	0.09	0.3	4.81	3.83	6.41	6.64
8 min	12.89	39.0	111	11.7	143.1	------------	.1	5.11	4.16	7.21	------------
30 min	12.94	43.3	107	10.4	144.2	.10	.2	5.07	4.23	6.96	6.96
60 min	12.93	42.0	112	9.5	143.2	------------	.2	5.13	4.23	7.00	------------
[a] 88 min	13.08	59.8	91.1	6.3	149.5	------------	.2	4.99	4.49	7.15	------------
[b] 127 min	13.23	85.1	59.7	3.7	153.2	------------	.3	4.89	4.88	7.18	------------
Takemoto and Suzuki [17]—Commercial cement B (1.51% SO_3), w/c=0.26, 20 °C											
30 sec	12.82	31.6	119	29.4	116.9	------------	0.08	4.79	3.76	6.94	------------
3 min	12.91	40.7	94.9	15.0	118.7	------------	.12	4.94	4.09	6.99	------------
8 min	12.93	42.1	91.5	14.3	119.1	------------	.09	4.92	4.12	7.13	------------
30 min	12.97	47.0	88.9	14.4	120.2	------------	.08	4.83	4.14	7.18	------------
[a] 95 min	13.00	49.8	98.2	12.9	127.9	------------	.06	4.84	4.15	7.36	------------
[b] 170 min	12.96	45.6	99.0	12.3	133.2	------------	.08	4.94	4.17	7.26	------------
Takemoto and Suzuki—Cement A, 24 hr aeration w/c=0.25, 20 °C											
30 sec	12.59	19.6	142	38.4	126.3	------------	0.06	5.23	3.59	6.97	------------
3 min	12.61	20.2	142	30.9	129.9	------------	.06	5.29	3.68	7.05	------------
8 min	12.81	32.2	111	11.8	129.9	------------	.06	5.25	4.14	7.41	------------
30 min	12.89	38.7	107	11.3	133.1	------------	.06	5.11	4.18	7.43	------------
60 min	12.93	42.5	103	10.3	132.2	------------	.06	5.07	4.24	7.47	------------
[a] 250 min	13.11	64.6	73	2.78	134.6	------------	.08	5.24	4.90	7.86	------------
[b] 320 min	13.39	122	40.5	1.27	139.1	------------	.10	5.03	5.50	8.11	------------
Takemoto and Suzuki—Clinker + hemihydrate (1.5% SO_3), w/c=0.25, 20 °C											
30 sec	12.91	40.8	149	38.8	140.2	------------	0.09	4.60	3.59	6.81	------------
3 min	12.66	22.8	148	29.7	140.5	0.1	.22	5.21	3.69	6.52	6.56
8 min	12.79	31.0	124	12.6	141.3	------------	.18	5.28	4.10	6.93	------------
30 min	12.82	32.8	117	9.1	142.0	.1	.12	5.36	4.25	7.24	7.01
60 min	12.93	42.1	123	10.2	145.7	------------	.11	5.11	4.19	7.24	------------
[a] 110 min	12.95	44.7	123	10.4	157.4	------------	.14	5.06	4.19	7.14	------------
[b] 197 min	12.86	36.5	115	9.2	158.4	------------	.16	5.28	4.27	7.13	------------
Steinherz and Welcman [20]—Cement A (0.9% $CaSO_4$), cement B (2.9% $CaSO_4$), cement C (3.4% $CaSO_4$) w/c=1.5, 20 °C											
(A) 1 min	12.6	28.3	28.9	21.5	35.6	0.69	0.665	4.97	4.20	5.83	5.62
(B) 1 min	12.4	24.5	71.0	46.1	49.2	------------	.164	4.93	3.66	6.29	------------
(C) 1 min	12.5	19.9	68.5	65.0	23.4	.70	1.00	4.96	3.53	5.37	5.26
Portland Cement Assoc. [23]—Type I, w/c=0.5, 25 °C											
10 min	12.76	39	17.5	30.9	25.6	0.005	0.027	4.46	4.24	7.06	7.50
30 min	12.40	17.1	39.5	31.2	25.3	.006	.072	5.20	3.93	6.67	7.48
70 min	12.90	105	10.4	32.7	25.0	.005	.053	4.25	4.55	6.84	7.56

[a] Initial set. [b] Final set.

Discussion

The principal source for the presence of calcium in solution is C_3S. The C_3A produces in solution the same number of ions that precipitate out in the high sulfate sulfoaluminate. Since the aluminum concentration is low, it may be concluded that C_3A does not increase the concentration of calcium appreciably. In addition the calcium sulfates present in normal cements contribute to the presence of calcium in solution. Free calcium oxide would be expected to contribute very little to the solution since it is probably dead-burned and therefore even the available oxide will be slow to react.

The hydroxyl ions in solution are produced from the hydration of C_3S and alkali. The sources of sulfate in solution are gypsum, hemihydrate and alkali sulfates. It is apparent that the immediate supersaturation of the solution must be caused by hemihydrate which is many times more soluble than gypsum. Gypsum with clinker, or clinker alone, will not produce supersaturation.

Calcium may be removed from the solution by the formation of hydrated calcium silicates, calcium aluminates, calcium sulfoaluminates, calcium hydroxide, and calcium sulfate. Hydroxyl ions are removed as calcium hydroxide. Sulfate ions are precipitated from the solutions as sulfoaluminate. In the presence of hemihydrate, false or plaster set is occasionally noticed which is usually interpreted as an indication of the formation of gypsum crystals.

Relatively high alkali content cements, by increasing the hydroxyl ion concentration, will accelerate the crystallization of calcium hydroxide from solution. The alkali sulfates present in cement or clinker may cause the precipitation of gypsum by forming supersaturated solutions; the resultant decrease in calcium ion concentration permits a higher hydroxyl ion content in the solution. Therefore, cements high in alkali sulfates may exhibit false set because of the formation of gypsum crystals.

In the initial stages of hydration the *p*H values of the aqueous phases are from 12.6 to 12.9. In the presence of high alkali cements the *p*H values after one hour of hydration may rise to approximately 13.2. It is clear from the results of Takemoto and Suzuki [17] and Kalousek, Jumper, and Tregoning [19], that high alkali clinkers produce aqueous phases with *p*H values up to 13.45. Apparently calcium sulfate reduces the hydroxyl ion concentration of solutions by removing calcium hydroxide. Reduction in *p*H is much more noticeable when calcium chloride is added to clinker. Although the solutions are usually supersaturated with respect to calcium hydroxide, any increase in calcium or hydroxyl ion concentration will accelerate the precipitation of calcium hydroxide.

The results of the present study are in accord with the solution theory for the hydration of ce-

TABLE 7. *Compositions of aqueous phases in contact with ground clinker plus additives*

Time	*p*H	Concentrations, moles/liter×10^3						pK_{sp_1}	pK_{sp_2}	pK_{sp_3}	pK_{sp_4}
		$2OH^-$	SO_4^{--}	Ca^{++}	2(Na+K)	Al_2O_3	SiO_2				
Takemoto and Suzuki [17]—Commercial cement A+alk. carbonates (0.2% K_2O, 0.2% Na_2O) w/c=0.26, 20 °C											
30 sec	12.93	42.5	297	18.8	327	------	0.04	5.02	3.78	7.65	------
3 min	12.87	37.2	320	27.8	327	------	.04	4.97	3.59	7.50	------
[a] 8 min	13.78	301	67.1	0.3	357	------	2.70	5.06	6.16	7.55	------
[b] 12 min	13.81	323	63.4	.3	375	------	.98	5.01	6.20	8.01	------
Kalousek, Jumper, and Tregoning [19]—Clinker 1+$CaCl_2$ (1.46%), w/c=0.35, 25 °C											
7 min	12.03	41	0.125	366	4.84	------	0.020	4.34	5.84	------	6.35
120 min	12.16	50	------	294	14.52	------	.020	4.22	------	------	6.39
Kalousek, Jumper, and Tregoning—Clinker 5+$CaCl_2$ (1.46%), w/c=0.35, 25 °C											
7 min	12.24	24	0.50	204	152	0.069	0.050	4.41	5.44	6.44	5.99
120 min	12.29	23	.25	169	171	.059	.033	4.51	5.80	6.67	6.12
Kalousek, Jumper, and Tregoning—Clinker 1+sucrose (0.05%), w/c=0.35, 25 °C											
7 min	12.64	56	0.25	28.2	1.45	0.029	0.033	4.65	5.95	6.83	6.45
120 min	12.72	68	.38	25.3	12.1	.069	.037	4.55	5.85	6.86	6.29
Kalousek, Jumper, and Tregoning—Clinker 5+sucrose (0.05%), w/c=0.35, 25 °C											
7 min	13.31	154	1.88	0.714	155	2.78	0.466	5.06	7.06	7.66	6.59
120 min	13.43	183	1.00	2.32	184	0.127	.333	4.43	6.87	7.35	7.47

[a] Initial set. [b] Final set

ment first proposed by Le Chatelier. Apparently calcium hydroxide crystallizes from a very supersaturated solution. However, no gypsum crystallizes from the solutions supersaturated with calcium and sulfate ions, except perhaps in the very early stages. False set may be evidence for the formation of gypsum. Almost all of the sulfate is found eventually in the very insoluble sulfoaluminates.

Both the silicate and aluminate phases are in contact with slightly supersaturated solutions. This is evidence that both the highly soluble C_3S and C_3A, after initial rapid reaction, react slowly by a diffusion mechanism. It may be concluded from these results that the rate of crystallization from solution is much more rapid than the slow hydration reactions which proceed by a diffusion mechanism through the layer of hydration products deposited on the unreacted portland cement. Therefore, the later rate of crystallization is controlled by the slow hydration reactions.

Thanks are due to Dr. Stephen Brunauer for his encouragement of this project and his helpful suggestions. The discussion of this paper with Dr. H. H. Steinour is gratefully acknowledged.

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Closure

Kenneth T. Greene

Dr. Hansen's suggestion that the coherence of pastes of quartz powder may result primarily from chemical rather than physical forces is entirely appropriate and strengthens the present author's belief that an intensive study of particle surfaces and the manner in which they may influence the properties of fresh portland cement pastes would be very valuable. It seems likely that some of the variable behavior of cements which appear to be very similar chemically and physically when judged by our present analytical methods may stem from differences of surface condition which we are unable at present to detect or measure.

I am indebted to Mr. Carlson for providing more recent data on the problem of the existence of calcium silicoaluminates corresponding to the formulas $3CaO \cdot Al_2O_3 \cdot CaSiO_3 \cdot 12H_2O$ and $3CaO \cdot Al_2O_3 \cdot 3CaSiO_3 \cdot 30\text{–}32H_2O$. The best evidence at present thus indicates that the occurrence of $3CaO \cdot Al_2O_3 \cdot CaSiO_3 \cdot 12H_2O$ is unconfirmed, while the existence of $3CaO \cdot Al_2O_3 \cdot 3CaSiO_3 \cdot 30\text{-}32H_2O$ is more likely but not firmly established. A reexamination of some of the original preparations of Flint and Wells, described by Mr. Carlson, suggests that their needle-shaped "silico-aluminate" crystals contained significant amounts of CO_2 as well as SiO_2.

Mr. Powers' discussion deals with an important point which should have been clarified in my paper. I am sure that he is correct in his opinion that there is no conflict between the conclusions of Powers and Steinour from their bleeding experiments and the data of the Soviet investigators, who used a method which would naturally give a different value for surface area since it measures a different thing.

The conclusion which the Soviet scientists draw from their data—namely, that the large increase in measured surface area results from a breakdown of the cement grains into much smaller particles—is another matter, as Mr. Powers points out. It appears that although there is necessarily no conflict regarding the data, there is a fundamental difference in conclusions.

The discussion of Dr. Greenberg and Mr. Mehra is a valuable contribution to our knowledge of the composition of the aqueous phase in the early stages of cement hydration. Studies of this kind are needed for a more complete understanding of the very early reactions and the manner in which they may influence the course of the setting and hardening phenomena as well as other physical properties of the fresh and hardened pastes.

In my original paper I stated that data on the concentration of components in solutions separated from cement pastes less than one minute after mixing are generally lacking. I wish to correct this statement since some results at 30 sec were published by Takemoto and Suzuki (reference 17 of Greenberg and Mehra). It is interesting to note that they show generally about the same concentration of SiO_2 in solution at 30 sec as at 1 min. It may be that this is an indication that the SiO_2 concentration is not much higher immediately after water contact, or it may mean that 30 sec after mixing is still not soon enough to detect such a higher concentration if it actually exists.

These discussers state, "However, no gypsum crystallizes from the solutions supersaturated with calcium and sulfate ions except perhaps in the very early stages. False set may be evidence for the formation of gypsum." I believe that under some circumstances hemihydrate may convert to gypsum in cement pastes without being manifested in a tendency to false set. DTA results obtained in our laboratories have indicated that in some cements, hemihydrate present before mixing converts to gypsum over a period of 10 min or more. These cements often show no false set by standard tests. Perhaps gypsum sometimes forms by crystallization from supersaturated solution and thereby causes false set, whereas at other times it arises by hydration of solid hemihydrate and does not induce false set.

Mr. Gaskin's experience regarding the influence of gases such as SO_2 on the setting behavior of cements is most interesting. Although it may be unlikely, as he says, that sufficient exposure to SO_2 will occur under normal manufacturing operations to become significant, it appears that the effect of different gases in the atmospheres of both kilns and grinding mills needs to receive greater attention than it has. As with the disturbed surfaces, mentioned by Dr. Hansen, adsorption of small amounts of gases and vapors may account for some of the presently unpredictable setting behavior of certain cements.

Paper IV–2. False Set in Portland Cement*

W. C. Hansen

Synopsis

Investigators generally agree that the crystallization of gypsum from cement pastes is the principal cause of false set in commercial cements. This paper reviews the literature on this subject, on the system $CaSO_4 \cdot 2H_2O$–$CaSO_4 \cdot 1/2H_2O$–water vapor, and on the system $CaSO_4 \cdot 2H_2O$–$Ca(OH)_2$–$NaOH$–H_2O.

This review shows that methods based on the stiffening of cement pastes and mortars as measured by the Vicat apparatus and on the sedimentation of slurries in water or other liquids have been used with success in studying the causes of false set. Also, that extracts from a cement paste can be studied to reveal whether or not gypsum is likely to crystallize in that paste. The use of these methods has resulted in investigators concluding that many suggested causes of false set are rarely, if ever, the cause of false set in commercial cements. Results with these methods have also shown that a type of false set can be developed by aeration in cements that do not contain dehydrated gypsum. The action of aeration appears to be one of altering the surfaces of the crystals of the aluminate and the aluminoferrite phases so that the retarding effect of calcium sulfate on the rates of their reaction with water is reduced. This area of the problem of false set requires additional study.

Résumé

On se trouve généralement d'accord sur le fait que la cristallisation du gypse dans les pâtes de ciment est la cause principale de la fausse prise des ciments du commerce. Cet exposé passe en revue ce qui a été écrit à ce sujet, sur le système $CaSO_4 \cdot 2H_2O$–$CaSO_4 \cdot 1/2H_2O$–vapeur d'eau et le système $CaSO_4 \cdot 2H_2O$–$Ca(OH)_2$–$NaOH$–H_2O.

Ce compte-rendu indique que les méthodes basées sur le procès du raidissement des pâtes de ciment et des mortiers tel que l'appareil de Vicat la mesure, et sur la sédimentation des schlamms dans l'eau ou dans des autres liquides, ont été employées avec succès dans l'étude des causes de la fausse prise. Cette revue montre également qu'il est possible d'étudier des fractions de la pâte de ciment dans le but de découvrir si le gypse est susceptible ou non de cristalliser dans cette pâte. Grâce à l'emploi de ces méthodes on conclut que des nombreuses causes de fausse prise proposées sont rarement—peut-être jamais—la cause de fausse prise dans les ciments du commerce. Les résultats que donnent ces méthodes indiquent aussi qu'un type de fausse prise peut se développer par aération dans des ciments qui ne contiennent pas de gypse déshydraté. Il semble que l'aération ait pour effet de modifier les surfaces des cristaux des phases d'aluminate et d'aluminoferrite de telle façon que l'effet retardateur du sulfate de calcium sur les vitesses de leur réaction avec l'eau est réduit. Cet aspect du problème de la fausse prise exige de l'étude supplémentaire.

Zusammenfassung

Die meisten Forscher nehmen an, daß die Kristallisierung des Gipses in Zementmassen der Grund für das falsche Abbinden der Handelszementsorten ist. Der Vortragende bespricht die Literatur, die darüber erschienen ist, über die Systeme $CaSO_4 \cdot 2H_2O$–$CaSO_4 \cdot 1/2H_2O$–Wasserdampf und $CaSO_4 \cdot 2H_2O$–$Ca(OH)_2$–$NaOH$–H_2O.

Man kann sehen, daß die Methoden, die auf dem Steifwerden der Zementpasten und Mörteln beruhen, wie sie mit dem Vicatapparat gemessen werden, und die Sedimentationsmethoden unter Benutzung von Wasser und von anderen Flüssigkeiten, sehr erfolgreich in der Erforschung der Grunde fur das falsche Abbinden benutzt worden sind. Auch kann man Zementpastenextrakte benutzen, wenn man ausfindig machen will, ob Gips vermutlich aus der Masse auskristallisieren wird, oder nicht. Die Anwendung dieser Methoden hat gezeigt, daß viele der angegebenen Möglichkeiten für das Vorkommen der falschen Abbindung für Handelszemente gar nicht in Frage kommen. Man kann das Phänomen auch mit Hilfe einer Belüftung an Zementen hervorbringen, die gar keinen hydratisierten oder unhydratisierten Gips enthalten. Diese Belüftung verändert vermutlich die Oberflächen der Aluminatkristalle und der Aluminoferritphasen, sodaß der Verzögerungseffekt des Kalziumsulfats auf deren Reaktionsgeschwindigkeiten mit Wasser verkleinert wird. Diese falschen Erstarrungserscheinungen müssen noch besser erforscht werden.

Introduction

In recent years, cement technologists have attempted to distinguish between "flash set" and "false set." The first is believed to be a manifestation of the lack of the required amount of sulfate in the cement to repress the rate of reaction of $3CaO \cdot Al_2O_3$ and water sufficiently to give a satisfactory time of set. Usually, in this type of set, the cement paste heats up excessively and reworking of the stiffened paste does not restore the original workability.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Universal Atlas Cement Division of the United States Steel Corporation, Gary, Ind.

False set is generally believed to be a manifestation of the presence in the cement of either calcium sulfate hemihydrate or soluble anhydrite or both, which dissolve rapidly and precipitate as gypsum. In this type of set, the cement paste heats up very little and reworking of the stiffened paste largely restores the original workability.

Attempts have been made to develop tests which would detect quick-setting tendencies in cements. One of these (ASTM C–359 [1] [1]) includes a reworking of a mortar for the purpose of distinguishing between flash and false set. Tests with this method have shown quick stiffening for some cements which contained very little, if any, dehydrated gypsum. (In this paper, the term "dehydrated gypsum" will mean either calcium sulfate hemihydrate or soluble anhydrite or a mixture of the two.) It appears, therefore, that the restoration of workability by reworking does not necessarily show that the stiffening was caused by the precipitation of gypsum.

In the early days of the manufacture of portland cement, it was believed by many that it was necessary to use plaster of Paris to control the set. For example, Meade [2] states "In spite of Le Chatelier's experiments, it has been a theory generally held in this country that gypsum would not retard the set of cement but that the only form of sulfate of lime which would do this is plaster of Paris; and that, where gypsum is ground in with the clinker, this is transformed into plaster of Paris."

Meade made tests with finely ground gypsum, plaster of Paris and dead-burned gypsum added to a powdered clinker with the following results:

Calcium sulfate added	Water used in pats	Initial setting time, Gillmore needle, for type of calcium sulfate indicated		
		Gypsum	Plaster of Paris	Dead-burned gypsum
Percent	*Percent*	*hr:min*	*hr:min*	*hr:min*
0	25	0:02	0:02	0:02
0.5	23	----------	0:05	----------
1.0	23	0:02	0:50	0:06
1.5	23	----------	2:50	----------
2.0	22	2:40	3:00	1:45
3.0	22	2:50	1:45	1:47
4.0	22	----------	0:35	----------
5.0	22	3:15	0:16	2:00
10.0	22	3:00	0:16	1:50
20.0	22	3:20	0:09	2:20

An examination of this table shows that cements with 1 percent of calcium sulfate as gypsum and as dead-burned gypsum had initial setting times of 2 and 6 min, respectively; whereas a cement with that amount of SO_3 added as hemihydrate had an initial setting time of 50 min. This demonstrates what is well known today that, with certain clinkers, the sulfate must get into solution at a very rapid rate to prevent the $3CaO \cdot Al_2O_3$ from causing some stiffening of the cement paste. Small amounts of dehydrated gypsum can do this because of the rapid rate at which they dissolve. Larger amounts of gypsum and still larger amounts of natural anhydrite are required to provide sufficient surface for the rapid rate of solution needed to give what might be called a normal initial set.

It seems that it is necessary to recognize that the term "normal initial set" has no definite meaning. If the setting caused by the reaction of $3CaO \cdot Al_2O_3$ with water is called flash set, then it is possible to have flash set that varies from severe to very mild, depending upon the extent to which the rate of the reaction of $3CaO \cdot Al_2O_3$ with water has been modified. It seems logical to believe that the stiffening caused by mild degrees of flash set can be destroyed by reworking of the paste.

Returning to the data by Meade, one observes that the cement made with plaster of Paris became fast setting when large quantities of plaster of Paris were used. This is a demonstration of the ability of dehydrated gypsum to produce what is now called false set.

There is a third type of quick stiffening that appears to differ from flash set or false set as defined above. This develops when some cements are exposed to the air (aerated) for some periods of time. Some of these cements are known to have contained very little, if any, dehydrated gypsum. Generally, this stiffening can be destroyed by reworking the paste.

Lhopitallier and Stiglitz [3] listed the following suggested causes of false set:

1. $CaSO_4 \cdot 2H_2O + heat = CaSO_4 \cdot \frac{1}{2}H_2O$.
2. Action of alkali carbonates contained in cements partially deteriorated by exposure to air.
3. Rapid hydration of a very high proportion of very fine particles of cement.
4. High content of $3CaO \cdot Al_2O_3$ in the latter.
5. Coating of gypsum by cement during grinding and the consequent neutralization of the gypsum (formation of lamellae).
6. Very high specific surface of the gypsum.

Lhopitallier and Stiglitz concluded from their experience that items 2 to 6 were not involved in false set. They measured false set by the penetration of the Vicat needle in pastes mixed to normal consistency.

Some of the items mentioned in this introduction will be discussed in more detail in the body of the report. The purpose of this introduction is to point out that this paper will deal with three types of quick stiffening in an effort to clear up one problem that was touched upon in the First International Symposium on the Chemistry of Cement. In his discussion of the papers, Cooper [4] made the following statement: "The question of the setting of cement is somewhat vexed, and I think that more disputes arise between the user, the engineer, and the manufacturer on questions of setting than on any other point. The manu-

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[1] Figures in brackets indicate the literature references at the end of this paper.

facturer tests his cement and gets certain results. A certificate is frequently issued to that effect but the first thing the manufacturer hears is that the cement which took two hours to set when it was tested at the works takes two minutes or two days on the job. In the result, the matter is referred to a third party, who usually obtains quite different results from those of the manufacturer, engineer, architect, or the party using it."

There seems to be no question about dehydrated gypsum being the principal cause of false set in commercial cements. Hence, this paper will be concerned primarily with this phase of the setting problem.

First Use of Calcium Sulfate With Portland Cement

According to Davis [5], portland cement as we know it today probably was manufactured by I. C. Johnson in the plant of White and Son in about 1845. He claims that France and Germany quickly followed Britain and that, by 1875, portland cement of fair quality was being produced on a fairly large scale.

Forsen [6] points out that Scott, in 1857, published a paper on the influence of sulfur-bearing fuels on the strengths of burned lime which resulted in an investigation by Schott (1871) of the influence of gypsum mixed with various kinds of lime. It would seem that Schott probably included something similar to portland cement in his study of limes.

Forsen states, "Berger claims that Scott was the first to suggest control of the setting of portland cement with gypsum, whereas this important discovery is attributed by Goslich to Michaelis." In this connection, Steinour [7] states, "Michaelis said in 1905 that for perhaps 25 years he had introduced wet gypsum into the grinding mills when otherwise the cement was flash setting."

It seems that the discovery of the retarding properties of calcium sulfate may actually have been made by masons who either accidentally or deliberately mixed plaster of Paris with their limes. According to Lesley [8], the first use of calcium sulfate in this country resulted from an observation of the addition of plaster of Paris to the batch when concrete was being mixed in Paris.

The work by Meade cited in the introduction was carried out to demonstrate that forms of calcium sulfate other than plaster of Paris could be used to prevent flash set. There has been some tendency to blame false set onto increases in the fineness to which a cement was ground which, in turn, increased grinding temperatures and resulted in the dehydration of the gypsum.

Bucchi [9] says that the first references in the technical literature pertaining to false set appeared with the widespread use of large compound mills, characterized by high output rate, with a low rate of heat dispersal, and of the tendency of the manufacturers to produce high strength cements by means of impact grinding. He suggested that this type of false set be called "false set of fine grinding" to distinguish it from other types of false set.

It seems that the problem of false set probably developed because of several changes in the manufacturing process. Among these are the following:

1. improvements in the burning of the clinker;
2. changes in the compositions of the kiln feeds, which resulted in clinkers with lower $3CaO{\cdot}Al_2O_3$ contents;
3. better quenching of the clinker, which decreased the amount of crystalline $3CaO{\cdot}Al_2O_3$;
4. increases in the amounts of SO_3 permitted in cements; and
5. increases in the fineness.

It seems very likely that most of the early clinkers actually required dehydrated gypsum to prevent flash set and combined with calcium sulfate at rates which permitted the crystallization of little, if any, gypsum in the paste.

The System $CaSO_4$–H_2O

The system $CaSO_4$–H_2O has been the subject of many investigations with some disagreement as to the nature of the compounds formed when gypsum ($CaSO_4{\cdot}2H_2O$) is dehydrated by heating in air. Weiser, Milligan and Ekholm [10] made a very thorough study of the dehydration of selenite at a constant vapor pressure of 23.6 mm (that of water at 25 °C). The products were studied by X-ray diffraction. They called the completely dehydrated product "dehydrated hemihydrate." They state, "the evidence seems conclusive that $CaSO_4{\cdot}2H_2O$ is dehydrated isobarically, a definite hydrate $CaSO_4{\cdot}1/2H_2O$ which adsorbs a small amount of water is first formed and this, in turn, dehydrates in a stepwise fashion to give dehydrated hemihydrate, calcium sulfate, which adsorbs water that is not completely removed at a vapor pressure of 23.6 mm until well above the decomposition temperature". "The X-radiograms of the two substances, calcium sulfate hemihydrate and dehydrated hemihydrate, are similar, showing that the structures are similar; but the existence of definite characteristic differences between the two patterns indicates that the water molecules in the hemihydrate occupy fixed positions in the lattice. These observations likewise support the view that calcium sulfate hemihydrate is a chemical individual and that the process of dehydration is not zeolitic in character."

Kelley, Southard, and Anderson [11] defined two forms of hemihydrate and the two forms of anhydrite as follows:

α-hemihydrate (stable) can be prepared in the presence of liquid water above 97 °C or in saturated steam. It loses water with formation of an anhydrous soluble anhydrite in one step and is to be considered nonzeolitic.

β-hemihydrate (metastable) can be prepared from the dihydrate by dissociation in a vacuum or in a nearly dry atmosphere, followed by annealing at 100 °C. It loses H_2O with formation of a soluble anhydrite containing several tenths of a percent of H_2O. From 0.9 percent H_2O down, the H_2O is removed with increasing difficulty. The two forms of soluble anhydrite are labeled α and β, depending on the variety of hemihydrate to which they are related.

Soluble α-anhydrite can be made by dissociation of α-hemihydrate in a vacuum or in a relatively dry atmosphere near 100 °C. It contains virtually no water.

Soluble β-anhydrite can be made by dissociation of β-hemihydrate in high vacuum at 100 °C and by rapid, nearly complete calcination of $CaSO_4 \cdot 2H_2O$ at 200 °C. It always contains several tenths of a percent of H_2O.

Gilliland [12] gives X-ray diffraction patterns that show very minor differences between the patterns of hemihydrate and soluble anhydrite. However, it appears from these X-ray diffraction patterns and those reported by Weiser, Milligan, and Ekholm that it would be extremely difficult by the use of such patterns to distinguish between β-hemihydrate and soluble β-anhydrite in portland cement.

From these studies, it appears that the cement technologists need consider only what Kelley, Southard, and Anderson class as β-hemihydrate and soluble β-anhydrite. They found that this type of hemihydrate did not lose all of its water when calcined at 200 °C (392 °F). Portland cement is rarely, if ever, either ground or stored at a temperature as high as 392 °F. Hence, any soluble anhydrite found in portland cement should contain a few tenths of a percent of water. (In this paper, the terms "hemihydrate" and "soluble anhydrite" will always refer to the β forms as defined by Kelley, Southard, and Anderson.)

Much has been written about the solubilities of the various forms of calcium sulfate and its hydrates. Gypsum ($CaSO_4 \cdot 2H_2O$) is the only one of these that has a true solubility in water at the temperatures at which portland cement concrete is placed, and in solutions of the compositions found in cement pastes. Hence, the cement technologist needs consider only the solubility of gypsum. He is, however, very much interested in the rates at which the other forms of calcium sulfate dissolve. Hemihydrate and soluble anhydrite dissolve very rapidly and produce solutions which are highly supersaturated for short periods of time with respect to gypsum. Natural anhydrite dissolves at a slower rate than does gypsum. Hansen and Hunt [13] give data that show differences between extracts of pastes of cements made with gypsum and with natural anhydrite.

One property of gypsum of great interest to the cement technologist is its stability with respect to temperature and water vapor. The following table was constructed from data by Mellor [14]:

Vapor pressure in the system $CaSO_4 \cdot 2H_2O$-$CaSO_4 \cdot 1/2H_2O$-*water vapor*

Temperature	Vapor pressure—ps	Vapor pressure of water—pw	Relative humidity ps/pw×100
°F	*mm*	*mm*	
32	1.17	4.57	25
50	2.78	9.14	30
68	6.24	17.4	36
104	26.3	54.9	48
110	91.4	149	61
176	272.4	355	76
212	710.8	760	93
230	1104	1075	-------------

Since portland cements are usually ground at temperatures [15] in the range of 100 to 300 °F, the relative humidity of the atmosphere would, in all cases, have to exceed about 50 percent to prevent some dehydration of the gypsum during grinding and storage. However, the rate of dehydration of gypsum depends upon both the temperature and the relative humidity. Hence, it seems possible that cements might be ground at temperatures above 200 °F without extensive dehydration of the gypsum and, if cooled as discharged from the mill to some temperature below 200 °F, the rate of dehydration might be reduced to a very low value. That cooling is effective is supported by the following statement from Blanks and Gilliland [16]: "As far as it has been possible to learn, there is not a single reported instance where adequate cooling of the grinding mills and of the cement prior to storage failed to relieve stiffening."

In this connection, Wilsnack [17] heated −200-mesh gypsum in 10-g portions at 150 °F for 0, 1, 2, and 4 days and found, respectively, the following water contents: 21.10; 21.02; 20.22 and 17.98 percent. When heated for 1 day at 200 °F, the water content was 7.34 percent.

Takemoto, Ito, and Hirayama [18] studied the dehydration of gypsum by means of differential thermal analysis during grinding of clinker and gypsum in an experimental mill. Their data are shown in figure 1. According to the authors, these data show formation of hemihydrate at 85 °C (185 °F) when the batch was ground for 40 min and the formation of soluble anhydrite at 130 °C (266 °F) when the batch was ground for 80 min.

There has been speculation as to whether or not dehydrated gypsum in portland cement would be converted to gypsum by combining with water vapor from the atmosphere after removal from the storage silo. Wandser [19] gives the following data for a sample of gypsum dehydrated by heating (to a loss on ignition of 4.07 percent) and then stored in an atmosphere of 65 percent relative humidity:

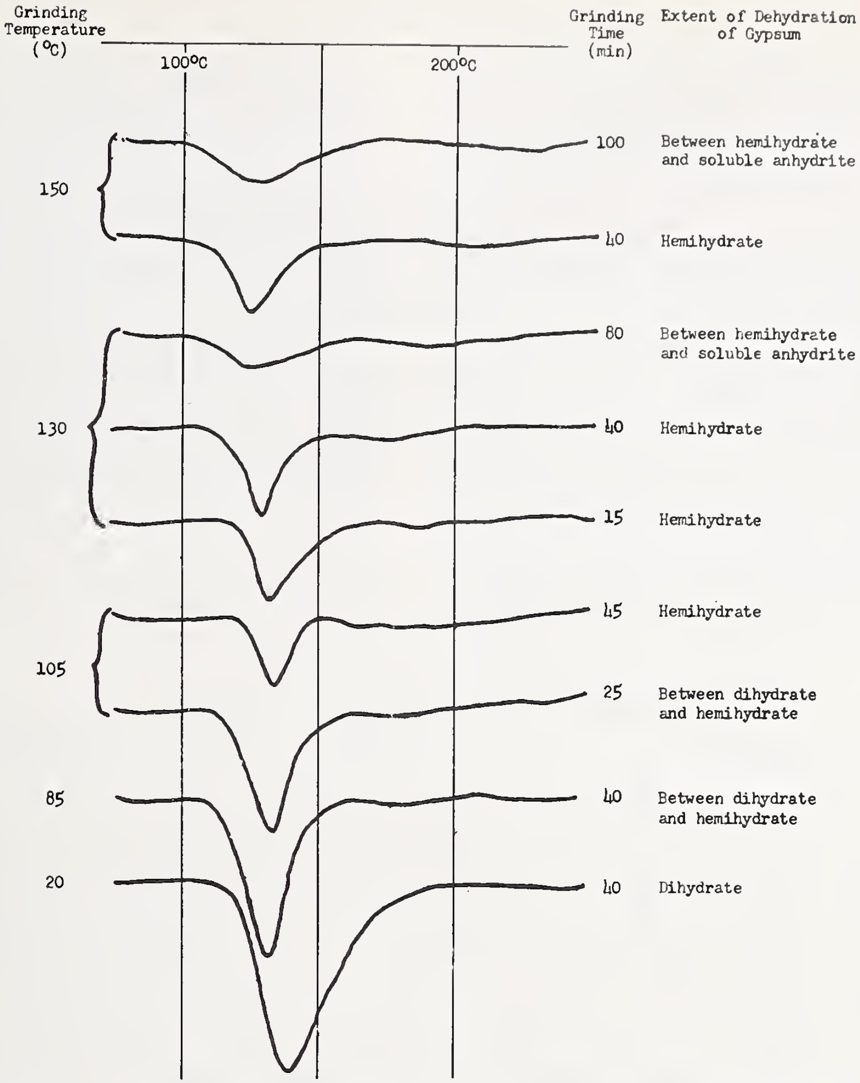

FIGURE 1. *Differential thermal analysis curves of cements ground with dihydrate (by Takemoto, Ito, and Hirayama).*

Heating rate: 5 °C/min, sensibility: 1/1.

Storage time	Water content
days	*percent*
1	7.11
2	7.41
28	7.42

The loss on ignition of pure hemihydrate is 6.2 percent.

Vikhter [20] exposed hemihydrate over solutions of sulfuric acid and found that, at relative humidities below 60 percent, the material adsorbed at the most about 1.3 percent H_2O and retained its activity practically indefinitely.

The small amount of water adsorbed by hemihydrate indicates that gypsum was not formed. The data by Mellor show that gypsum is converted to hemihydrate at a relative humidity of 61 percent and a temperature of 110 °F. It seems from these data that hemihydrate in cement would remain as hemihydrate during the handling of cement under the procedures which are normal to most projects in which cements are used.

As will be brought out later, some cements become false setting upon aeration. One explanation for this has been that the cement contained dehydrated gypsum but did not show false set until the cement was aerated because of the absence of gypsum crystals upon which to crystallize. From the above data, it seems unlikely that gypsum crystals would be formed under what might be considered normal conditions of aeration because it appears that soluble anhydrite hydrates in air to hemihydrate and that hemihydrate does not hydrate to gypsum under these conditions.

Early Work on False Set

During the years 1929 to 1933, a number of reports were published in *Cement and Cement Manufacture* on false set. According to these reports, false set is caused by the following:

1. rapid absorption of water by finely-ground cement [21];
2. dehydration of the gypsum to an anhydrite with a rate of solution insufficient to prevent flash set [22, 23, 24];
3. partial or complete dehydration of the gypsum [25, 26, 27];
4. "balling up of bundles of tiny particles which become wetted on the outside of the bundle only and give a plastic mortar; but after a few minutes the water percolated into the interior of the bundles with an apparent stiffening of the pat which is mistaken for an initial set" [28];

   (a) "False set is due to insufficient gauging; that is, every particle of cement has not been brought into contact with gauging water".

   (b) "False set occurs chiefly when the clinker is of a soft nature and tends to clog and flake in the mill, a tendency which is aggravated by high temperature, whereas with hard gritty clinker high temperature does not produce false set"; and
5. improperly burned clinker [29].

Blank [30] describes tests made with wet clinker. Cement made from wet clinker was very fast setting and this could be corrected only by drying the clinker. Blank concluded that there was no "cut-and-dried explanation" for the causes of false set. However, it appears that he was dealing with a very unusual case which was different from the conditions under which most cases of false set were observed.

Data reported by Schachtschabel [27] are interesting in showing that some cements may require dehydrated gypsum to prevent flash set. His data are as follows:

Variation of setting time due to gypsum, hemihydrate, and soluble anhydrite

Water, 26 to 28 percent. Times of mixing, 1 and 3 min

Percent addition	Gypsum				Hemihydrate				Soluble anhydrite			
	Mix 1 min		3 min		1 min		3 min		1 min		3 min	
	Init.	Final	Init.	Final	Init.	Final	Init.	Final	Init.	Final	Init.	Final
	h. m.	*h. m.*	*h. m.*	*h. m.*	*h. m.*	*h. m.*	*h. m.*	*h. m.*	*h. m.*	*h. m.*	*h. m.*	*h. m.*
0.75	------	------	------	------	------	------	------	------	0 3	0 4	0 2	0 3
1.00	0 3	0 4	------	------	0 3	0 5	------	------	4 15	6 45	5 25	8 20
1.25	0 2	0 6	0 9	0 12	4 40	6 40	4 50	8 0	------	------	------	------
1.50	0 8	2 50	1 45	3 30	------	------	------	------	------	------	------	------
2.00	2 4	5 50	3 30	5 30	4 50	7 35	5 0	7 50	4 50	7 30	5 0	7 40
2.50	6 20	9 7	5 15	8 0	0 45	6 30	4 30	7 20	------	------	------	------
3.00	------	------	------	------	0 29	6 0	3 45	6 45	0 34	5 50	1 42	6 35
4.00	6 45	10 0	5 25	8 25	0 25	5 25	0 27	5 45	0 33	5 0	0 29	5 7
6.00	------	------	------	------	0 17	0 33	0 16	0 30	------	------	------	------
8.00	6 0	10 30	5 55	8 40	------	------	------	------	------	------	------	------

It required between 1.5 and 2.0 percent SO_3 as gypsum to prevent flash set with this clinker when freshly ground, whereas 1.0 percent SO_3 as soluble anhydrite and 1.25 percent SO_3 as hemihydrate were as effective as about 2.5 percent SO_3 as gypsum. Aging of the ground clinker in bags for 3 weeks reduced the amount of SO_3 as gypsum required for normal set to 0.5 percent.

These data also show that amounts of SO_3 above about 2.0 percent as either hemihydrate or soluble anhydrite produced a rapid initial set.

It appears from this review of the work reported between about 1928 and 1935 that investigators had clearly shown that dehydration of gypsum during either grinding or storage could cause false set in portland cement. Some investigators erroneously attributed false set caused by dehydration of gypsum to the formation of a relatively insoluble anhydrite.

Two investigators [21, 28] suggested that false set was due to rapid adsorption of water by the finely ground cement. The data by Schachtschabel indicate that some cases of fast stiffening might be classed as false set because of the rapid reaction of $3CaO{\cdot}Al_2O_3$ with water. For example, the clinker used by Schachtschabel when mixed with 1.5 percent SO_3 as gypsum gave an initial set of 8 min when mixed for 1 min and 105 min when mixed for 3 min. These results raise the question as to what is meant by normal setting. The cement paste mixed for 1 min probably would be classed either as flash or false setting whereas that mixed for 3 min probably would be classed as normal setting. It appears that the gypsum could not dissolve fast enough in the 1-min mixing period to prevent all traces of flash set. However, the additional mixing of the 3-min mixing period either maintained a higher rate of solution of the gypsum or else destroyed some of the set. If one were to class this cement with 1.5 percent SO_3 in the form of gypsum as false setting when mixed as a paste for 1 min, then one might be led to the conclusion that false set was caused by some factor such as rapid adsorption of water.

It has been a rather common belief that fast setting could be corrected by increasing the gypsum content of the cement. This was effective with this clinker as shown by the results for 1.5 and 2.5 percent SO_3 added as gypsum. However, when the SO_3 was raised from 2.0 to 2.5 percent by use of hemihydrate, the cement became fast setting. These results show why one practice might work satisfactorily in one cement plant and not in another.

The Liquid Phase of Cement Pastes

Studies on the constitution of portland cement have rather clearly defined the compositions of the crystalline phases in such cements. One such phase is a solid solution of K_2SO_4 and Na_2SO_4 which dissolves very quickly when the cement is mixed with water. Also, calcium hydroxide splits off very rapidly from the calcium silicates and aluminates. The liquid phase of cement paste, therefore, tends to satisfy the following equation within a very short time after the cement and water are mixed:

$$\underset{\text{Solid}}{CaSO_4{\cdot}2H_2O} \rightleftharpoons CaSO_4 + 2MOH = M_2SO_4 + Ca(OH)_2 \rightleftharpoons \underset{\text{Solid}}{Ca(OH)_2},$$

where M equals either K or Na or both.

The solubility of $Ca(OH)_2$ and $CaSO_4{\cdot}2H_2O$ in solutions of alkalies has been investigated by Hein [31] and by Hansen and Pressler [32]. The data by the latter authors are given in table 1.

In recent years, investigators in a number of countries have studied the problem of false set by means of extraction tests. Gilliland [12] used a test in which 250 g of cement was mixed in a Waring Blendor for 2 min with 125 ml of distilled water and filtered on a Buechner funnel. The extract was analyzed for CaO, $(OH)_2$, SO_3, K_2O and Na_2O. The quantity of SO_3 in such a solution at equilibrium was taken from the data by Hansen and Pressler. The following table gives data by Gilliland for four cements heated for 24 hr at various temperatures:

Penetration tests and extract compositions for heated cements

Cement No.	Heated 24 hr	Penetration test			Data for extracts—moles/liter			
		Water	½ min	5 min	Na_2O+K_2O	SO_3	Sat. SO_3	Excess SO_3
	°C	*Percent*	*mm*	*mm*				
9939		27.2	34	2	0.0271	0.0294	0.0227	0.0067
	128				.0250	.0510	.0216	.0294
	200	28.0	35	1	.0230	.0543	.0206	.0337
	300	26.0	38	0	.0240	.0543	.0211	.0332
	350	27.6	37	21	.0286	.0248	.0235	.0013
	650	29.2	37	30	.0343	.0202	.0268	.0066
9940		29.6	37	0	.0136	.0433	.0166	.0267
	128				.0138	.0461	.0166	.0295
	350	27.0	38	31	.0140	.0364	.0167	.0197
A–112		28.6	37	15	.0773	.0626	.0562	.0064
	128	29.0	35	0	.0739	.0906	.0537	.0369
	200	33.0	33	3	.0733	.0741	.0532	.0209
	300	28.0	37	0	.0707	.0946	.0514	.0432
	350	28.0	34	26	.0758	.0717	.0551	.0166
	650	28.2	36	28	.0823	.0533	.0600	.0067
A–215		28.0	33	17	.0472	.0424	.0346	.0078
	128	27.2	33	0	.0468	.0689	.0344	.0345

These data show that all of the extracts from the original cements contained SO_3 in excess of that required by a solution saturated with respect to gypsum. Small degrees of supersaturation might be accounted for by increased solubility of broken crystals. Hence, some of the original cements may have contained very little, if any, dehydrated gypsum.

Heating the cements at 300 °C generally increased the amount of SO_3 in the liquid phase. Heating at 350 °C appears to have converted some of the calcium sulfate to natural anhydrite and heating at 650 °C appears to have fairly well completed this conversion.

Gilliland used this extraction test to help prove that alkali carbonate does not cause false set during aeration as suggested by Bogue [33]. The results of his tests are as follows:

Treatment	Penetration Test		Data for extracts—moles/liter			
	½ min	5 min	K_2O $+Na_2O$	SO_3	Sat. SO_3	Excess SO_3
	mm	*mm*				
As received	33	15	0.0736	0.0658	0.0535	0.0123
Aerated 10 days at 50 percent RH	36	0	.0733	.0875	.0532	.0343
Heated to 350 °C for 24 hr after aeration	37	20	.0582	.0371	.0421	−.0050

Severe false setting was induced by aeration but heating at 350 °C, which is sufficient to convert gypsum and hemihydrate to natural anhydrite but insufficient to decompose alkali carbonates, destroyed the false set. This seems to demonstrate for this high-alkali cement that false set, upon

Table 1. *Solubility of* $Ca(OH)_2$ *and* $CaSO_4 \cdot 2H_2O$ *in solutions of* KOH *and* NaOH *at 25 and 30 °C (data by Hansen and Pressler* [32]*)*

Composition of original solution moles/liter			Composition of solution in contact with solid $Ca(OH)_2$ and solid $CaSO_4 \cdot 2H_2O$—moles/liter				
K_2O	Na_2O	K_2O+Na_2O	CaO	SO_3	OH	Na_2O	K_2O+Na_2O Calc.[a]
DATA FOR 30 °C							
None	None	None	0.0319	0.0125	0.0387	-------------	0.0001
0.0050	None	0.0050	.0298	.0141	.0419	-------------	.0053
.0025	0.0025	.0050	.0294	.0141	.0393	-------------	.0044
.0150	.0050	.0200	.0256	.0191	.0529	0.0052	.0199
.0100	.0101	.0201	.0236	.0196	.0477	-------------	.0199
.0251	None	.0251	.0228	.0223	.0523	-------------	.0256
.0125	0.0125	.0250	.0226	.0219	.0514	-------------	.0250
.0150	.0151	.0301	.0226	.0236	.0585	-------------	.0302
.0251	.0050	.0301	.0231	.0241	.0587	0.0052	.0303
.0150	.0151	.0301	.0216	.0252	.0536	-------------	.0304
.0301	None	.0301	.0214	.0253	.0524	-------------	.0301
.0401	None	.0401	.0211	.0299	.0626	-------------	.0399
.0200	0.0202	.0402	.0198	.0303	.0602	-------------	.0406
.0150	.0252	.0402	.0195	.0303	.0589	0.0251	.0401
.0501	None	.0501	.0185	.0373	.0618	-------------	.0497
.0251	0.0252	.0503	.0188	.0376	.0633	-------------	.0502
.0251	.0252	.0503	.0194	.0363	.0672	0.0253	.0505
.0050	.0500	.0550	.0184	.0395	.0698	.0504	.0561
.0500	.0050	.0550	.0190	.0398	.0689	.0052	.0552
.0601	None	.0601	.0187	.0430	.0710	-------------	.0598
.0301	0.0302	.0603	.0180	.0425	.0711	-------------	.0599
.0150	.0504	.0654	.0175	.0468	.0734	0.0502	.0659
.0501	.0252	.0753	.0174	.0544	.0771	.0255	.0756
.1002	None	.1002	.0162	.0710	.0806	-------------	.0951
.1002	0.0050	.1052	.0167	.0783	.0884	0.0056	.1058
.1002	.0252	.1254	.0164	.0951	.0940	.0259	.1257
.1504	None	.1504	.0162	.1167	.0972	-------------	.1491
None	0.1448	.1448	.0150	.1151	.1024	-------------	.1513
0.1504	.0050	.1554	.0162	.1211	.1011	-------------	.1553
.1504	.0252	.1756	.0162	.1382	.1048	-------------	.1744
.2005	None	.2005	.0164	.1626	.1062	-------------	.1991
None	0.1930	.1930	.0149	.1586	.1146	-------------	.2010
0.2506	None	.2506	.0161	.2055	.1136	-------------	.2462[b]
.1253	0.1250	.2503	.0169	.2040	.1188	-------------	.2465[b]
.3750	None	.3750	.0094	.2121	.1455	-------------	.2555[b]
None	0.3750	.3750	.0051	.2629	.2279	-------------	.3718
0.5012	None	.5012	.0093	.2083	.1386	-------------	.2683[b]
1.0023	None	1.0023	.0034	.3662	.2752	-------------	.5000[b]
DATA FOR 25 °C							
None	None	None	0.0331	0.0123	0.0414	-------------	0.0001
0.0100	None	0.0100	.0292	.0151	.0488	-------------	.0103
.0200	None	.0200	.0240	.0190	.0502	-------------	.0201
.0401	None	.0401	.0211	.0289	.0649	-------------	.0403
.0601	None	.0601	.0183	.0426	.0726	-------------	.0606
.1002	None	.1002	.0161	.0722	.0888	-------------	.1005
.2005	None	.2005	.0165	.1562	.1164	-------------	.1979[b]

[a] Calculated from determined values for CaO, SO_3 and OH.
[b] $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ probably formed as a solid phase.

aeration, is not caused by forming alkali carbonates.

It is now well known that, generally, a fairly large part of the alkalies in cement clinkers exist in these clinkers as the sulfates. The remaining alkalies probably exist as a solid solution of $23CaO \cdot K_2O \cdot 12SiO_2$ with $2CaO \cdot SiO_2$ and as a solid solution of $8CaO \cdot Na_2O \cdot 3Al_2O_3$ with $3CaO \cdot Al_2O_3$. It seems very unlikely that any significant amount of alkalies can be released from these phases as carbonates during normal exposure to air and, of course, alkali sulfates will not be converted to carbonates by exposure to air. Hence, it appears that the formation of alkali carbonates by aeration cannot be a cause of false set. However, when alkali carbonates are added to cement pastes, they precipitate $CaCO_3$, which might in itself cause stiffening of the paste just as the precipitation of gypsum does. Also, it seems that calcium sulfate requires the presence of some $Ca(OH)_2$ to prevent $3CaO \cdot Al_2O_3$ from reacting at a sufficient rate to cause some stiffening of the paste. Hence, it appears that the early stiffening of a cement paste observed by a number of investigators when they added alkali carbonates to a cement is a type of stiffening that would not be obtained in practice.

Schachtschabel [27] attributed the action of alkali carbonates added to the cement to the changing of the calcium sulfate to alkali sulfate by precipitation of $CaCO_3$.

The data by Gilliland indicate that the cement used in his study contained dehydrated gypsum as received because, at equilibrium, a solution containing 0.0736 moles K_2O+Na_2O should contain 0.0535 moles SO_3 instead of the 0.0658 moles which it contained. Aeration increased the SO_3 content to 0.0875.

Hansen [34] performed a somewhat similar experiment in which 200 g of cement was shaken with 150 ml water for 1 and 3 min. The cement was tested as received and after aeration in laboratory air for 24 and 48 hr. The results of these tests were as follows:

Treatment	Time of shaking	Composition of extract—moles/liter					
		SO_3	$(OH)_2$	CaO	Na_2O	Sat. SO_3	Excess SO_3
	min						
As received	1	0.0245	0.0279	0.0286	0.0238	0.021	0.004
	3	.0157	.0433	.0279	.0311	.025	−.009
Aerated 24 hr	1	.0523	.0238	.0589	.0172	.019	.033
	3	.0401	.0239	.0458	.0182	.020	.020
Aerated 48 hr	1	.0533	.0232	.0621	.0144	.018	.035
	3	.0431	.0234	.0512	.0153	.018	.025

This sample of cement must have contained dehydrated gypsum as received but, in the unaerated sample, the $3CaO \cdot Al_2O_3$ combined with the calcium sulfate at a rate such that, at 3 min, the solution was not saturated with respect to gypsum. When the cement was aerated, the solution was highly supersaturated at 3 min with respect to gypsum. This indicated that aeration reduced the rate at which $3CaO \cdot Al_2O_3$ reacted with calcium sulfate.

Hansen demonstrated that aeration reduced the rate of reaction of $3CaO \cdot Al_2O_3$ with calcium chloride by grinding the clinker without added calcium sulfate and then making extraction tests in which 200 g of the powdered clinker was shaken for 1, 5, 15, and 30 min with solutions of calcium chloride. The extracts were analyzed for chloride and the amounts combined during the shaking period were calculated with the following results:

Treatment	Grams Cl_2 combined with 100 g clinker for minutes indicated			
	1	5	15	30
As received	0.22	0.28	0.34	0.36
Aerated 24 hr	.08	.14	.22	.24
Aerated 48 hr	.03	.11	.22	.26

These data show that aeration retards the rate at which the cement combines with $CaCl_2$.

Manabe [35] showed, by studies with calcium sulfate made with radio-isotope sulfur-35, that aeration decreased the rate at which calcium sulfate combined in cement pastes.

Returning to the data by Gilliland, it is seen that these data also indicate that the rate at which $3CaO \cdot Al_2O_3$ reacts with the calcium sulfate has been decreased by aeration.

The presence of excess SO_3 in extracts from cement pastes does not always indicate the presence of dehydrated gypsum in the cement. If cements contain relatively large amounts of alkali sulfates, these sulfates may dissolve very rapidly to give solutions from which $CaSO_4 \cdot 2H_2O$ will precipitate by the reaction of the alkali sulfate with $Ca(OH)_2$ to give the equilibrium of eq (1). Hansen and Pressler [32] give the following data for the liquid phases of slurries of four cements after reaction periods of 3 min:

Cement No.	Composition of liquid phase			Composition of solution at equilibrium for given M_2O content		
	Moles/liter			Moles/liter		
	SO_3	CaO	M_2O	SO_3	CaO	M_2O
1	0.0127	0.0417	0.0018	0.0130	0.0310	0.0018
2	.0151	.0412	.0028	.0140	.0320	.0028
3	.0777	.0259	.0879	.0640	.0162	.0879
4	.0883	.0481	.0705	.0490	.0170	.0705

From these data, it is seen that the extract from

1. Cement No. 1 is slightly supersaturated with $Ca(OH)_2$;
2. Cement No. 2 is slightly supersaturated with $CaSO_4 \cdot 2H_2O$;
3. Cements Nos. 3 and 4 are supersaturated with respect to $CaSO_4 \cdot 2H_2O$ and unsaturated with respect to $Ca(OH)_2$. Hence, they will have to dissolve more $Ca(OH)_2$ and precipitate gypsum to attain equilibrium.

It appears that these cements contained large quantities of alkali sulfates that dissolved at very rapid rates.

Bucchi [9] developed a method of studying the rate at which SO_3 combined in the cement paste. In this method, samples of the paste after various periods of reaction were mixed with a sufficient amount of saturated $Ca(OH)_2$ solution to dissolve all of the SO_3 in the cement if it still remained as gypsum. The solutions were filtered and the filtrates were analyzed for SO_3. The results showed a very rapid combination of SO_3 in the first few minutes. Bucchi determined by this method the quantity of $SO_4^=$ remaining uncombined in the paste at the end of this initial rapid reaction. This value he called Q' and the original total $SO_4^=$ content of the paste he called Q. Then, $Q-Q'=X$, the amount of SO_4 combined during the first few minutes. According to Bucchi, if a cement shows rapid set when Q is equal to or less than X, the rapid set will be flash set. Generally, rapid set that occurs when Q is greater than X will be false set.

Bucchi prepared a number of cements by grinding the clinker separately and then blending them with either powdered gypsum or plaster of Paris or mixtures of the two. Results for one clinker, which are typical of those for all clinkers studied, are as follows:

SO_3 content of cement—percent				Time of set Vicat needle		$SO_4^=$ ion concentration [a] in the paste—percent		
SO_3 in clinker	SO_3 added as gypsum	SO_3 added as hemihydrate	Total	Init.	Final	Q	Q′	Q−Q′
0.52	0.66		1.18	0:08	0:18	1.09	0.00	--------
.52	1.37		1.89	2:35	4:25	1.75	0.42	1.33
.51	2.17		2.68	2:35	4:25	2.48	1.16	1.32
.50	3.00		3.50	2:34	4:17	3.23	1.90	1.33
.48	3.92		4.40	2:20	4:10	4.06	2.71	1.35
.48	4.97		5.45	2:41	4:30	5.03	3.71	1.32
.52		0.69	1.21	0:10	0:19	1.12	0.00	--------
.52		1.17	1.69	2:34	4:26	1.56	0.23	1.33
.52		1.66	2.18	2:35	4:29	2.01	0.69	1.32
.51		2.19	2.70	2:33	4:21	2.49	1.16	1.33
.51		2.56	3.07	1:59	4:22	2.84	1.50	1.34
.50		2.99	3.49	0:15	4:20	3.22	1.86	1.36
.49		4.22	4.71	0:12	0:27	4.35	2.99	1.36
.48		4.91	5.39	0:12	0:30	4.97	3.64	1.33
.52		0.42	2.19	2:31	4:30	2.02	0.69	1.33
.52		0.83	2.18	2:30	4:41	2.01	0.70	1.31
.52		1.16	2.18	2:00	3:50	2.01	0.70	1.31
.52		1.50	2.19	1:00	3:00	2.02	0.68	1.34
.52		1.58	2.18	0:40	2:31	2.01	0.72	1.29

[a] Q is initial concentration as calculated from $SO_4^=$ content of the cement and Q′ is the concentration at the end of the initial rapid reaction.

These results show that, for this clinker, gypsum and hemihydrate produced similar initial setting times until 2.56 percent SO_3 as hemihydrate was added. A very fast set was obtained with 2.99 to 4.91 percent SO_3 as hemihydrate.

Lhopitallier and Stiglitz [3] made an extensive study of false set by grinding clinkers with gypsum and then heating the cements to form dehydrated gypsum. They analyzed extracts from pastes for K_2O, Na_2O, CaO, SO_3, and $(OH)_2$ and compared them with the data published by Hein and by Hansen and Pressler and used the penetration of the Vicat plunger to indicate false set. The following conclusions were reached:

1. "The set of hemihydrate, formed by dehydration of gypsum in overheated grinding mills, suffices by itself to explain the phenomenon of false set of cements."
2. "The intensity of false set is a function of the absolute content of hemihydrate present in cement."
3. "In the case of partial dehydration, the fraction of non-dehydrated gypsum acts as seed for crystallization and accelerates the set of the hemihydrate."
4. "If mixing is continued beyond the set of the hemihydrate, the skeleton formed by the crystals of gypsum is broken and the paste becomes plastic again without further addition of water. The period of mixing necessary to break up false set is shorter the higher the proportion of particles of gypsum."
5. "Analysis of cement liquors taken at intervals of time allows one to ascertain the beginning of the phenomenon and to estimate the minimum time of mixing needed to break up the stiffening."

Murakami [36] found that false set due to hemihydrate could be explained by determining the chemical compositions of extracts from pastes taken immediately and 10 min after mixing with the amounts of water required for normal consistency. Takemoto and Suzuki [37] also studied extracts from neat pastes.

Manabe [35] added powdered clinker to solutions of $CaSO_4$ in which the $CaSO_4$ had been made with sulfur 35. By measuring the specific activity of the S in the original solution and in extracts made at various periods of time, he was able to study the rate at which SO_3 combined with the cement. As pointed out previously, he found that aeration decreased the rate of combination of SO_3 with the cement.

The development of methods based on the flame photometer for the determinations of alkalies has made it relatively easy to analyze the extracts from cement pastes. However, one can calculate the alkali contents of these extracts with sufficient accuracy for use in deciding whether or not an extract is supersaturated with respect to gypsum. These extracts are essentially solutions of alkali and calcium hydroxides and sulfates. Hence

$$\text{Moles } SO_3+\text{Moles } (OH)_2-\text{Moles } CaO=\text{Moles } M_2O.$$

The extremely small amounts of Al_2O_3, SiO_2, and other oxides present in such extracts do not seriously interfere with these calculations. The results of many tests in our laboratories show good agreement between determined and calculated values.

These extraction methods have made it possible for investigators to determine whether or not a cement could produce false set by precipitating gypsum. This has led most, if not all, recent investigators to conclude that dehydrated gypsum is the principal cause of false set. The knowledge that mixing of the paste can destroy false set has led them to the realization that the mixing period in the tests designed to test for false set should be short if the maximum amount of stiffening is to be determined.

Methods of Testing for False Set

An anonymous [38] investigator appears to have been the first to publish a method designed principally to detect false set. The proposed method was based on the sedimentation of slurries of the cement with water and with white spirit of turpentine. The results obtained were as follows:

	Spirit		Water		Vicat set		
Sample	Time taken to settle	Volume after settlement	Time taken to settle	Volume after settlement	Init.	Final	Volume after settlement [a]
	min.	*cc*	*min.*	*cc*	*min.*	*min.*	%
Fine sand	20	14	20	14¾	--------	--------	6.2
Fine emery	20	10	20	10½	--------	--------	5.0
Cement 1	100	13	45	17¼	90	210	32.7
Cement 2	65	12¾	3	39½	--------	5	209.8
Cement 3	165	13½	55	17½	45	120	29.6
Cement 4	80	12¾	3	38½	--------	5	201.9
Cement 5	100	13¼	40	16½	105	220	24.5
Cement 6	75	12¾	35	17½	30	110	37.2
Cement 6 (after ignition)	65	12	16	19¼	--------	--------	60.4
Cement 7	80	13	50	16½	115	230	26.9
Cement 7 (after ignition)	85	12	21	18¾	--------	--------	56.2

[a] Increase in water over that in spirit.

At about this time (1929), the U.S. Bureau of Reclamation began to work on a test method and a specification by which false setting cements could be rejected. It appears that the difficulties with false set became acute for this user primarily from the use of cements with low potential $3CaO \cdot Al_2O_3$ contents and the necessity of transporting the concrete some distance from the mixer before placing it in the forms.

In March 1937, the U.S. Bureau of Reclamation printed Specification No. 898D which developed into the present Federal Method 2501—"Early Stiffening of Cement, Paste Method" [39]. In No. 898D, 500 g of cement was kneaded for 3 min with 26 percent water in accordance with ASTM Designation C 77–32 [1]. The paste was molded into the Vicat ring and tested for depth of penetration of the 1-cm plunger of the Vicat apparatus. The cement was considered to be false setting when the plunger failed to penetrate 2 mm below the original surface 2½ min after mixing was completed.

Experience with this method showed that some cements required more than 26 percent water to produce workable pastes. The method was therefore changed to permit the use of the amount of water required to give a penetration of 35±2 mm. Also, the time at which the final penetration was determined was changed from 2½ to 5 min after mixing was completed. Cements may be rejected by specifications based on this method when the difference between the initial and final penetrations is less than 17 mm.

The State of Washington Department of Highways [40] checks all cements used in their work for stiffening characteristics and warns the resident engineer on construction that additional work may be required in placing concrete made with certain cements. In their method, which was revised in 1950, they mix a mortar of one part cement and two parts graded Ottawa sand with sufficient water to give a flow of 101 to 110 percent, ASTM Method C 109 [1]. They mix the water and cement for 30 sec in a bowl with a spoon. The sand is then added and the mortar is mixed for 60 sec. The Vicat mold is then filled and the depth of penetration of the Vicat plunger is measured 5 min after completion of the mixing. If the depth of penetration is less than 30 mm, the cement is considered to be false setting.

In 1955, the State of Nebraska [41] included a method of determining false set in a specification for portland cement. This method of test consists of determining the depth of penetration of the 1-cm plunger of the Vicat apparatus in a neat cement paste of normal consistency, ASTM Designation C 187 [1]. Penetrations are determined at 3, 4½, and 8 min after the water is added to the cement. The paste is remixed and remolded after the third reading and a final reading is taken at 10¼ min after the initial contact with water. A cement is classed as false setting when either the second or third penetration is less than 50 percent of the first penetration, and the fourth penetration is 90 percent or over, of the first penetration.

The American Society for Testing Materials [1] adopted a method in 1955 known as ASTM Designation C 359, "Tentative Method of Test for False Set of Portland Cement". This has been adopted in slightly modified form as Federal Method 2511 [39], "Tentative Method of Test for Early Stiffening of Portland Cement, Mortar Method".

This method, which was patterned after the Nebraska method [41], measures the depth of penetration of the 1-cm plunger of the Vicat apparatus in a 1:1 mortar. The mortar is mixed by machine and placed in a mold in slightly less than 3 min. Penetrations are determined at 3, 5, 8, and 11 min after mixing is started. After the 11-min reading is taken, the sample is remixed and remolded and the penetration is measured to determine whether or not the original workability of the mortar can be restored.

It appears that no other country has either adopted a standard method of test for false set or included limits for false set in their specifications for portland cement. However, many investigators in other countries have studied the problem of false set and some have introduced methods of testing for false set.

Manabe [42] used a method in which 10 g of cement was shaken with 15 ml of water in a 30-ml graduated cylinder for a prescribed period of time. The rate of sedimentation was measured and the results were correlated with results obtained by Federal Method 2501.

Sulikowski and Ziarno-Czamarska [43] used an electrical conductivity method to show false setting in cements which had been heated to dehydrate the gypsum. They found that the slurry of the unheated cement showed a rapid and then progressively slower decrease in electrical resistance whereas the slurry of the heated cement showed a pronounced maximum on the curve.

Bucchi [44] distinguished between false and flash set by an extraction test. In this test, two 5-g samples of the initial setting pat are weighed to the nearest 1 mg at the moment the pat shows initial set by the Vicat needle. One sample is extracted in saturated lime water and analyzed for SO_3, which is called S and expressed as percent of paste. The other sample is ignited at 950 °C to obtain loss on ignition, called Pa. Then, the SO_3 content in terms of anhydrous cement is

$$\frac{S}{100-Pa}\times 100$$

In the case of flash set, the extract gives only a faint opalescence when treated with $BaCl_2$ to precipitate $BaSO_4$, whereas, with false set, a measurable amount of $BaSO_4$ is precipitated.

Steinour [7] and Blanks and Gilliland [16] discuss some methods of testing for false set which they obtained by personal communications with the investigators.

A number of investigators have demonstrated the ability of small amounts of dehydrated gypsum to produce stiffening in pastes of inert powders. Typical of these are the results obtained by Hansen [34]. In these studies, quartz was ground in a cold mill to about the fineness of portland cement. One sample was ground without any additions; one was ground with gypsum equivalent to 2.0 percent SO_3; and one was ground with molding plaster equivalent to 2.0 percent SO_3. These were blended to give mixtures with varying SO_3 contents and the mixtures were tested for false set by ASTM Method C 359. The results were as follows:

False set in quartz paste as determined by ASTM Method C 359

	Paste containing gypsum penetration—mm					Paste containing molding plaster penetration—mm				
SO_3	Initial	5 min	8 min	11 min	Re-mix	Initial	5 min	8 min	11 min	Re-mix
%										
0	50+	45	46	44	50+	50+	45	46	44	50+
0.25	47	43	42	42	47	49	40	38	30	50+
0.50	46	44	40	48	46	46	38	27	20	50+
1.00	46	45	41	43	47	48	10	8	7	50+
1.50	47	47	42	40	46	47	5	0	0	50+
2.00	48	44	41	41	48	41	0	0	0	50+

These results indicate that about 0.5 percent SO_3 as dehydrated gypsum could produce a mild stiffening in a cement paste provided the cement did not combine with more than traces of SO_3 during the test period. However, the cements that combine with SO_3 at very rapid rates during the first few minutes might not show false set, except when most or all of the gypsum has been dehydrated.

False Set Produced by Aeration

Swayze [45] demonstrated that certain clinkers which do not require calcium sulfate to prevent flash set may develop quick-stiffening tendencies when the powders are aerated. The clinker used had the following calculated compound composition—percent by weight:

$3CaO\cdot SiO_2$	73.9	Free CaO	0.6
$2CaO\cdot SiO_2$	9.9	MgO	.6
$3CaO\cdot Al_2O_3$	None	SO_3	.01
$4CaO\cdot Al_2O_3\cdot Fe_2O_3$	11.2	Na_2O+K_2O	.04
$2CaO\cdot Fe_2O_3$	3.7	Loss on ignition	.08

This was ground in a laboratory mill to specific surfaces of about 2700 cm²/g without calcium sulfate, with sufficient gypsum, and with sufficient natural anhydrite to give 2.5 percent SO_3. Each grind was made without and with either 0.5 or 0.2 percent water added to the mill. The results obtained by Swayze are as follows:

False set in cold ground laboratory cements, ASTM Method C 359: 32 percent water in mortar

Sample condition	Penetration—mm					Penetration—mm				
	Init.	5 min	8 min	11 min	Remix	Init.	5 min	8 min	11 min	Remix
	Clinker Only—Dry Grind					Clinker Only—0.5% Water				
Fresh sample	50	50	50	47	50	50	50	50	50	50
Aerated 16 hr	50	1	0	0	50	50	50	49	12	50
Heated 260—7 da [a]	50	1	0	0	50	50	50	42	5	50
Aerated 16 hr	50	11	0	0	50	50	50	33	2	50
	Clinker+Gypsum—Dry Grind					Clinker+Gypsum—0.5% Water				
Fresh sample	50	50	50	50	50	50	50	50	50	50
Aerated 16 hr	50	3	0	0	50	50	2	1	1	50
Heated 260—7 da [a]	50	0	0	0	50	50	0	0	0	50
Aerated 16 hr	50	0	0	0	50	50	0	0	0	50
	Clinker+Anhydrite—Dry Grind					Clinker+Anhydrite—0.2% Water				
Fresh sample	50	50	5	2	50	50	50	50	50	50
Aerated 16 hr	50	50	2	0	50	50	50	2	0	50
Heated 260—7 da [a]	50	39	3	0	50	50	50	38	3	50
Aerated 16 hr	50	50	2	0	50	50	50	50	35	50

[a] Fresh sample.

Swayze points out that it was difficult to grind the clinker plus anhydrite mixture because of ball-coating and that, accordingly, the powdered clinker was aerated before grinding was completed. The cements produced in all of the other grinds showed no quick-stiffening tendencies in this test until they had been aerated. Then, all developed quick-stiffening tendencies.

The fresh samples of all grinds when heated to 260 °F for 7 days in an open can and cooled in a closed can developed quick-stiffening tendencies. Aeration of these samples produced no changes in them as determined by the method of testing.

Swayze supplied the writer with a sample of the clinker ground dry without calcium sulfate. This was tested as received and after aeration in laboratory air for 48 hr. The latter was tested with 2 percent SO_3 added as powdered gypsum and with 2 percent freshly burned CaO. The results were as follows:

Sample	Additions	Water	Penetration—mm				
			Init.	5 min	8 min	11 min	Remix
		%					
A—As Received	None	32	50+	50+	37	2	50+
B—Aerated 48 hr	None	32	50+	6	1	1	50+
C—Aerated 48 hr	2% SO_3	32	50+	11	1	0	50+
D—Aerated 48 hr	2% CaO	32	50+	37	3	1	50+

The A and B samples were tested to determine the rate at which they combined with $CaCl_2$ by shaking 200 g with 150 ml of a 3 percent $CaCl_2$ solution. The results were as follows:

Sample	Grams Cl_2 combined for 100 g of clinker in time indicated	
	1 min	3 min
A—As Received	0.003	0.002
B—Aerated 48 hr	.002	.002

Swayze concluded from his studies that aeration increased the reactivity of the crystals of $3CaO{\cdot}SiO_2$ toward water. The results of the tests with the reaction toward $CaCl_2$ indicate that the aluminate phase combined with this salt at a very slow rate. It is believed that this cement should react with $CaCl_2$ because Swayze (personal communication) says that this cement combines with about 2.5 percent SO_3 in 24 hr.

Following this work by Swayze, tests were made in our laboratories with a number of clinkers. The clinkers were collected so that most of them did not come in contact with any water. These were then ground in a cold laboratory mill with gypsum. The freshly ground and aerated cements were tested by the extraction test for an indication of whether or not gypsum would precipitate from the liquid phase of the cement pastes, and for false set by ASTM Method C 359. The results for false set are given in table 2.

The results of the extraction tests did not indicate presence of either dehydrated gypsum or of excessive amounts of alkali sulfates in any of these cements. There is no reason to believe that more than traces of dehydrated gypsum could have formed during the grinding of these cements.

The results of the false set test show that some of the freshly ground samples stiffened somewhat during the test. For example, the penetration at the 11-mm period was 28 mm for sample B–1. It is believed that some stiffening in this test can be classed as normal stiffening for some cements.

A number of the cements show some stiffening during aeration. In some cases, the stiffening produced in 24 hr of aeration was not present in the cement which was aerated for 48 hr. Swayze and others claim that this happens frequently.

In this study, this type of false set was obtained with Types I, II, and III cements. Hence, it does not appear to be characteristic of any one type of clinker.

One must remember that grinding at temperatures below about 200 °F is never done commercially and that results similar to those obtained with cements ground at low temperatures may never be obtained in practice. This might be particularly true if the clinker contains some water. Many people have felt that water released from gypsum during grinding and storage has an influence on the behavior of the cement.

Takemoto, Ito, and Hirayama [18] obtained the data given in table 3 for cements aerated for 0, 5, and 15 hr.

A general statement by these authors regarding gypsum is as follows: "Gypsum shows a remarkable effect as a grinding aid. It seems to reduce cement coating on grinding media, flakes in cement, and total grinding time at temperatures below 105 °C (221 °F)."

They found that cements ground below 105 °C with gypsum, as compared with cements ground above 105 °C had many more medium size particles (between 15 and 40μ), less tendency to false set by aeration, and greater mortar strength.

Regarding false set, they state "Generally, cement ground at 20 °C had slight tendency to false setting, and even cement ground at 20 °C with hemihydrate showed normal setting after aeration for 15 hr. Cement ground at 20 °C with dihydrate had scarcely any tendency to false set by aeration. These cements ground at 85 or 105 °C with dihydrate had a tendency to false set by aeration, but the tendency disappeared after aeration for 15 hr. Cement ground at 130 or 150 °C with natural gypsum had a remarkable tendency to false set by aeration. The tendency to false set when ground at 85 or 105 °C with hemihydrate was similar to that of cement ground above 130 °C with gypsum."

"The poorer the particle size distribution of cement, the greater the tendency to false setting by aeration, even for cement ground at 20 °C

Table 2. *Data for clinkers ground in a cold mill with gypsum to give SO_3 contents of approximately 2.0 percent*

Data for clinker						Data for penetration test penetration—mm [b]				
Sample [a]	Type	SO_3	K_2O	Na_2O	Loss on ignition	Initial	5 min	8 min	11 min	Remix
		%	%	%	%					
A–1	I	0.03	0.41	0.13	0.30	50 50 50	50 47 38	50 46 31	50 43 16	50 50 50
A–2	II	0.17	0.36	0.09	0.39	50 50 50	50 50 50	50 50 50	50 50 44	50 50 50
A–3	III	0.10	0.28	0.10	0.72	50 50 50	50 13 50	50 7 45	50 5 38	50 50 50
B–1	I	0.53	0.56	0.10	0.12	50 50 50	50 42 38	32 15 15	28 8 5	50 50 50
C–1	I	0.35	0.63	0.36	0.75	50 45 50	43 24 41	40 10 28	39 5 12	50 24 44
C–2	II	0.63	0.79	0.22	0.36	50 50 50	50 45 46	50 12 34	45 8 10	50 50 50
D	I	0.49	0.11	0.10	0.03	50 50 50	50 50 50	50 41 50	50 39 50	50 50 50
E	I	0.09	0.39	0.24	0.22	50 50 50	50 50 45	45 43 42	44 41 38	50 50 50
F	I	0.11	0.46	0.11	0.53	50 3 16	50 1 8	50 0 7	42 0 5	50 50 50
G	I	0.48	0.08	0.14	0.05	50 50 50	44 50 50	40 50 44	37 48 44	50 50 50
H–1	I	0.87	0.49	0.10	0.10	50 33 50	50 5 50	50 2 50	50 1 50	50 50 50
H–2	II	0.90	0.47	0.08	0.26	50 4 50	50 2 50	50 1 50	50 1 39	50 50 50
I	III	0.46	0.77	0.25	0.54	50 50 50	50 50 50	50 50 47	50 50 34	50 50 50

[a] Letter indicates plant.

[b] First line original cement; second line cement aerated 24 hr; third line cement aerated 48 hr. Types I and II cements tested with 30 percent water; type III cements tested with 32 percent water.

with gypsum. Therefore, we must conclude that not only the extent of the dehydration of gypsum but also the size composition of the cement affects its tendency to false set by aeration."

It appears that it is not possible to predict what aeration might do. In an experiment in our laboratories, a clinker was ground without water in a mill at about 200 °F with natural anhydrite equivalent to 2.0 percent SO_3 (cement A). A similar grind was made, except that 2.0 percent water was added to the mill as grinding was started (cement B). These were tested for false set as follows:

1. A as ground
2. A+2.0 percent SO_3 as gypsum
3. A aerated 48 hr
4. B as ground
5. B+0.5 percent SO_3 as plaster of Paris
6. B aerated 48 hr

The results with ASTM Method C 359 were as follows:

Cement	Water	Penetration—mm				
		Initial	5 min	8 min	11 min	Remix
	%					
A — No water in mill						
As ground	30	27	12	3	3	10
2.0% SO_3 as gypsum	30	50+	41	30	15	50+
Aerated 48 hr	30	(a)	----	----	----	----
B — 2.0% Water added to mill						
As ground	30	40	9	3	2	6
0.5% as plaster	30	50+	50+	50+	50+	50+
Aerated 48 hr	30	(a)	----	----	----	----

[a] The mortar became dry and crumbly in the mixer and the temperature rose from 71 to 95 °F and from 71 to 84 °F for cements A and B, respectively.

These results indicate that the original cements were flash setting because the anhydrite could not dissolve fast enough to react with the $3CaO \cdot Al_2O_3$. The addition of 2.0 percent of SO_3 as gypsum to cement A almost eliminated the flash setting and the addition of 0.5 percent SO_3 as plaster of Paris

TABLE 3. *Data from paper by Takemoto, Ito, and Hirayama*

Cement No.[b]	W/C	Penetration—mm			Aeration[a] 5 hr				Aeration 15 hr			
					W/C	Penetration—mm			W/C	Penetration—mm		
		Init.	5 min	10 min		Init.	5 min	10 min		Init.	5 min	10 min
	%				%				%			
1	23.9	35	29	26	24.5	34	1	1	24.2	35	25	15
2	23.6	33	6	6	24.8	34	2	2	25.0	34	6	5
3	24.3	35	8	4	25.0	15	1	1	25.0	34	2	1
4	23.5	36	21	8	24.3	34	3	1	24.3	35	1	1
5	23.1	36	23	24	23.9	34	1	1	24.0	37	1	1
6	25.8	35	31	33	27.0	35	28	32	27.8	36	30	18
7	24.5	35	32	29	25.8	34	6	5	26.5	36	31	23
8	25.5	36	35	36	26.8	7	3	4	25.0	35	27	15
9	24.3	34	14	14	26.0	8	4	5	24.2	34	1	1
10	24.0	36	12	16	25.5	9	4	4	24.5	34	0	0
11	28.5	32	8	2	29.5	38	17	9	29.5	8	3	2
12	26.0	33	1	0	28.0	35	0	0	27.8	30	3	2
13	25.0	34	30	30	26.3	33	15	14	26.0	35	29	24
14	24.2	35	16	12	24.5	6	0	0	25.0	34	1	0
15	24.2	34	30	20	25.3	34	11	7	26.0	37	31	26
16	23.7	36	16	4	23.0	35	0	0	24.0	35	1	0
17	26.3	34	33	30	27.4	33	27	23	28.3	35	33	28
18	24.2	22	12	12	25.0	15	1	0	25.8	25	6	5

[a] Aeration layers 2 mm thick exposed at temperature of 20 °C and relative humidity of 85 percent.
[b] Blaine surfaces varied between 3500 and 3400 cm^2/g.

to cement B did eliminate the flash setting. Aeration appears to have greatly increased the reactivity of the $3CaO \cdot Al_2O_3$ toward water in both cements.

The composition of this clinker was as follows:

Complete oxide analysis—percent									Free CaO—percent
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	SO_3	Loss on ignition	Total	
22.9	6.0	2.5	64.3	3.0	0.54	0.23	0.11	99.58	0.88

Calculated compound composition—percent					Alkalies—percent			
C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	K_2O	Na_2O	Total	Na_2O Equiv.
43.0	33.3	11.7	7.6	0.4	0.33	0.17	0.50	0.39

Clinker of similar composition was ground in a commercial mill under conditions that were expected to dehydrate some or all of the gypsum. This cement was tested as received and, then, a sample was aerated for 24 hr. Samples of the aerated cement were stored in sealed containers for tests at later ages to determine whether or not the false set would disappear with age when not exposed to air and moisture. The cements were tested for false set by ASTM Method C 359 and extracts of slurries of 200 g of cement in 150 ml of water shaken for 1-, 3-, and 10-min periods were analyzed for SO_3, CaO, and $(OH)_2$, and the equivalent Na_2O content was calculated. The results of these tests are shown below.

The liquid phase of the paste of the cement as received was highly supersaturated with respect to gypsum at the 1-min period but only slightly, if at all, at the 3- and 10-min periods and the cement showed no false setting tendencies. The liquid phase of the pastes made with the cement after aeration for 24 hr and with the aerated cement stored for periods up to 4 weeks was highly supersaturated with respect to gypsum at both the 1- and 3-min periods. These results indicate that aeration decreased the rate at which the cement could combine with SO_3. Storage of the aerated cement in sealed containers up to 4 weeks did not change the cement with respect to its ability to combine with SO_3.

Extraction data for period indicated—moles/liter								Penetration data—mm			
Sample[a]	Storage, weeks	1 min		3 min		10 min		Initial	5 min	8 min	Remix
		SO_3[b]	Na_2O	SO_3[b]	Na_2O	SO_3[b]	Na_2O				
C	None	0.0347	0.0163	0.0210	0.0127	0.0188	0.0172	50	50	50	50
D	None	------	------	------	------	------	------	3	0	0	50
E	1	.0442	.0141	0.457	.0170	.0207	.0175	2	0	0	50
F	2	.0419	.0150	.0376	.0177	.0210	.0193	3	0	0	50
G	3	.0432	.0153	.0380	.0169	.0214	.0182	3	0	0	50
H	4	.0430	.0155	.0373	.0171	.0208	.0186	3	0	0	50

[a] C = Sample as received; D is C aerated 24 hr; E to H are D stored for weeks indicated.
[b] SO_3 at equilibrium should be about 0.019 moles/liter.

When a cement shows flash set, it is generally assumed that this is the result of a rapid reaction of $3CaO{\cdot}Al_2O_3$ with water. However, the tests by Gilliland, Hansen, and Manabe indicate that the reactivity of the $3CaO{\cdot}Al_2O_3$ with calcium sulfate and chloride is decreased when the cement is aerated. This, of course, does not necessarily show that the reactivity of the $3CaO{\cdot}Al_2O_3$ with water has been decreased by aeration. Swayze showed that aeration caused flash set with a clinker that contained no calculated $3CaO{\cdot}Al_2O_3$ and assumed that aeration increased the reactivity of the $3CaO{\cdot}SiO_2$.

The fact that pastes of cements A and B made with clinker and natural anhydrite after aeration for 48 hr became extremely hot and crumbly, whereas the pastes of the cements before aeration showed milder flash set indicates that aeration increased the reactivity of the $3CaO{\cdot}Al_2O_3$ toward water. Actually, the reactivity of the $3CaO{\cdot}Al_2O_3$ toward water may not have been increased but the ability of the natural anhydrite to retard the reaction of $3CaO{\cdot}Al_2O_3$ with water probably was decreased. These results indicate that, in the cases cited, where the rates at which the cements combine with sulfate and chloride were decreased, the ability of the $3CaO{\cdot}Al_2O_3$ to react with sulfate and chloride had been decreased.

Hansen [34] concluded from work reported in 1958 that aeration by reducing the rate at which the cement combined with calcium sulfate permitted the dehydrated gypsum to precipitate as gypsum and produce false set. Actually, the precipitation probably was largely responsible for the rapid stiffening but its effect may have been augmented by a rapid reaction of the $3CaO{\cdot}Al_2O_3$ with water.

This raises the question as to why aeration either increases the reactivity of $3CaO{\cdot}Al_2O_3$ towards water or decreases the ability of calcium sulfate to combine with $3CaO{\cdot}Al_2O_3$ and prevent flash set. Hansen [46] has postulated that Ca^{++} and O^{-} ions in the surfaces of $3CaO{\cdot}Al_2O_3$ crystals can chemisorb water molecules from which H^+ and OH^- ions migrate into the crystals and split off $Ca(OH)_2$ and rearrange the ions in the crystals to form $2CaO{\cdot}Al_2O_3{\cdot}xH_2O$. It is conceivable that these partially reacted crystals cannot chemisorb $SO_4^{=}$ and Cl^- ions and, accordingly, cannot react with calcium sulfate and calcium chloride. It is also conceivable that these partially reacted crystals can chemisorb H_3O^+ and OH^- ions and, in that way, react rapidly with water. In general, cement appears not to become very badly flash setting upon aeration and, since prolonged aeration often destroys the flash setting tendencies developed by shorter periods of aeration, it appears that the reaction with H^+ and OH^- ions either from water vapor or from liquid water tends to form a layer of hydrated material on the surfaces of the crystals that retards further reaction.

Swayze suggested that the reactivity of the $3CaO{\cdot}SiO_2$ with water is increased by aeration. However, it seems from these new data that the reactivity of the calcium aluminoferrite phase may have been increased by aeration and that the fast stiffening was caused by a rapid reaction of this phase with water and not by increased reactivity of the $3CaO{\cdot}SiO_2$. The data from our laboratories given in table 2 show that some Type II cements develop false set when aerated and indicate that both $3CaO{\cdot}Al_2O_3$ and the calcium aluminoferrite phase can be modified by chemisorption of water vapor so that their reactions with water cannot be retarded by calcium sulfate.

Cement technologists have long known that aeration produced false set in some cements. It seems that the scarcity of data bearing on the mechanism of this behavior probably resulted from the lack of methods of detecting what might be called mild cases of either flash or false set. ASTM Method C 359 appears to be able to detect very mild degrees of fast stiffening and has given investigators a tool by which the stiffening characteristics of cements can be studied in more detail.

There is a need for additional work to determine the exact mechanism by which aeration causes false set. However, it seems from a practical standpoint that the false set that causes trouble in the field is produced by dehydrated gypsum, because it appears that cements will seldom be aerated sufficiently to become false setting from the aeration reaction. It should be pointed out, however, that there is a great need for the samplers and testers to handle their samples in ways that do not permit aeration to develop false set in samples when the cements are not false setting.

Summary

Since the time of the First International Symposium on the Chemistry of Cement, progress regarding false set seems to have been as follows:

1. Rapid stiffening of cement pastes has been separated into (a) flash set produced by rapid reaction of $3CaO{\cdot}Al_2O_3$ with water; (b) false set produced by crystallization of gypsum.
2. A number of suggested causes of false set such as rapid absorption of water by clusters of cement particles, formation of alkali carbonates during aging, and so forth, have been considered and discarded.
3. Several methods of testing for false set have been developed.

4. Most evidence points to the conclusion that false set in commercial cements is almost entirely the result of dehydrating gypsum to either or both hemihydrate and soluble anhydrite during either or both grinding and storage.
5. A new problem has been created by the finding that aeration produces a false set that is not connected with dehydrated gypsum.

The writer wishes to express his appreciation to the management of the United States Steel Corporation and the Universal Atlas Cement Division for permission to publish this paper and to his colleagues in the research laboratories for their assistance in its preparation.

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Discussion

Toshio Manabe

Cement chemists may be interested in the problem of false set in cement, not only because it causes troubles in the field, but because it gives many important suggestions to study the reaction of the initial hydration period of cement.

I agree with Dr. Hansen in considering that "the crystallization of gypsum from cement paste is the principal cause of false set in commercial cements." However, as to the consideration of mechanism of false set, there are some questions on which I cannot agree. Especially I would not support Dr. Hansen's theory that in fresh cement C_3A combines with calcium sulfate at a rate which permits the crystallization of little, if any, gypsum in the paste, whereas aeration retards the rate of combination and consequently increases the amount of crystallization of gypsum.

In my experiments [1], it was found that a fair amount of calcium sulfate was rapidly combined with cement in the first few minutes and then the rate of combination became very slow. The time at which the rapid combination of calcium sulfate with cement began was delayed a few minutes by aeration, but the amount of calcium sulfate rapidly combined was nearly equal to that in the unaerated cement, as shown in figure 1. That is, by aeration, the time at which the rapid combination of calcium sulfate with cement occurs is shifted, but the amount of calcium sulfate rapidly combined within the first 10 min or so is scarcely decreased.

It seems that these results are considerably different from that obtained with $CaCl_2$ by the author. It is probable that the reactivity of aerated clinker compounds towards calcium sulfate may be much greater than that towards calcium chloride.

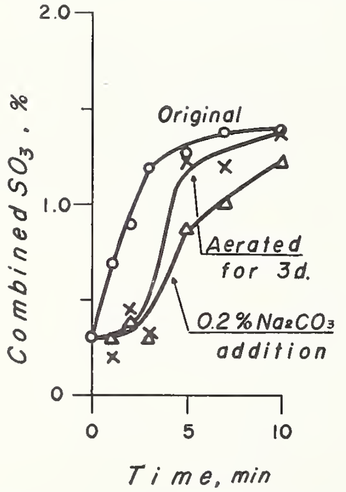

FIGURE 1. *Amount of* SO_3 *combined as sulfoaluminate during the initial hydration period.*
(Total SO_3 of the cement, 2.22%; W/C=50%)

Now, let us consider a cement which contains 2.0 percent SO_3, for example. When the unaerated cement is mixed with water, 0.6–1.0 percent SO_3 would be rapidly combined with cement in a few minutes, and the rest, 1.0 percent or more SO_3, may be precipitated as dihydrate, if all SO_3 is present as dehydrated gypsum. Therefore, even in the fresh cement, a tendency to false setting would be expected. But in practice the cement probably would not show any false-setting tendency. What can be the reason?

If the gypsum in cement is only partly dehydrated during grinding and about 1.0 percent of SO_3 is present as gypsum, and if the dehydrated gypsum preferentially combines with cement, false set would not appear in the unaerated cement. As will be mentioned later, however, if gypsum remains partly unchanged in cement, it acts as crystal nuclei and effectively accelerates the rate at which the dehydrated gypsum converts to dihydrate. In this case, it seems that the precipitation of gypsum takes place during mixing, and then false set would not appear even if the cement is aerated.

From the data reported by Takemoto, Ito, and Hirayama [2] and Murakami [3], it is conceivable that gypsum in commercial cement is nearly completely converted to hemihydrate and, in some cases, even to soluble anhydrite during grinding. However, since soluble anhydrite has a very strong hygroscopic property, it reconverts easily to hemihydrate when exposed to air. Accordingly, it may be regarded as pretty certain that in most commercial cements, almost all calcium sulfate may be present in the form of hemihydrate.

From results of many penetration tests I came to the following conclusion:

Almost all commercial portland cements have a tendency to stiffening caused by dehydrated gypsum at a certain period after contact with water, and the stiffening is fully developed within a few minutes. The rate of development of stiffening may be pictured as in figure 2. If the paste is mixed until the time denoted by "e" in the figure, the stiffening tendency does not appear, because the structure formation which causes

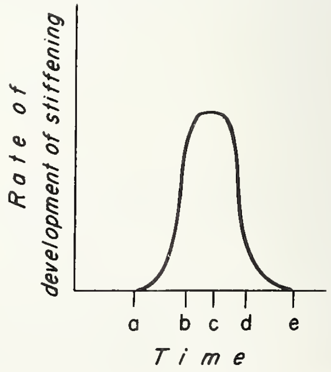

FIGURE 2. *Rate of development of stiffening.*

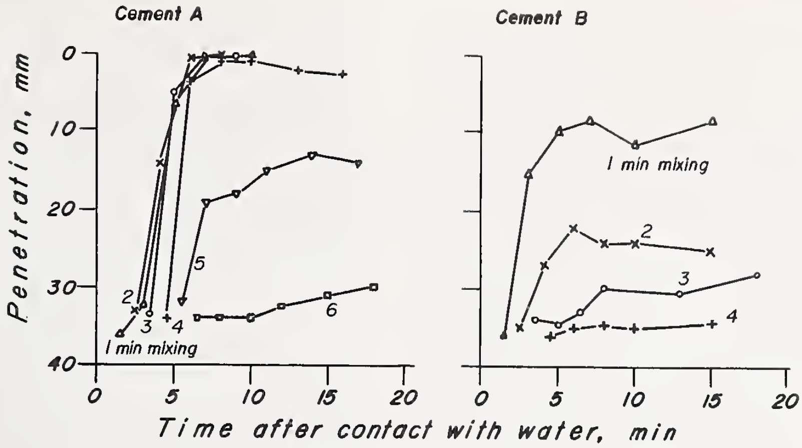

FIGURE 3. *Effect of mixing time on development of stiffening.*

the stiffening of the paste is destroyed by mixing. If the paste is mixed until "a", the stiffening is fully developed and if mixed until "b", "c", or "d", the stiffening is partly developed.

Figure 3 shows examples of the results of penetration tests which were carried out in neat cement pastes of approximately normal consistency by varying mixing time. In the case of cement A, "a" in figure 2 corresponds to 1 min, "e" corresponds to 6 min, and "b"–"d" correspond to 2–5 min. In cement B, the stiffening was developed immediately after mixing with water, and 3-min mixing corresponds to "e".

Further, the results of experiments on the chemical compositions of extracts from paste and also on the amount of SO_3 combined with cement permitted the drawing of a diagram, figure 4. This figure shows the distribution of SO_3 among the various forms in paste. When unaerated cement is mixed with water, the combination of SO_3 with cement immediately takes place, and the precipitation of gypsum follows at once; this process is shown by the solid line in the figure. But the time taken for this rapid combination and precipitation to begin ("a" in the figure) is progressively increased by aeration, as shown by the broken line. In comparison with the results of the penetration test, it is found that the time at which the stiffening occurs corresponds to that at which the combination and the precipitation rapidly appear.

Therefore, even if all the gypsum is converted to dehydrated gypsum, in the unaerated cement, the precipitation of gypsum takes place completely during mixing, the structure formation does not develop in the paste, and a tendency to false setting is not observed. If the precipitating time is delayed by aeration, however, the precipitation of gypsum occurs partly or wholly after mixing is completed, and the stiffening appears.

From these considerations it seems important to know when the precipitation of gypsum occurs after mixing with water. In the case of commercial plaster of Paris, the precipitation of gypsum usually occurs at about 15 min after contact with water. Plaster of Paris is commonly manufactured by the "kettle process", in which gypsum is almost converted to soluble anhydrite during heating and then reconverted to hemihydrate by the process of aging. However, it was found that when gypsum was converted only to hemihydrate or partly to soluble anhydrite by heating at rather lower temperature, the dehydrated gypsum reconverted to gypsum 4 or 5 min after contact with water. If gypsum was almost completely converted to soluble anhydrite, the reconversion to gypsum was retarded progressively, and even if the soluble anhydrite was converted to hemihydrate by exposing to air, the time at which the precipitation of gypsum occurred was almost unchanged, as in the case of commercial plaster of Paris.

By adding pulverized cement clinker, the setting time of plaster of Paris is considerably accelerated. This result indicates the ability of the clinker to accelerate the precipitation of gypsum. This could be the reason why fresh cement in which all of the gypsum is converted to dehydrated gypsum does not manifest false-setting tendency.

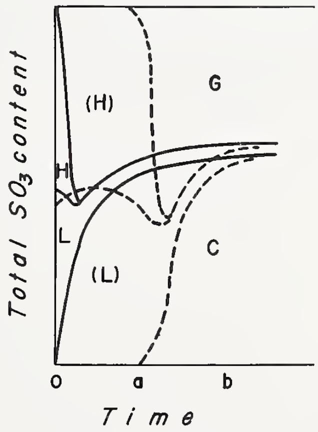

FIGURE 4. *Distribution of* SO_3 *among the various forms.*
Solid line, fresh cement; broken line, aerated cement; H, hemihydrate; G, gypsum; C, calcium sulfoaluminate; L, liquid phase.

When the cement is aerated, the accelerating ability of clinker is weakened, so that the precipitating period of gypsum is delayed and false set appears.

Then, what part of the clinker acts as the accelerator? It is likely that the formation of the high-sulfate form of calcium sulfoaluminate gives rise immediately to the precipitation of gypsum.

The author has postulated that $2CaO{\cdot}Al_2O_3{\cdot}xH_2O$ is formed by aeration and that it cannot react with calcium sulfate. In this connection it would be interesting to note some results obtained in my experiments. A portion of cement which did not manifest false set was exposed to air which had been passed through dilute sulfuric acid solution to regulate the humidity. (The relative humidity was about 60 percent.) Another portion of the cement was exposed to air which was passed through potassium hydroxide solution first to remove carbon dioxide and then through the sulfuric acid solution. The results of penetration tests with these aerated cement were as follows:

	Aerated with air containing CO_2 penetration—mm			Aerated with air not containing CO_2 penetration—mm		
	Init.	5 min.	10 min.	Init.	5 min.	10 min.
As received	35	34	35	------	------	------
Aerated 12 hr	34	1	2	36	35	35
Aerated 24 hr	35	3	1	34	35	35

These results show that if the air does not contain carbon dioxide, false set does not appear by aeration. Therefore, it is probable that the products formed by hydration and subsequent carbonation play an important role in the false-setting phenomena caused by aeration.

It is well known that an addition of a small amount (0.1 percent or less) of alkali carbonates to a cement produces early stiffening of the paste. The author states that alkali carbonates precipitate calcium carbonate which might, in itself, cause stiffening of the paste just as the precipitation of gypsum does. But it seems to me that the amount of calcium carbonate precipitated is too little to make the paste stiffen.

Murakami [4] showed that addition of chemicals which acted as retarders of setting of dehydrated gypsum produced a tendency to false setting in cement paste, and concluded that alkali carbonates which retarded the precipitation of gypsum were formed in cement by aeration, and early stiffening resulted.

When alkali carbonates were added to cement paste, the rate of combination of SO_3 with the cement was decreased as in the case of aeration (fig. 1). But this similarity does not necessarily indicate that alkali carbonates are formed in cement by aeration. As mentioned by the author, it is probable that very little, if any, alkali carbonate is formed by aeration. Then I would rather consider that the addition of alkali carbonates and aeration act similarly only in the retardation of the rate at which SO_3 combines with the cement.

When a small amount of calcium lignosulfonate, which is often used in the field as dispersing agent or retarding agent, was added to cement pastes, a tendency to false setting appeared as shown in figure 5. In this case it was also found from the results of extraction tests that the rate of combination of SO_3 with cement was reduced by addition of calcium lignosulfonate and the precipitation of gypsum was retarded.

Another experiment on the ability of C_3A to accelerate the precipitation of gypsum also showed that the ability was reduced by aeration. The C_3A used in the study was prepared from reagent-grade calcium carbonate and aluminium oxide and, consequently, contained only a trace of alkali. Hence, it is clear that the reduction of the accelerating ability of C_3A is not caused by the formation of alkali carbonates.

Accordingly, it seems that the following conclusion could be drawn, that is, any conditions which retard the combination between calcium sulfate and cement have a tendency to produce false set.

In the next place, I should like to consider the degree of early stiffening of the paste. If

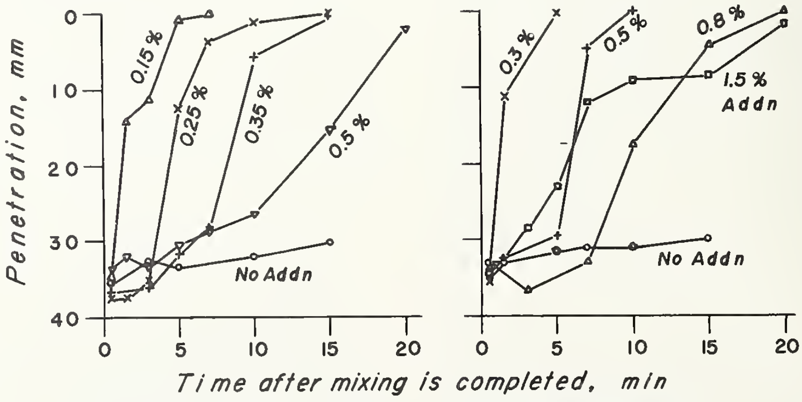

FIGURE 5. *Effect of addition of calcium lignosulfonate.*

the precipitation of gypsum causes the early stiffening, the degree of stiffening may be proportional to the amount of gypsum precipitated after mixing is completed.

The case of cements in which gypsum is completely dehydrated will be first considered. In these cases it is conceivable that if the precipitation of gypsum wholly occurs after mixing is completed, the degree of stiffening is at its maximum for the cement and may depend on the amount of SO_3 which does not rapidly combine with cement at the initial hydration period and precipitates as gypsum. This hypothesis may be confirmed by the following experiments.

Two grinds were made with a commercial portland cement clinker and a natural rock gypsum. The first one had an SO_3 content of about 0.7 percent, the second about 2.0 percent. The cements were then blended to obtain the desired intermediate SO_3 contents. Six cements thus obtained were heated to 140 °C for 2 hr to completely dehydrate the gypsum, then they were aerated for 2 days in small paper bags. Penetration tests were carried out for these cements using the Vicat apparatus. For the purpose of determining the maximum degree of stiffening, the pastes were mixed for 1½ min and then molded into the Vicat ring and tested for depth of penetration of the 10-mm plunger and the 5-mm plunger.

The results are given in figure 6.

Cement No. 1 showed a quick set accompanied by the evolution of considerable heat. Cement No. 2 did not manifest a tendency to false set. Cement No. 3 and the rest manifested the tendency to stiffening, and the degree of stiffening increased with the SO_3 content.

The amount of SO_3 which does not rapidly combine with the cement during the initial hydration period can be estimated by extracting the paste with lime solution. The results of the extraction tests on the pastes at the age of 20 min were as follows:

Cement No.	1	2	3	4	5	6
SO_3 content in cement percent of cement	0.70	0.79	1.00	1.21	1.56	2.13
Extracted SO_3 percent of cement	0.07	0.08	0.25	0.51	0.84	1.40
Combined SO_3 as sulfoaluminate percent of cement	0.64	0.71	0.75	0.70	0.72	0.73

The amount of SO_3 precipitated as gypsum can be estimated by subtracting the amount of SO_3 present in the liquid phase of the paste from the amount of extracted SO_3. The amount of SO_3 present in the liquid phase depends on the concentration of alkali in the liquid phase. In the case of the clinker used in the study the amount of SO_3 present in the liquid phase was estimated to be about 0.08 percent. These values represent the amount of SO_3 at the time "b" in figure 4.

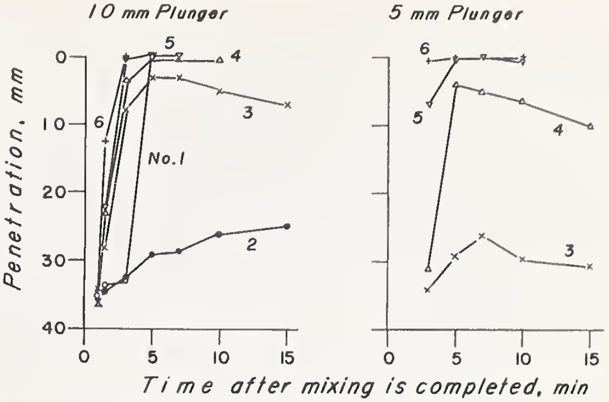

FIGURE 6. *Effect of calcium sulfate content.*
(Numerals in figure represent number of cement in table.)

From the table, it seems that the clinker used required about 0.75 percent of SO_3 for normal set. Hence the quick set shown in cement No. 1 was caused by the lack of SO_3. It also was clearly found that in cement No. 2 which did not show the stiffening, there was precipitation of little, if any, dihydrate, and that in cement No. 3 and the rest, the degree of stiffening increased nearly proportionally to the amount of precipitation of gypsum. Furthermore, it seems that the depth of penetration of the 10-mm plunger in paste is considerably prevented by the precipitation of gypsum equivalent to only 0.2 percent of SO_3.

When gypsum in cement is not completely dehydrated, that is, the calcium sulfate is a mixture of gypsum and dehydrated gypsum, the manner in which the dehydrated gypsum may behave during the first few minutes of the initial hydration period will be considered with an example.

A cement was prepared from a commercial clinker, gypsum, and hemihydrate labeled with S–35. The cement contained 2.32 percent of SO_3, which was made up of 0.14 percent from the clinker, 1.02 percent from the gypsum, and 1.06 percent from the labeled hemihydrate. The specific activity of SO_3 of the hemihydrate used in the study was 212.5 reg/min (register of 256 scaler), and the specific activity of the SO_3 in the cement was calculated to be 97.1 reg/min. One g of the cement was mixed with 0.5 ml of distilled water, and after 10 min it was shaken with 100 ml of lime solution for 4 min. Then the slurry was filtered on a Buchner funnel, and from 20 ml of the filtrate SO_3 was determined and from 70 ml the specific activity of SO_3 was determined. The activity of SO_3 in the filtrate was 84.2 reg/min, and the amount of SO_3 extracted was 1.70 percent. Consequently, the amount of SO_3 rapidly combined with cement within 10 min was 0.62 percent. From these data, it was calculated that 0.23 percent SO_3 from the gypsum and 0.39 percent SO_3 from the hemihydrate were combined with the cement within 10 min and also that the amount of hemihydrate preferentially combined with cement was only 0.23 percent as SO_3. Since the alkali content (R_2O) of the liquid phase at the age of 10 min was about 60 mM/l, 43 mM SO_3 should be contained in the liquid phase, corresponding to 0.17 percent of the cement.

From the result it is probable that when the cement comes in contact with water, the dehydrated gypsum preferentially dissolves but immediately transforms to dihydrate owing to the coexisting gypsum which acts strongly as crystal nuclei, and after that, the cement reacts at first with the SO_3 left in the liquid phase, which comes from dehydrated gypsum, and then the successive reaction occurs with the gypsum which is composed of gypsum present from the first and dihydrate precipitated from dehydrated gypsum. When the cement is not aerated, the reactivity of the cement is so strong that the amount of hemihydrate preferentially combined with the cement may be somewhat increased.

The effect of gypsum as crystal nuclei, of course, depends on the proportion of gypsum to dehydrated gypsum. If the proportion of gypsum is less than 25 percent of the total SO_3, the effect of the gypsum is obviously reduced.

The foregoing considerations about false set caused by the dehydrated gypsum may be briefly summed up as follows:

Gypsum in cement is usually dehydrated, during grinding, almost all to hemihydrate or even partly to soluble anhydrite. Such a dehydrated gypsum ought to reconvert to dihydrate in about 5 min after contact with water. But in case of cement, clinker, probably the aluminate phase, accelerates the precipitating period of gypsum to within 3 min. Hence, the structure developed by the precipitation of gypsum is destroyed by mixing, and the false-setting tendency does not appear. However, by aeration the accelerating ability of clinker is reduced and the precipitation of gypsum wholly or partly occurs after 3 min. Consequently, the structure formation develops after mixing is completed and the stiffening appears. If almost all the gypsum in the cement is dehydrated to soluble anhydrite owing to the high grinding temperature, it would be expected in some cases that clinker could not accelerate the precipitating period of gypsum to within 3 min; then even a fresh cement would manifest the false-setting tendency. If the grinding temperature is so low that 25 percent or more of the gypsum remains undehydrated, the undehydrated gypsum acts as crystal nuclei and accelerates the precipitation of gypsum. Hence, even the aerated cement does not manifest the false-setting tendency.

Therefore, in consideration of the false-setting phenomenon, the time at which the precipitation of gypsum occurs and the amount of gypsum precipitated are the important factors. The former depends on the degree of dehydration the gypsum is subjected to during grinding or storage and also the accelerating power of clinker for the precipitation of gypsum.

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Discussion

P. Seligmann and N. R. Greening

The purposes of this discussion are to confirm and to extend certain portions of the interesting line of reasoning developed in the discussion by Mr. Manabe.

The State of Hydration of Calcium Sulfate in Cement

Mr. Manabe states ". . . it is conceivable that gypsum in commercial cement is nearly completely converted to hemihydrate and, in some cases, even to soluble anhydrite during grinding." Data obtained at the Portland Cement Association Laboratories indicate that, because of the effectiveness of clinker as a dehydrating agent, this conclusion is more likely to be valid than might usually be supposed.

The technique used in these studies was the determination of the evaporable and nonevaporable water by the method of Copeland and Hayes [1],[1] involving drying at a water vapor pressure of 0.5 μ (over ice at the temperature of solid CO_2). As a standard for comparison, the room temperature dehydration of gypsum was studied; a sample of Mallinckrodt Analytical Grade gypsum (fine powder) was dried by this procedure and then successively equilibrated at 36 and 50 percent relative humidity. As shown in table 1, the gypsum loses well over 90 percent of its water at 0.5 μ water vapor pressure; consequently, if a cement containing calcium sulfate dihydrate were subjected to this drying procedure, most of the hydrate water would be classed as evaporable.

TABLE 1. *Room temperature dehydration of gypsum*

The mole ratio H_2O/SO_3 in the following table was computed on the assumption that the material after ignition at 950 °C was pure anhydrite.

Condition	Mole ratio H_2O/SO_3
As received	1.964
Dried at 0.5 μ water vapor pressure	0.083
Equilibrated at 36% relative humidity	.649
Equilibrated at 50% relative humidity	.663

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[1] Figures in brackets indicate the literature references at the end of this paper.

Evaporable water, nonevaporable water, and carbon dioxide were determined on 26 of the cements used in the Long-Time Study of Cement Performance in Concrete [2]. These values were then used in an analysis of the ignition loss of each cement, which was also measured. Since the SO_3 in the clinker is known for these cements [3] the contribution of the water and SO_3 by the added calcium sulfate could be accounted for separately. Table 2 shows, for each cement, the total loss on ignition and the mole ratios H_2O/SO_3 for the evaporable water and total water in the cement based both on the total sulfate present and on the added calcium sulfate. It is apparent that in all cases the mole ratio for the evaporable water is considerably less than 1.8–1.9, the range of values expected for dihydrate, and in many cases is less than that expected for the hemihydrate.

For reference, the last two columns of table 2 show the average and maximum temperatures of the cements in the streams from the finishing mill systems at the commercial plants where they were prepared [4]. No definite relationship between grinding temperature and water content is apparent.

The cements of table 2 had been stored in sealed containers for about 20 yr; it could be argued that this storage provided an abnormally favorable environment for the dehydration of gypsum by the clinker.

Further evidence on this point was obtained from tests made on four cements purchased from commercial sources in the Chicago area. For these cements, neither the grinding temperature nor the SO_3 content of the clinker was known. The results, shown in table 3, do not differ appreciably from those previously obtained.

X-ray diffraction patterns of the four commercial cements were made. Hydration products were detectable only in the pattern for cement 19737. In addition to the lines for the clinker compounds in this cement the diffraction pattern had a line at 3.50A, attributable to the anhydrite, and a line at 4.90A, presumably due to calcium hydroxide. These assignments were verified when a pattern of the cement after heating at 600–650 °C for 12 hr showed a disappearance of the 4.90A line, an intensification of the 3.50A line, and the presence of other anhydrite lines.

The same four commercial cements were examined petrographically.[2] In all four samples, the predominant form of calcium sulfate was the hemihydrate. In addition, traces of anhydrite and gypsum were found in cement No. 19737 and small quantities of calcium hydroxide in cements No. 19737 and No. 19738. The petrographic and X-ray examinations of No. 19737 thus appear to be relatively consistent. In the interpretation of these results, it must be pointed out that the crystal structure associated with calcium sulfate hemihydrate can be maintained by calcium sulfate over a considerable range of moisture contents without any appreciable change in optical or X-ray diffraction characteristics [5, 6].

Attempts have been made to measure the rate of dehydration of gypsum by ground clinker or by cement directly. The process appears to be very slow unless ball-milling is used. Thus, a sample of gypsum stored in a desiccator over ground clinker lost 0.1 percent of its water after 64 days at 70 °F.

TABLE 2. *Water content of the long-time-study cements*

Cement No.	Loss on ignition	Mole ratio H_2O/SO_3 based on				Cement temperature, °F	
		SO_3 in gypsum		Total SO_3		Average	Maximum
		Evap. water	Total water	Evap. water	Total water		
	Percent						
11	0.89	0.63	2.80	0.47	2.09	222	236
11–T	.86	1.14	2.95	.84	2.18	222	226
12	.37	0.00	0.56	.00	0.49	209	230
12–T	.58	.46	1.08	.43	1.01	229	245
13	1.60	.88	3.92	.88	3.92	240	248
14	0.83	.67	2.10	.51	1.62	228	245
15	.95	1.20	2.10	1.13	1.99	192	200
16	.70	0.62	2.02	0.44	1.43	[a] 209, 215	[a] 226, 232
16–T	.75	.83	2.05	.60	1.50	[a] 209, 215	[a] 226, 232
17	.37	.00	0.47	.00	0.41	[b] 247–264	[b] 278–292
18	1.04	1.62	2.80	1.26	2.18	183	225
18–T	0.83	1.56	2.50	1.19	1.90	[c] 187, 125	[c] 200, 130
21	.69	0.68	2.40	0.57	2.01	191	214
21–T	.65	.54	2.16	.45	1.82	209	221
22	.48	.41	0.85	.38	0.79	216	235
23	.42	.34	1.03	.30	.89	211	227
24	1.26	.85	3.45	.61	2.46	107	113
25	0.35	.42	1.03	.26	0.64	325	370
31	1.17	.35	1.83	.34	1.75	221	224
33	1.20	.00	2.34	.00	2.04	[a] 235, 209	[a] 254, 225
34	1.34	.56	2.95	.49	2.61	178	225
41	1.05	.39	2.43	.29	1.82	214	185
42	0.67	.98	1.71	.85	1.49	168	242
43	.77	.50	1.86	.33	1.25	273	284
43A	.71	.49	1.95	.36	1.42	259	274
51	.66	.23	1.33	.21	1.19	193	198

[a] Values for 2 mills used.
[b] Range of values for 3 mills used.
[c] The second value is for a regrind.

TABLE 3. *Water content of recently purchased cements*

Lot No.	Mole ratio H_2O/SO_3 based on	
	Evaporable water	Total water
19737	0.64	3.06
19738	.70	1.17
19739	.55	1.48
19740	.79	2.04

The Role of Carbon Dioxide in Cement Aeration

Recent work at these laboratories on the properties of calcium carboaluminate hydrate provides a possible mechanism for the inactivation of the surface of tricalcium aluminate during aeration of cement and also for certain effects of carbonate ion in solution that have been previously discussed.

Results obtained with an X-ray technique indicate that calcium carboaluminate is a material

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[2] The petrographic examinations were made by J. E. Cox and B. Erlin of the Portland Cement Association Petrographic Laboratory, whose assistance is gratefully acknowledged.

of exceedingly low solubility which can be formed preferentially when tricalcium aluminate is hydrated in a solution containing both sulfate and carbonate ions. The phenomenon has also been observed in hydrating cement paste at a normal water-cement ratio. Consequently, it is to be expected that a chemical reaction of tricalcium aluminate with carbon dioxide and moisture in the atmosphere would produce a carbonated coating that would be unreactive toward sulfate ions in solution. The experimental details are as follows.

Calcium carboaluminate hydrate, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10.5H_2O$ has an X-ray diffraction pattern with a very intense line at 7.60 A which is easily identified in carbonated samples of hydrated cement paste. This intense line persists during drying and has been observed in samples equilibrated over calcium chloride dihydrate. This diffraction line therefore provides a means for determining the presence of the calcium carboaluminate phase.

Recently, several observers [7, 8] have noted the formation of calcium carboaluminate hydrate during the hydration of tricalcium aluminate in the presence of solid calcium carbonate. It appears, consequently, that calcium carboaluminate hydrate is less soluble than calcium carbonate.

In the present work, a mixture of equimolar quantities of tricalcium aluminate and calcium carbonate in a sodium sulfate solution was agitated continuously on a rotating wheel. After 10 days, an X-ray pattern of the solid phase showed the presence of a large quantity of calcium carboaluminate hydrate and no indication whatever of the calcium carbonate or tricalcium aluminate originally present. Lines also appeared for both forms of calcium sulfoaluminate hydrate and for tetracalcium aluminate hydrate, but all these lines were quite weak. It may therefore be concluded that the carbonated compound forms in preference to the other reaction products and is definitely less soluble than calcium carbonate.

In order to study this phenomenon in relation to cement hydration, a paste was made with Long-Time-Study cement No. 18 (C_3A: 13.2%; SO_3: 1.8%) with 5 percent calcium carbonate at 0.50 water-cement ratio. This paste was moist cured. At intervals up to 6 months, the superficial layer was removed and X-ray diffraction patterns were made of the underlying material. Experience has shown that in the absence of the calcium carbonate, the X-ray diffraction patterns of pastes prepared in this manner would not include the line for the calcium carboaluminate hydrate. In the presence of the carbonate, however, the line was quite intense. The pattern also contained the main line for the high form of calcium sulfoaluminate hydrate, rather than that for the low form which would have been expected in this case in the absence of the carbonate. The result obtained verifies that the added calcium carbonate reacted with the tricalcium aluminate in the cement, but indicated that the specific conditions were favorable for production of a sulfoaluminate as well.

Finally, it can be seen that if larger amounts of carbonate ion were present in solution, a rapid reaction of these ions with the tricalcium aluminate phase in cement would account for the retardation of the reaction of cement with sulfate ion that was postulated by Mr. Manabe.

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Discussion

Jean Laneuville

I think Dr. Hansen's paper has shown that the fundamental mechanism by which some cements become fast setting upon aeration is still obscure. This problem is undoubtedly a real challenge to the initiative of cement chemists for the coming decade.

I wonder why some valuable contribution could not be derived by tackling the problem under another angle, say, the search for conditions under which false-setting tendency cannot be developed.

In our laboratory, we have made a few experiments on this matter by using selected rotary-kiln clinkers made under determined burning conditions. Clinker A was made under normal burning conditions. Clinker B, of a very high SO_3 content, was lightly burnt with a large excess of air prevailing in the rotary kiln. These clinkers were ground at 70 °F in a laboratory ball mill to a Blaine fineness of 2750 cm^2/g. Four percent of gypsum was added to clinker A before grinding, and the chemical composition of the resulting cement A is given in table 1. The lightly burnt clinker was ground without gypsum to give "cement" B. The fast-stiffening properties of these cements were tested according to the ASTM method C359 on the fresh samples, on the samples heated in closed tin cans to 293 °F during 6 hr, on samples aerated in the laboratory air in one-half-inch layers for different periods of time, and on samples heated 6 hr at 293 °F and subsequently cooled and aerated for periods of 10 and 19 days.

The data shown in the table indicate that under the test conditions, it was possible to produce fast stiffening by heating or aerating cement A, but it was impossible to develop the least stiffening either by heating or aerating cement B. Although the discrepancy between the oxide analysis of the two cements is not large, their stiffening properties are very dissimilar.

Of course, as cement B contained no gypsum and all the SO_3 was presumably bound in the form of potassium sulfate, sodium sulfate, and dead-burnt anhydrite, it seems normal that no false set could be induced by heating this cement. The fact that cement B could not be made fast stiffening by aeration under the same conditions which rendered cement A false setting is somewhat intriguing.

We came to the fact that two cements of quite similar oxide composition, made from clinkers burnt in the same kiln, with the same raw materials, thereafter ground in the same mill, aerated under the same conditions do develop very dissimilar fast-stiffening properties.

I wonder if these properties would not originate to a large extent in the conditions prevailing in the rotary kiln and cooler during the process of burning and cooling the clinker.

I would appreciate the author's comments on this topic.

TABLE 1. *Chemical composition and false-set test of two cold ground laboratory cements*

Cements	Oxide analysis—%										Calculated compound composition—%			
	Ign. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Free CaO	C_3S	C_2S	C_3A	C_4AF
A	1. 14	21. 68	4. 95	3. 38	62. 49	3. 05	2. 30	0. 67	0. 34	0. 39	45	28	7	10
B	0. 13	21. 58	4. 79	3. 68	63. 47	3. 08	2. 50	0. 68	0. 33	0. 73	49	25	6	11

ASTM method C359—30% water in mortar

Cement	Condition	Penetration—mm				
		Init.	5 min	8 min	11 min	Re-mix
A	Fresh	50	50	50	50	50
A	Heated 293 °F, 6 hr	50	0	0	0	50
A	Aerated, 3 days	50	50	50	48	50
A	Aerated, 5 days	50	40	39	10	50
A	Aerated, 10 days	5	2	0	0	50
A	Heated 290 °F, 6 hr, and aerated 10 days	38	0	0	0	50
B	Fresh	50	50	50	50	50
B	Heated 293 °F, 6 hr	50	50	50	50	50
B	Heated 293 °F, 22 hr	50	50	50	50	50
B	Aerated, 5 days	50	50	50	50	50
B	Aerated, 18 days	50	50	50	50	50
B	Aerated, 31 days	50	50	50	50	50
B	Heated 293 °F, 6 hr, and aerated 19 days	50	50	50	50	50

Discussion

Renichi Kondo

The valuable paper presented by Dr. W. C. Hansen explained systematically the causes of false setting. I can agree with him that false setting is generally due to the existence of dehydrated gypsum in cement, and that the false set induced by aeration is partly due to inactivation of the C_3A which increases the amount of effective dehydrated gypsum. I like to think, however, that aeration reduces the reactivity of the C_3A not only toward sulfate but also toward water, and that before aeration the paste of cement containing C_3A can be kneaded down almost to the texture produced by the immediate hydration during mixing, while after aeration the cement hydrates a little after the mixing period and, accordingly, the rapid setting may be brought about. Then the expression, "Increasing of the reactivity of C_3A with water by aeration", seems to be rather superficial.

In addition, the results of the determination of setting time of the components of cement showed that $C_{6.2}A_{2.2}F$, C_4AF, and the glass phase in clinker and its devitrified product set almost as rapidly as C_3A [1].

Furthermore, he concluded that the formation of alkali carbonate during aging is to be discarded as the cause of false setting. It is considered possible, however, that the alkali carbonate produced by aeration behaves as a retarder, under the influence of calcium hydroxide, on the plaster setting even if the amount of the carbonate is very small. Decreasing the amount of alkali sulfate in cement by aeration also retards the plaster setting. If retarding action undesirably prevents the setting of the plaster from taking place during mixing, as mentioned by Messrs. T. Yoshii and Y. Murakami [2], then false set should appear. Of course, I believe as Dr. Hansen does that the alkali carbonate itself is not the main factor of false setting through the formation of calcium carbonate.

The false setting on aeration can hardly be explained by a single mechanism, because there seem to exist so many factors and complicated mutual interactions, for instance, some cements give rise to complexity, showing the cycles found by Mr. Miyatake [3] along with the progress of aeration. The degree of false setting is changed successively with aeration, i.e., in the first stage it is very weak, in the second, intensive, in the third, decreased, in the fourth, strengthened, and finally the hardenability is lost.

Moreover, I have verified [4] that the velocities of moisture absorption of the cement components decrease in the following order: portland cement clinker$>$dehydrated gypsum$>C_3A \gg C_4AF$, glass phase in clinker, anhydrite, et cetera, especially in the initial stage.

In some cases, sodium carbonate in such a small amount as less than 0.1 percent remarkably intensified the false setting, while the further addition of about 5 percent of powdered C_3A weakened it to some extent. From the above results, therefore, the effect of carbonation seems to be much stronger than that of the aeration of C_3A, and also the moisture absorption of C_3A is unexpectedly low.

An accelerated test can be performed by means of the penetration test in which alkali carbonate is added in amounts up to 0.1 percent or 0.1–0.3 percent to the cement, the former amount being selected in order to detect the latent property of false setting due to the existence of dehydrated gypsum, and the latter amount to cause possible rapid setting of C_3A in some conditions.

On the other hand, it was also ascertained that portland blastfurnace cement did not set rapidly, even when it contained no gypsum. Then the addition of insoluble anhydrite was preferable, to reduce the tendency of false setting due to gypsum for this kind of cement as mentioned by L. Blondiau and Y. Blondiau [7]. In this connection, the high-slag type of portland blastfurnace cement had very low 3-day strength, but it could be about doubled without reducing the long-time strength by the further addition of 5 to 10 percent of anhydrite which simultaneously increased the expansion due to hydration until it just compensated the amount of drying shrinkage.

As for the measures taken to reduce the trend of false setting of portland cement, water is usually sprayed into the grinding mill for the purpose of lowering the temperature of the cement; however, the air-tight paper bag has been successfully used by a cement manufacturer in Japan. It is also believed to be efficacious to minimize the amount of gypsum so that normal initial setting would just take place, and at the same time, to make a further addition of insoluble anhydrite, i.e., dead-burnt gypsum, natural, or byproduct anhydrite, up to the optimum SO_3 content for improving the other characteristics of cement, such as strength, shrinkage, and chemical resistivity.

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Discussion

R. R. Hattiangadi

Dr. Hansen's valuable paper on false set in cement touches a very important, yet illusive, field of cement technology. From talks with several fellow members during the last 2 or 3 days, I am led to believe not only that the phenomenon of false set is a matter of anxiety to many cement manufacturers and cement chemists, but also that the understanding of the subject is undoubtedly obscure. There are apparently a very large number of situations where false set is encountered. I am aware that in narrating our own views based on observations, and a certain amount of fragmentary experimentation, I may only be contributing further confusion to the subject.

In two of our factories in India, situated more than 800 miles apart, employing limestone and other raw material of dissimilar geological and physical characteristics, but using similar wet process kilns, false set in plant cement used to occur spasmodically. The clinker in one factory was fairly high in lime and high in C_3A, whereas the other could be regarded as normal average portland clinker. The composition of the clinker at these two factories was approximately as follows:

	I	II
	Percent	*Percent*
CaO	65.0–66.0	63.0–64.0
Free CaO	1.0– 2.0	1.0– 2.0
C_3A	11.0–13.0	7.0– 9.0

The shortening of the initial and final setting times of the cement and slight stiffening were first observed at these two factories, in perfectly good mill samples of cement after they were left out in layers of ½ in. to 1 in. in open trays in a corner of the laboratory for periods of 24 to 48 hr. For want of a suitable expression, I am referring to this procedure, in my discussion hereafter, as "exposure" to the atmosphere. In other words, a freshly ground, normally setting cement at times acquired this peculiar characteristic within a day or so when kept exposed or aerated in the laboratory. The stiffened paste of the cement, showing false set, became normal setting on reworking. Also, the samples of cement became normal setting after further exposure to the atmosphere for about a week or so. This stiffening effect of the sample exposed for only short periods of 24 to 48 hr was observed, however, only during the dry winter months (less than 50 percent humidity), and even then, only occasionally, and never in the hot humid summer, nor in the rainy season. Then again, the samples showing false-set characteristics when later kept either in a 100 percent humid atmosphere and/or a CO_2 atmosphere for a few hours again became normal setting. Likewise, a freshly ground sample of plant cement when kept either in 100 percent humid atmosphere or a CO_2 atmosphere for the initial period of 24 to 48 hr at varying temperatures (between 5 °C and 40 °C) did not show any signs of stiffening or false set. While, thus, this erratic behavior of the cement was being observed in the laboratory, it was fortunate and remarkable that no complaints whatsoever reached us about this erratic setting-time behavior from any of the consumers. It would therefore appear that in actual field practice no false set was ever encountered. In fact, a large number of samples drawn from the field from various points and tested did not reveal any false-set characteristics; but—there was always the danger that any reference laboratory testing samples in accordance with the prevailing specifications might fail the cements in question. In this context, I am inclined to agree with one of the speakers who made a suggestion earlier somewhat to the effect that talk on this subject of false set might be kept in cold storage for some time, at least until one could write a specification which could boldly state that false set when encountered in laboratory testing should be ignored!

Reviewing the observations, the following common features could be listed in respect of both the factories cited above.

1. Exposure of the cement samples in layers ½ inch to 1 inch thick for only 24 to 48 hr in an atmosphere of low humidity and comparatively low temperature brought about false set in the cement.
2. Longer exposure for 8 to 10 days under the same conditions as above removed the false set.
3. Exposure for short or long periods, in atmospheres of (a) high humidity, (b) higher than normal CO_2 concentration and/or (c) higher temperatures (over 35 °C) did not impart false set to the cement.
4. The finer the cement was ground the greater was the proneness to false set.

The following experiments were carried out in a laboratory ball mill in an attempt to determine the principal factors which contributed to the development of false set.

1. Samples of clinker were ground in the laboratory ball mill with 4 percent of gypsum, but the resulting cement did not show any signs of false set, though the same clinker when ground in the plant mill with 4 percent of gypsum tended to show false set. This behavior indicated that the conditions of grinding in the plant were conducive to the occurrence of false set.
2. Ground gypsum was dehydrated, partially or completely, at various temperatures in a current of dry air, in a humid atmosphere, and also in an autoclave, and varying proportions of these samples of dehydrated gypsum were blended separately with ground clinker, but no false set was observed in any of the samples. In the above set of experiments, addition of larger proportions of partially dehydrated gypsum did give a permanent flash-set effect to some of the samples but not false set. The flash set or "plaster set" observed was quite different from false set as the samples with the flash-set effect did not normalize after prolonged exposure of 8 to 10 days. This result indicated that partial dehydration of gypsum was not necessarily the cause of the false set.
3. To simulate the conditions of plant grinding in the laboratory, samples of ground clinker were heated at temperatures of 100–120 °C in a current of steam for 10 to 20 min, and these samples were mixed with various proportions of gypsum and partially dehydrated gypsum. The sample of artificial cement so prepared showed signs of false set when exposed to dry cold atmosphere for 24 to 48 hr.

From the above it would appear that clinker and gypsum (cement) when ground under the conditions obtaining in a normal mill, i.e., in an atmosphere of comparatively high humidity (due to moisture present in the clinker and moisture evolved by dissociation of gypsum) and high temperature (say 100 °C or so) tends to show an effect of false set when exposed to dry cold atmosphere for 24 to 48 hours.

In trying to envisage the mechanism of the occurrence of false set, I have made two assumptions, which I believe are based on generally accepted theories regarding the retardation of setting time in cement. These assumptions are:

a. $Ca(OH)_2$ is the primary retarder of setting time in portland cement.
b. If the paste does not contain enough sulfate to produce calcium sulfoaluminates, which immediately envelop and protect the aluminate phase from water attack, rapid setting occurs due to quick hydrolysis and precipitation of most of the silica-alumina hydrogels.

Arguing from the above assumptions, it would appear that for a fresh plant cement ground under conditions of comparatively high humidity and temperature (100–120 °C) the cement grains would be covered with a thin layer of $Ca(OH)_2$ and, with the calcium sulfoaluminates in the contact solution, it would behave normally as to setting time.

As regards the temporary stiffening or false-set effect observed on exposed samples I would offer the following explanation, which may sound quite fantastic. When cement which is normal setting to start with is exposed to the atmosphere at temperatures of 5–10 °C for short periods, the grains of cement are perhaps coated by a continuous molecular layer of small crystals of $CaCO_3$ due to the combined action of the low atmospheric concentrations of CO_2 and H_2O. Such a sample of cement would show signs of false set because the cement grains are enveloped by a continuous layer of $CaCO_3$ crystals which does not permit the gaging water to come in contact with cement constituents to form $Ca(OH)_2$ in the contact solution immediately, but when this cement paste is worked vigorously for a longer time, the $CaCO_3$ film is broken and the required amounts of $Ca(OH)_2$ solution are formed and the cement paste regains normal set.

On the other hand when the cement is exposed to either (a) saturated atmosphere or (b) a higher concentration of CO_2 than that normally prevailing in the atmosphere, it does not show any signs of false set. In the first case (a), perhaps higher quantities of $Ca(OH)_2$ are formed on the surface of the cement grains, which go into solution immediately when the cement paste is prepared, and no effect of false set is observed. Perhaps in the second case (b), due to higher concentration of CO_2, comparatively larger crystals of $CaCO_3$ are formed on the surface of the cement grains, which perhaps concentrate themselves discontinuously, and this discontinuity permits more of the surface of the cement grains to be acted upon by the contact solution and produces more $Ca(OH)_2$ solution, giving normal set effect. A similar mechanism may seem to explain the fact that no false set starts to occur in these cements in the humid summer months or the rainy season, or when the cement is exposed for a period of a week or more even during the winter months. The spasmodic occurrence of false set in the plant cement could be explained by the fact that at times the dehydration of cement grains in the plant mill proceeds to such an extent that later aeration or exposure effect is not sufficient to cover the grains of cement with very fine crystals of $CaCO_3$ and the cement shows normal set even after 24 to 48 hr exposure.

Roller, Swayze, and others have worked on the effect of exposure of cement to humid atmosphere, but do not appear to have studied the problem from the angle represented in the above discussion. I would venture to suggest that if further work were to be done on determination of stiffening effect of cement exposed to the atmosphere at various temperatures and various periods of time under controlled conditions of humidity and CO_2 concentration and the composition of the contact solution within a few minutes of gaging were studied simultaneously, together with a study of surface reactions which seem to play an important part, a better answer to the reasons for false set might be obtained.

I take this opportunity to thank my associates, D. D. Murdeshwar, V. N. Pai, and R. Padmanabhan, in helping me carry out the various experiments.

Discussion

L. Santarelli

Dr. Hansen in his paper on false set illustrated the methods known till now to identify this phenomenon. I wish to add to Dr. Hansen's already complete documentation the results obtained by the use of an apparatus known as the "Automatic Penetrometer" which was presented at the XXXI Congrès de Chimie Industrielle [1][1].

The principle of this apparatus is as follows: if a rod with a conical head and loaded with a definite weight is sunk into a cementitious paste at a uniform rate, it will stop when the viscosity of the paste is such as to oppose the weight applied. If the total weight is regulated so that the stopping corresponds to the initial set shown by the Vicat needle, we can determine the setting times in concordance with the Vicat needle. This standard weight is equal to 320 g.

The same may be said for the final setting (standard weight 2200 g). It has been later ascertained that there is the following relation between the weight (P) and stopping time (T): $\log P = aT + b$. Hence, if the test data are plotted on a semilogarithmic diagram of weight vs. time the result is a straight line. Thus, the final setting time is readily extrapolated, if we have two points which characterize the straight line at lower stopping times.

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[1] Figures in brackets indicate the literature references at the end of this paper.

This apparatus, suitably modified, has been used with success to follow the hardening process of calcium sulfate hemihydrate in a cement in order to obtain useful information on the phenomenon of false set [2].

Since it was found that with a weight corresponding to the initial set of the Vicat needle it is often impossible to identify false set, it was decided to initially reduce the weight of the penetrometer to zero (by a special return spring) and to follow the course of the growing viscosity by loading the penetrometer with small weights as soon as the downward movement of the needle should come to a stop. At a certain point it can be seen that penetration can be continued by decreasing the weights instead of increasing them: this point corresponds to the appearance of the phenomenon of false set.

The results summarized in figure 1 clearly show the phenomenon: curve 1 corresponds to a normal setting cement, while the curves 2, 3, and 4 correspond to three cements with false set in which the phenomenon appears at 150 g, 280 g, and 550 g, respectively. If the measurement had been made with a penetrometer calibrated for "initial set", that is, having a weight of 320 g, it is evident that the cements which correspond to curves 2 and 3 would not show any anomalies.

The net difference between the curves 1 and 2, 3, 4 is characteristic. In fact, the three curves are made up of three distinct sections, the first very steep, which corresponds to the setting of the calcium sulfate hemihydrate. This short first period is followed by the phenomenon of recovery, due most probably to the destruction of the structure formed by the dihydrate crystals, due to the effect of alumina which reacts with $CaSO_4$ forming sulfoaluminate. This results in the formation of a distinct "knee" which is followed by the third section, which ends in a straight line and corresponds to the real setting of the cement.

With the above mentioned method it is possible to identify in a cement the hydration of the hemihydrate and the stiffening which is a consequence of this hydration. Furthermore, the method indicates the consistency reached by the structure formed by the dihydrate crystals formed during hydration and the time elapsed to obtain this structure.

I believe that the above is of interest toward a better knowledge of the phenomenon of false set.

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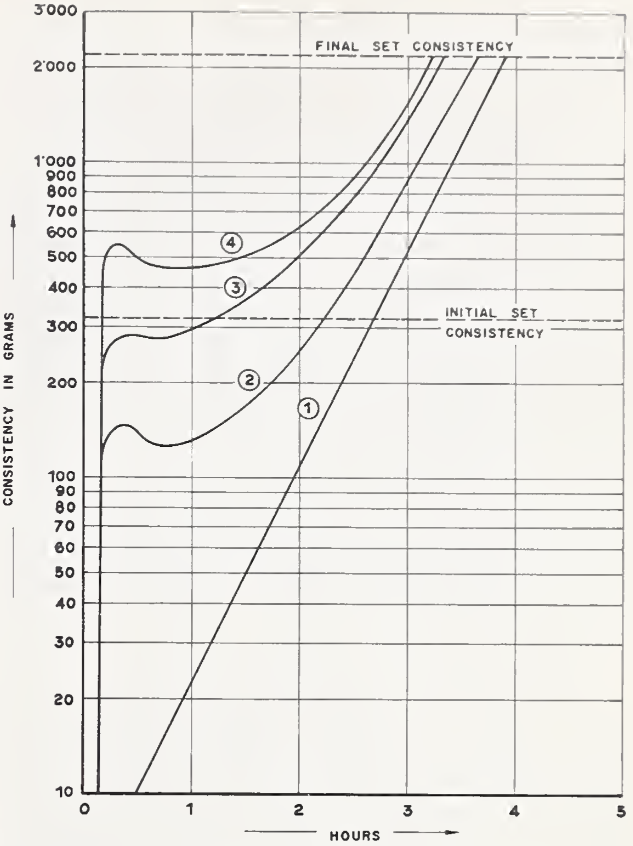

Figure 1. *Consistency curves obtained by automatic penetrometer on pastes of four cements.*

Curves 2, 3, and 4 are for cement showing false set

Discussion

Guenter Ahlers

Introduction

The purpose of this discussion is to report the results of some experiments which are believed to illuminate interestingly Dr. Hansen's paper, as well as the discussions of this paper by P. Seligmann and N. R. Greening, and by T. Manabe. The work to be presented here consists of quantitative analyses of cements for gypsum, and of a study of the gypsum precipitation in pastes by means of X-ray diffraction.

Gypsum Analyses

Quantitative analyses for gypsum by means of X-ray diffraction were carried out on 34 cements, chosen from 10 mills, most of which are located in the western United States. The analyses were performed on the 7.6-A line, without the use of an internal standard. The accuracy is estimated to be about 20 percent of the amount present, except at the very low concentrations, where it approaches ±0.3 percent gypsum. Of the cements examined 16 were found to contain less than 0.5 percent, 11 between 0.5 and 1.0 percent, 2 between 1.0 and 1.5 percent, 3 between 1.5 and 2.0 percent, and two cements contained 2.1 and 2.8 percent gypsum. The SO_3 contents of these cements ranged from 1.5 to 2.4 percent, corresponding to 3.2 to 5.2 percent gypsum. It is thus seen that it is the rule rather than the exception that almost all the gypsum has been dehydrated at least to the hemihydrate. The hemihydrate line at 6.0 A was always found, but no quantitative measurements were made on it. These results suggest that most cements contain enough hemihydrate to show stiffening due to gypsum precipitation, provided that this precipitation is not prevented by other factors. The occurrence of false set due to gypsum can thus be expected to depend primarily on factors which control the rate of precipitation of gypsum, and the rate of consumption of SO_3 by other reactions.

Gypsum Precipitation in Pastes

The precipitation of gypsum in pastes was observed as it occurred by measuring the 7.6-A line intensity in the paste as a function of time. Whereas these measurements could not yield quantitative results, because the surface of a paste cannot be expected to be representative of the entire sample, it is felt that they give an indication of the relative amounts of gypsum at different times. Such measurements were made on a cement paste which showed false set and on a mixture of finely ground Ottawa silica sand and 2.5 percent hemihydrate. The hemihydrate line at 6.0 A was also followed. In the cement paste the hemihydrate concentration began to drop immediately (the first measurement was made at 2 min after mixing), and gypsum began to precipitate. Both processes came to completion between 5 and 10 min after mixing. The sand sample behaved similarly, but the process was somewhat slower. It was completed after 20 min.

In order to relate gypsum precipitation to the degree of stiffening, a simple test was devised to measure relative stiffening. A 2.6-g rod with 0.3 cm^2 cross section was dropped onto the paste from such a height that it barely made an indentation. This height was taken as a measure of the stiffening. Such a simple test had the advantage that it could be performed repeatedly on the same paste. The stiffening as measured in this fashion on the cement reached a maximum after 8 min. For the sand-hemihydrate mixture this maximum was reached after 20 min. The agreement between the time at which maximum gypsum concentration and maximum stiffening were reached is believed to be a strong indication of a relation between the two processes.

A mixture of ground sand and 3 percent gypsum, and sand alone, showed no stiffening. The addition of 2 percent gypsum to the cement did not appreciably affect its stiffening characteristics. A sample of the cement was heated to 380 °C for 4 hr in order to convert all SO_3 to orthorhombic $CaSO_4$. After heating, 3 percent gypsum was added to the cement. The stiffening was then much less severe; however, other properties of the sample besides the hemihydrate contents may have been affected by this treatment.

Conclusions

It is believed that this work indicates that usually cements contain little or no gypsum. This finding might have been expected from the thermodynamic properties of gypsum and hemihydrate.[1] Most cements are ground at temperatures in excess of 100 °C, and at these temperatures gypsum is unstable. Especially in air-swept mills the dehydration should proceed with fair ease during grinding.

It is further felt that strong indications of a direct relation between gypsum precipitation and stiffening exist for the cement investigated here. The factors which determine whether or not excessive gypsum precipitation will occur seem as yet to be only partially understood. When gypsum precipitation does occur, it may or may not result in false set as measured by ASTM methods, depending on whether or not the precipitation is completed before the mixing is over.

Discussion

Myron A. Swayze

The purpose of this discussion of Dr. Hansen's paper is twofold: first to correct some of his present conclusions from my discussion of his 1958 ASTM paper on "Aeration Cause of False Set" (Hansen's references [34] and [45]); and second, to advance another explanation for development of false set due to aeration which I overlooked in 1958.

The corrections necessary in Dr. Hansen's present remarks on my 1958 discussion are as follows:

1.—Hansen's paper states, "Swayze showed that aeration caused *flash* set with a clinker that contained no C_3A". This is not correct. Both grinds of the zero-C_3A clinker alone had prolonged setting times compared with grinds containing gypsum or anhydrite. Clinkers of this type require no calcium sulfate to control set. The false set induced by aeration or heating and aeration of these grinds could, therefore, not be attributed to inactivation of C_3A or dehydrated gypsum, since both materials were absent.

2.—Hansen's paper states that only the grind of clinker plus anhydrite *without water* produced ball coating and thus became aerated during

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[1] K. K. Kelley, J. C. Southard, and C. T. Anderson, Bureau of Mines Technical Paper 625, 1941.

grinding from frequent opening of the mill. The grind with 0.2 percent water pulverized readily and displayed no false set in fresh condition.

The second part of this discussion deals with a new approach to the explanation of development of false set in cements due to aeration. Our experience with all commercial cements tested is that this property is always induced by relatively short exposures to moist air, and is worse in high C_3S cements than in low C_3S.

In an unpublished 1940 report on "Colloidal Aspects of Portland Cement Behavior" made by Dr. L. S. Brown to the Lone Star Cement Corporation, Brown recognized that the cement particles in a paste are from 100 to 1000 times larger than those found in typical colloidal suspensions, their concentration is much greater, and while the classic suspensions are of solids inert to the dispersion medium, the cement grains are reactive. Last, the composition of cement grains is complex, while the usual suspensions contain a single dispersed solid. Nevertheless, in freshly mixed pastes, the relatively enormous cement particles still follow the behavior of colloidal materials in reaction to forces that cause dispersion, flocculation, and peptization in colloidal suspensions.

In observations with a cataphoresis cell under the microscope, Brown found fresh suspensions of C_3S in water to be poorly dispersed and faintly electronegative. Calcium hydroxide suspensions could not be observed due to their strong electrolytic action. C_3A hexahydrate was well dispersed and strongly electropositive. Since gypsum had no electrolytic action, it should peptize cement grains, causing dispersion. While calcium hydroxide is sparingly soluble, that part in solution is about 90 percent ionized.

In a study of flash set, companion cements with and without gypsum were made from a fresh clinker containing 60 percent C_3S and 8 percent C_3A. Both cements had Wagner surface areas of 2150. Both were mixed rapidly with 25 percent water and made into setting-time pats. The paste without gypsum was stiff and dry, and had an initial set in 10 min. The paste with gypsum was smooth and fluid, with initial set in 3½ hr. After moist storage of the pats for 24 hr and in air for several days, thin sections were prepared. The sections showed only moderate but approximately equal hydration. The cement grains in the pat without gypsum were strongly flocculated, while those in the pat with gypsum were well dispersed.

The cement with gypsum was then aerated for a day and a third pat made with 25 percent water. The paste was materially drier and stiffer than that with the fresh cement, and study of the dried pat in thin section showed evidence of flocculation, although not as striking as in the case of flash set without gypsum.

Brown stated that the prehydration during aeration makes a certain amount of calcium hydroxide very quickly available to form a saturated solution on mixing with water, sufficient to cause flocculation of the cement grains. This flocculated structure did not have the strength and rigidity of that observed in the flash set pat, due to absence of hydrated C_3A, a product inhibited by the gypsum present.

This counteraction of the dispersing effect of gypsum in a cement paste by the electrolytic action of quickly available hydrated lime can easily be broadened to cover not only false set induced by aeration, but also false set in fresh cements in which gypsum has been converted to hemihydrate by the heat of grinding. From grinding tests we know that gypsum is a good grinding aid. Its action in this respect is very probably due to its dispersing action, with air as the dispersion medium. Hemihydrate, on the other hand, actually retards grinding beyond what is found for straight clinker grinds. Flocculation of cement grains is very evident by development of heavy coating on the mill and grinding media. We have no knowledge of the action of hemihydrate on cement particles in pastes, but the inference is strong that, if it flocculates them in air, it should show the same action in water. If this inference is correct, then we do not need the theory of "plaster" setting to explain the early gelling of cement pastes after mixing with water.

In modern cement grinding, temperatures are high enough to convert most of the gypsum to hemihydrate. The moisture liberated by this conversion can easily prehydrate C_3S grains if it remains in contact with them for an appreciable length of time, liberating very fine grained and quickly soluble calcium hydroxide. The combination of these two active agents in promoting flocculation may well be the principal sources of false set in freshly ground cements.

It is hoped that research on the electrostatic properties of hemihydrate and cement minerals will be stimulated by this discussion, so that a more logical explanation of false set can be derived by use of the principles of colloid chemistry.

Discussion

A. Rio and R. Turriziani

The observation made by several investigators that some cements show false set after air exposure, as detectable by ASTM method C359, has put in evidence a new type of phenomenon which seems to differ from the usual false set, appearing in freshly prepared cements after grinding, and due to the presence of dehydrated calcium sulfate in cement.

In Hansen's paper, false set by aeration is ascribed to the transformation which aluminates undergo after air exposure, by which they become less reactive towards sulfates and more towards water. According to this assumption, false set by aeration should be due to a precipitation and crystallization of gypsum, facilitated by a lower reactivity of aluminates to it, as well as to their more rapid reaction with water.

In his contribution to the discussion of false set, Manabe points out the fact that the aeration does not reduce the ability of aluminates to combine with calcium sulfate, but only affects the accelerating action of aluminates on the precipitation of gypsum.

Observations made in our laboratory, though confirming Hansen's and Manabe's conclusions that the false set by aeration is also essentially a false set by gypsum, suggest that the causes of the phenomenon are independent of the mineralogical compounds of clinker and therefore of any passivation of the aluminates.

Experiments carried out on cements of different origins showed the following:

1. When a cement gives false set after aeration, it also presents such a phenomenon before aeration, which may be seen by using a shorter mixing time (1 min, 10 sec) than the usual (3 min) (tables 1–2).
2. An addition of calcium sulfate to the cement giving false set (fresh or aerated) causes, generally, the disappearance of this phenomenon (tables 1–2).
3. False set remains in the cements which are reground 1 hr and this leaves out any action due to phenomena concerning films, or the surface of cement grains (table 2).
4. Generally, the extraction tests carried out according to Hansen and Pressler [1], but with the shaking time prolonged up to 10 min, confirm what has already been stated by Hansen and others, that the extracts of aerated cements show a larger $CaSO_4$ supersaturation than those of fresh cements (figures 1–2, table 1).

Furthermore, by observing the different types of commercial cements to be tested for false set, we noted as follows:

a. Some cements never presented false set, even after a long exposure to air.
b. On the contrary, other cements giving false set at the start lacked it completely after aeration.
c. Other cements showed false set after 24 hr aeration, while the phenomenon disappeared after 48 hr.

Experiments and observations we carried out suggest that the false set by aeration might depend on the different forms of calcium sulfate contained in the commercial cements.

In fact, according to what some authors [2, 3] have already shown, the precipitation rate of calcium sulfate is closely connected with the ratio that can be established between dihydrate and forms of dehydrated calcium sulfate occurring in cement.

At first the grinding conditions and later the aeration would affect the values of these ratios, varying the relative percentages of dihydrate and dehydrated calcium sulfate. Particularly the aeration by its action on the dehydrated forms of

TABLE 1. *Composition of extract and depth of penetration for fresh and aerated cements*

Sample condition	H_2O	Time of shaking	Composition of extract—moles/liter								Penetration—mm [c]					
			$(OH)_2$	SO_3	CaO	K_2O–Na_2O	Sat. CaO	Excess CaO	Sat. SO_3	Excess SO_3	1 min, 10 sec	3 min	5 min	8 min	11 min	Remix
	%	*min.*														
Cement A [a]																
Fresh	34	0.5	0.0250	0.1129	0.0166	0.1213	0.0164	0.0002	0.0905	0.0224	-------	48	48	48	48	48
		1	.0262	.1100	.0171	.1191	.0164	.0007	.0885	.0215	48	0	0	0	0	48
		3	.0337	.1087	.0215	.1209	.0164	.0051	.0895	.0192						
		5	.0367	.1062	.0151	.1278	.0164	−.0013	.0960	.0102						
		7	.0397	.1062	.0153	.1306	.0164	−.0011	.0980	.0082						
		10	.0385	.1062	.0131	.1316	.0164	−.0033	.0985	.0077						
Aerated 24 hr [b]	34	0.5	.0220	.1170	.0460	.0930	.0165	.0295	.0670	.0500	-------	48	17	0	0	48
		1	.0220	.1140	.0314	.1046	.0165	.0149	.0760	.0380	48	0	0	0	0	48
		3	.0237	.1180	.0301	.1116	.0164	.0137	.0822	.0358						
		5	.0280	.1180	.0207	.1253	.0164	.0043	.0935	.0245						
		7	.0320	.1110	.0143	.1287	.0164	−.0021	.0963	.0147						
		10	.0342	.1087	.0142	.1287	.0164	−.0022	.0963	.0124						
Aerated 24 hr +2% $CaSO_4 \cdot 2H_2O$	34	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	48	48	48	48	48
											48	4	0	0	0	48
Cement B [a]																
Fresh	34	0.5	.0295	.0885	.0153	.1027	.0165	−.0012	.0745	.0140	-------	48	48	48	48	48
		1	.0292	.0885	.0150	.1027	.0165	−.0015	.0745	.0140	48	48	29	15	9	48
		3	.0410	.0800	.0146	.1064	.0165	−.0019	.0775	.0025						
		5	.0415	.0745	.0117	.1043	.0165	−.0048	.0760	−.0015						
		7	.0412	.0745	.0093	.1064	.0165	−.0072	.0775	−.0030						
		10	.0450	.0745	.0097	.1098	.0164	−.0071	.0805	−.0060						
Aerated 24 hr	34	0.5	.0295	.0920	.0215	.1000	.0165	.0050	.0720	.0200	-------	48	48	0	0	48
		1	.0300	.0920	.0210	.1010	.0165	.0045	.0730	.0190	48	30	2	0	0	48
		3	.0310	.0885	.0185	.1010	.0165	.0020	.0730	.0155						
		5	.0355	.0863	.0171	.1047	.0165	.0006	.0760	.0103						
		7	.0410	.0800	.0141	.1069	.0165	−.0024	.0775	.0025						
		10	.0437	.0790	.0143	.1084	.0164	−.0021	.0795	−.0005						
Aerated 24 hr +2% $CaSO_4 \cdot 2H_2O$	34	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	48	48	29	4	48
											48	48	0	0	0	48

[a] Blaine surfaces varied between 3400–3600 cm²/g.

[b] Aeration layers 1.5 cm thick exposed at temperature of 20 °C and relative humidity of 85 percent.

[c] The penetration values were determined by A.S.T.M. Method C 359 after mixing time of 3 min or 1 min, 10 sec.

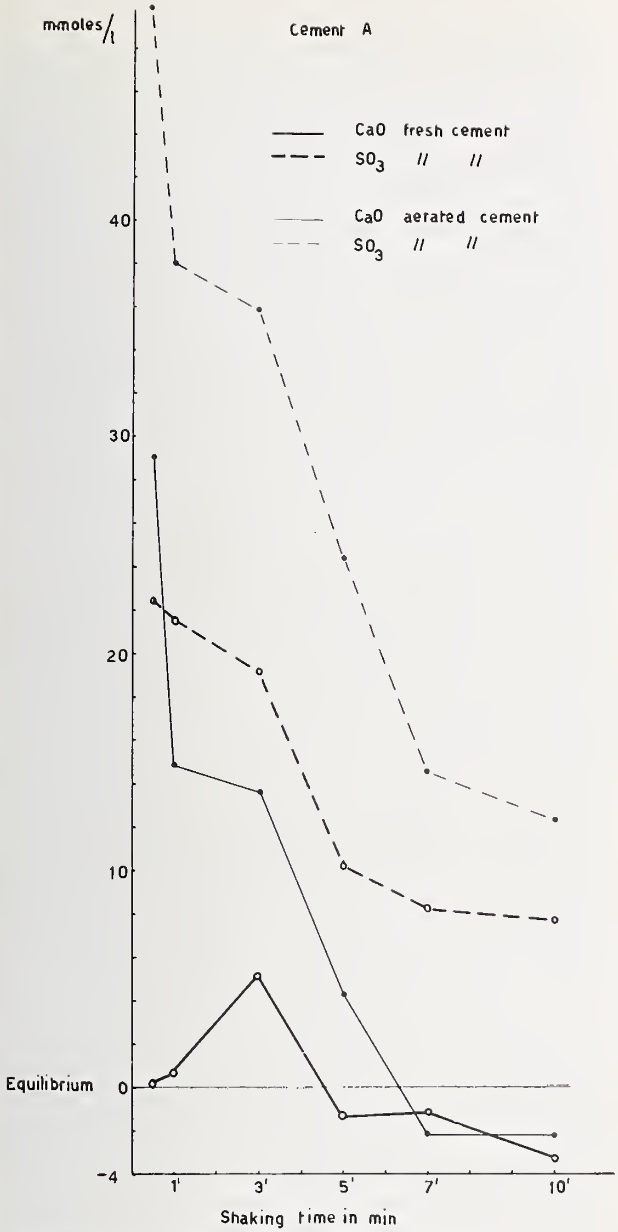

FIGURE 1. *Concentration of* CaO *and* SO_3 *in extracts from cement A after different periods of shaking.*

TABLE 2. *Depth of penetration for fresh and aerated cements*

Sample condition	H_2O	Penetration—mm [a]					
		1 min, 10 sec	3 min	5 min	8 min	11 min	Re-mix
Cement C							
	%						
Fresh	34	-------	48	48	48	48	48
	34	48	48	48	25	15	48
Aerated 24 hr	34	-------	48	48	48	45	48
	34	48	48	48	45	43	48
Aerated 24 hr and reground 1 hr	34	-------	48	48	40	35	48
Aerated 24 hr + 2% $CaSO_4 \cdot 2H_2O$	34	-------	48	48	48	48	48
	34	48	48	48	48	46	48
Cement D							
Fresh	34	-------	48	48	48	48	48
	34	48	48	48	48	48	48
Aerated 24 hr	34	-------	48	48	48	48	48
	34	48	48	48	48	48	48
Aerated 24 hr and reground 1 hr	34	-------	48	48	48	48	48
Aerated 24 hr + 2% $CaSO_4 \cdot 2H_2O$	34	-------	48	48	48	48	48
	34	48	48	48	48	48	48
Cement E							
Fresh	34	-------	48	48	48	48	48
	34	48	48	31	16	7	48
Aerated 24 hr	34	-------	48	48	29	19	48
	34	48	0	0	0	0	48
Aerated 24 hr and reground 1 hr	34	-------	48	45	20	15	48
Aerated 24 hr + 2% $CaSO_4 \cdot 2H_2O$	34	-------	48	48	48	48	48
	34	48	48	1	0	0	48
Cement F							
Fresh	34	-------	48	48	46	46	48
	34	48	48	3	0	0	48
Aerated 24 hr	34	-------	48	45	42	44	48
	34	48	21	0	0	0	48
Aerated 24 hr and reground 1 hr	34	-------	48	36	30	48	48
Aerated 24 hr + 2% $CaSO_4 \cdot 2H_2O$	34	-------	48	48	48	48	48
	34	48	48	4	0	0	48
Cement G							
Fresh	34	-------	48	48	42	42	48
	34	48	48	25	2	0	48
Aerated 24 hr	34	-------	48	3	0	0	48
	34	48	0	0	0	0	48
Aerated 24 hr and reground 1 hr	34	-------	48	0	0	0	48
Aerated 24 hr + 2% $CaSO_4 \cdot 2H_2O$	34	-------	48	48	43	39	48
	34	48	0	0	0	0	48

[a] The penetration values were determined by ASTM Method C 359 after mixing time of 3 min or 1 min, 10 sec.

calcium sulfate would tend to transform the latter into the stable form of dihydrate. During this process it would be possible to pass through stages where these ratios become such as to give rise to false set and of the supersaturation in SO_3 in the contact solutions.

On the basis of our supposition we should have a clear interpretation of the phenomena treated in sections 1, 2, 3, 4 and a, b, c.

Moreover, the smaller supersaturation values of fresh cements, which we attribute to a greater precipitation rate of calcium sulfate, are not only confirmed by the penetration tests after a mixing time of 1 min and 10 sec, but also agree with the combination rate of sulfate with aluminates, measured according to Bucchi [4, 5].

Actually, in agreement with Manabe, we do not find a difference between the combination rates of aerated and fresh cement. Therefore, the lower sulfate concentrations measured by extraction tests can be attributed only to a higher precipitation rate of the calcium sulfate, rather than to the lower ability of aluminates to combine with sulfates, as Hansen asserts.

Ultimately, the aeration, at least under the time and exposure conditions usually considered, would cause a variation in the relative quantities of dihydrated and dehydrated calcium sulfate

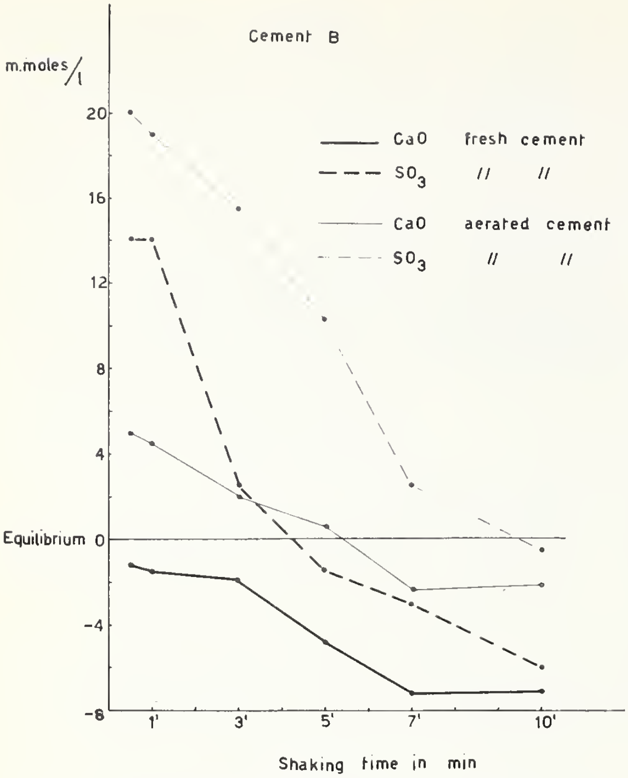

Figure 2. *Concentration of* CaO *and* SO_3 *in extracts from cement B after different periods of shaking.*

bringing about a different precipitation rate of gypsum which, since it occurs after the mixing, produces the characteristic stiffening of the paste. Of course, at the stage of our present experience, we cannot exclude the existence of concomitant effects due to phenomena of colloidal nature or of different type, as has already been pointed out by other authors, although such phenomena do not agree with the results of our experiments

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Discussion

A. J. Gaskin and J. K. McGowan

In general we agree with Hansen in ascribing the phenomenon of false set to the crystallization of gypsum in cement pastes, but we find that our views on the mechanism involved accord more with those expressed by Manabe [1][1] and by Seligmann and Greening [2].

During the past few years, examination of the behavior of 10 different cements of Australian origin has left us with the impression that the presence of more or less dehydrated remnants of gypsum in commercial cements must be regarded as a typical feature, that this material inevitably crystallizes as gypsum at a very early stage of paste preparation, and that most false-set effects are due to delays in this crystallization stage, extending it beyond the standard 3-min mixing period into the subsequent rest period.

Whether false set will be found in any given paste then becomes a question of the time at which gypsum crystallization begins, and the rate at which the crystallization of this phase proceeds, as well as a function of the amount of dehydrated material in the cement used.

These variables are separately influenced by various independent factors, and the resultant picture is quite complex. An ill-defined "flocculation" factor which temporarily increases the consistency of all cement pastes during the first few minutes of preparation, and the rare occurrence of a type of delayed "flash" set due to sulfate deficiency, are additional mechanisms which further confuse the main issue. Considering only the main process of gypsum crystallization, our broad view of the factors involved is as follows:

Commercial cement milling always appears to destroy the structure of gypsum to some extent. Mechanical as well as thermal action could be involved. The disordered product dissolves and crystallizes as gypsum during the mixing stage of paste preparation, the resultant stiffening effects being mixed out unless delayed for various reasons. In normal fresh cements, abundant nuclei for gypsum crystallization are present, and the onset and subsequent rate of the crystallization process can be accelerated by calcium ions supplied from C_3S and C_3A surfaces. Delayed crystallization resulting in false set can be caused by lack of sufficient nuclei, filming of accelerator sources, or by specific retardation effects of dissolved materials, principally carbonates. Adsorbed CO_2, released from clinker surfaces into the liquid phase of pastes, is the most potent retarder in practice, being supplied in sufficient quantities to the clinker surfaces during aeration.

Some of the experimental data from which this view has been evolved are given below.

The Nature of Gypsum in Cements

An X-ray study, made by Dr. J. Graham in this laboratory, of all commercial cements used in our investigation showed that the proportion of gypsum added during manufacture always exceeded that which we could recognize in the product. Results on laboratory cements did not show such discrepancies, and indicated that the technique of examination was sensitive and fairly precise.

Some commercial cements gave no indication that gypsum was present, most showed from 0.2

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[1] Figures in brackets, indicate the literature, reference at the end of this paper.

to 1.0 percent of recognizable gypsum, and a few gave higher values, ranging up to 60 percent of the amount originally added at the mill.

The proportion of gypsum preserved in any sample was generally characteristic of the plant of origin, but no correlation with mill temperatures could be found even though these varied from plant to plant over the range 100 to 125 °C.

Thermal effects could have been masked by variations in mill humidity, but no clear evidence was obtained in regard to the action of mill atmospheres. A mill with internal water addition, for instance, produced cement with no recognizable gypsum fraction.

Although some samples gave distinct patterns of the "hemihydrate-soluble anhydrite" type, suggesting that thermal dehydration had been occurring, it is possible that mechanical effects, which lead to similar types of dehydrated material, had also been operative.

It has been shown by Larsen and Bridgman [3] that gypsum may be dehydrated at room temperature by pressure alone, and Kiyama and Yanagimoto [4] demonstrated that the effect occurred below 65,000 psi, a pressure which could conceivably be applied to small particles caught between impacting balls in a large mill. The fact that gypsum may be dehydrated by ultrasonic vibration at 40 °C as shown by Zolotov and Kurochkin [5] is another aspect of the ease with which the water "sheets" may be encouraged to diffuse out of the gypsum structure.

If mechanical as well as thermal effects are important in large mills, it will not generally be possible to correlate the results of commercial cement milling with those from small laboratory mills run at equivalent temperatures. Closer correspondence would be expected when the small mills are run at higher than equivalent temperatures. This may account, in part, for the results of Takemoto, Ito, and Hirayama [6], who found little false-set tendency in cement ground at 105 °C in a small mill. Large mills at this temperature, however, can produce cements developing severe false set.

The nature of the "cement gypsum" components will probably be determined, therefore, not by mill temperature alone, but by such factors as the size of the mill, the size and type of grinding media, and the nature of the circuit, particularly as it affects the residence time of the finest particles.

In this connection it is of interest to note that open-circuit mills, loaded with a large proportion of small balls and fed with a hard clinker, gave cements with least recognizable gypsum, and worst false set, in our study, whilst the cement with the highest proportion of "retained" gypsum, and least false set, came from a carefully compartmented closed-circuit mill with a very high power efficiency, running at as high a temperature as the open-circuit mill.

The practical implications seem to be that the "cement gypsum" component will be in a more critical state when it is mechanically disorganized and dehydrated by overgrinding, particularly if the clinker components, which we believe to be accelerators of gypsum crystallization, are not also overground. By "critical" we mean having a slightly delayed setting time, through lack of nuclei or impairment of rate of solution. There seems to be no way of estimating these nucleation and solution factors except by paste trials. A "cement gypsum" or even a gypsum heated at 120 °C, may show no trace of dihydrate structure by X-ray diffraction, but may still be highly nucleated.

Particles of "gypsum" large enough to be picked out of cements for microscopical examination appeared to be of composite structure, with a mosaic appearance, due to variable birefringence, when viewed in polarized light using crossed Nicols, and showed a higher refractive index than gypsum. It is probable that this component of commercial cements contains fragments of the dihydrate structure intimately associated with material in all states of dehydration down to anhydrite. It cannot be simply described as "soluble anhydrite" or "hemihydrate," and may best be referred to as "cement gypsum" or some such arbitrary term.

Crystallization of Gypsum in Pastes

Although "cement gypsum" is more heterogeneous than most normal products of purely thermal dehydration of gypsum, some of its properties may be approximated by partially dehydrating very fine crystalline gypsum at 105–140 °C, to obtain materials in various "states of nucleation." Structurally, these thermal products are well organized and nucleate gypsum crystallization immediately when made into pastes. The nuclei may be progressively destroyed by more severe thermal treatments, and the solubility reduced by exposure to water vapor, both effects resulting in the development of induction periods and consequent setting delays when the materials are incorporated in pastes.

Commercial plasters of all types show long-delayed set compared with that of interest in false-setting cement systems. Some samples can be accelerated by addition of very fresh clinker, or mixtures of clinker and gypsum, to such an extent that the resultant pastes pass through the stiffening stage during mixing and hence do not exhibit false set, but we found such great variations in this respect even for consecutive samples from the same source that the use of this type of material was discontinued.

The most significant features of the gypsum crystallization process are the intensity of stiffening which can be caused by a small amount of material and the short time in which the setting reactions can be completed.

As little as 0.5 percent, by weight, of a well-nucleated dehydrated gypsum when added to a pure silica-water paste, can produce severe stiffening if mixing is stopped at 2 min. At 3 min, if mixing is resumed for a few seconds, the paste softens and remains soft on standing.

Replacement of the ground silica by larger proportions of highly nucleated dehydrated gypsum does not change the picture in respect to time of set and effect of mixing, but simply increases the intensity of the stiffening. Pastes made from all proportions of these two components will set rapidly enough to pass a false set test of the ASTM C 359 type.

By varying the nature of the "gypsum" component through more or less severe thermal treatment, but keeping the amount constant at 4 percent, a series of model paste systems exhibiting a range of stiffening periods from 2 to 5 min was prepared and used as a standard from which to deduce the efficiency of accelerating or retarding additives.

Accelerators in Model Pastes

In theory, high concentrations of calcium and sulfate ions in solution should accelerate gypsum crystallization. The particle size and solubility of dehydrated gypsum must therefore be important factors in determining the rate of attainment of suitable concentrations of these ions to initiate and promote the rate of growth of gypsum crystals in pastes.

External sources of calcium or sulfate ions will tend to overcome any delays due to inactivity of the dehydrated components, for reasons discussed by Schierholtz [7] and by Ridge [8].

Cement pastes contain ample sulfate in solution from the first moments of mixing, because of the presence of alkali sulfates. Conditions affecting the supply of calcium ions, therefore, become the main rate-determining features.

The clinker components C_3S and C_3A both supply calcium ions to solution rapidly and in quantity, and as expected, proved to be efficient accelerating agents, when added in a freshly ground condition to our model pastes.

Poorly nucleated pastes, incapable of passing a false-set test, were changed, by accelerating the stiffening stages, into normal-setting systems by addition of C_3A or C_3S in quantities as small as 5 percent by weight of the total paste solids.

Increasing the amount of dehydrated gypsum greatly in excess of the amount of added C_3A did not change the behavior of such pastes markedly, except to reduce the degree of acceleration slightly. If an initial period of sulfoaluminate crystallization preceded that of gypsum, it was not apparent in the form of a lengthened induction period. Nor did the stiffening phase of a paste containing equal quantities of C_3A and dehydrated gypsum appear to differ in any characteristic from the same phase in a paste, without C_3A, accelerated to the same extent with extra nuclei. No evidence could be obtained to show that sulfoaluminate formed rapidly enough to prevent the usual gypsum crystallization stage from occurring at the usual time.

Aged samples of C_3A and C_3S lost accelerating power, presumably by losing surface solubility through the buildup of hydrate and carbonate films.

Retardation in Model Pastes

Agents which reduce the surface solubility of dehydrated gypsum, block the activity of nuclei, or temporarily drive the ionic concentration of calcium or sulfate in solution to low levels so as to extend the induction period or decrease the rate of growth of gypsum crystals, retard set.

Surface solubility or the activity of nuclei seems to be impaired by traces of water vapor taken up during cooling, storage, or grinding of gypsum dehydration products made in the temperature range 105–120 °C. The effect, in model pastes, appears as the addition of up to an extra minute to the stiffening period. In ordinary cement pastes it appears to be overcome by the accelerating action of clinker. It is not likely to be a major variable controlling the incidence of false set in ordinary cements.

Carbonate ion in solution, however, is a very potent retarder, and is considered to be the main activator of false set in all ordinary commercial cement pastes containing dehydrated gypsum.

In the absence of C_3S and C_3A accelerators, model pastes could be changed from "normal" to "false" setting by the addition of as little as 0.001 percent, by weight, of CO_2 to the system. The gas was either introduced into the mixing water, or "adsorbed" on a small amount of an additive such as calcium hydroxide.

Pastes in which fresh finely ground clinkers rich in C_3S and C_3A were substituted for the ground silica component tolerated more carbonate in the form of CO_2, or equivalent alkali carbonate, because of the more rapid restoration of the calcium ion concentration.

With the most active clinker particles available, the limit of tolerance of pastes for CO_2 was 0.03 percent by weight, when 4 percent of poorly nucleated dehydrated gypsum was present, before false set appeared.

Commercial Cement Pastes

The combined thermal and mechanical effects of milling were found in the X-ray study of our plant samples to give as much as 4 percent of a dehydrated gypsum component in the worst-affected cements.

From the model-paste results, such samples could be expected to tolerate 0.03 percent by weight of CO_2, if very well nucleated, or less if deficient in nuclei, before developing false set. This was found to be so experimentally. The requisite quantities of CO_2 were taken up by the cements when exposed to the pure dry gas at atmospheric pressure, within a few minutes.

Samples which contained smaller amounts of dehydrated gypsum and a moderate proportion of recognizable dihydrate, remained normal setting until larger quantities of CO_2 were taken up during longer exposure periods. The best sample required 10 min exposure, taking up 0.15 percent of CO_2, before false set could be induced.

The behavior of the cements on aeration corresponded generally with the effects of exposure to CO_2. Those which failed after exposure periods of 1 to 3 min in the gas, failed the ASTM C 359 test after 2½ hr aeration, and those which survived longer periods in CO_2 survived aeration.

Carbonate added to pastes as sodium carbonate in quantities equivalent to the amounts of CO_2 found critical did not appear to be as effective in causing false set as "adsorption" of the gas. It is not proposed that alkali compounds in cements enter into the CO_2-adsorption or aeration processes to any major extent.

The mechanism of the "adsorption" of CO_2 on clinker compounds rich in lime is rather obscure. The gas must be retained at the surfaces in some state from which it can be released into solution rapidly. It is held as well on analytical reagent grade calcium hydroxide as it is on pure C_3S or C_3A, or commercial clinker. Grinding does not remove it, nor is its effectiveness as a retarder decreased by prolonged storage as long as water vapor is absent.

Flocculation Due to Carbonation of Clinker

Pastes containing only clinker and pure precipitated $CaSO_4 \cdot 2H_2O$ can be made to exhibit false set by exposure to CO_2, or even by long aeration. This is not the severe false set typically associated with dehydrated gypsum, but it is probably a minor component of false set in many cements.

The mechanism appears to involve delays in the attack of water on clinker surfaces, and consequent attainment of the normal state of "slight" flocculation. Cements generally pass through an initial stage of "severe" flocculation during mixing, but hydration effects at clinker surfaces and the stabilization of electrolyte concentration in the solution, then result in a weakening of the floc structure, although not to the point of dispersion.

If the rheological equilibrium normally established within 3 min is delayed by the presence of blocking films of carbonate on clinker particles, the intensity of flocculation may still be increasing during the subsequent rest period, so causing false set. Centrifuge sedimentation volumes were used to show that floc strengths reached maxima in periods of 1 to 3 min after addition of water when fresh cements containing the pure dihydrate were used at 0.6 water/cement ratio. With increasing exposure to CO_2, or aeration, these maxima were progressively displaced towards the 7-min mark on curves relating the sedimentation volumes (at "10 g") to time of mixing.

Dehydrated gypsum added to fresh-clinker systems intensified the floc strength at an early stage, if well-nucleated. If severely retarded by soluble carbonate in the system, or by deficiency of nuclei, such additions could produce a second floc-strength maximum at a later time than the "flocculation-effect" maximum.

Prevention of False Set

False set primarily caused by dehydrated gypsum retarded with carbonate is difficult to treat. Water vapor is the only agent, in our experience, which will reduce the effect of CO_2, once it has been adsorbed on cement. Carbonated cements stored over water in CO_2-free air in sealed containers revert towards normal set after 12 hr storage or longer. This behavior may be linked with the amelioration of milder degrees of false set commonly observed on prolonged aeration, particularly if humidity is high.

If cement contains dehydrated gypsum but has not already taken up CO_2, later adsorption of the gas may be blocked to some extent by treating the cement for a few minutes with a gas which is strongly "adsorbed" but otherwise innocuous, such as SO_2 or acetic anhydride. Cement takes up 0.1 percent of these gases rapidly, and this is sufficient to reduce the amount of CO_2 it will take up to the 0.03 percent level or even less. In favorable instances, this removes the tendency towards false set. The treatment may cause severe retardation of initial and final set, though it has little or no effect on 7-day strengths.

Prevention is better than cure where false set is concerned, and this implies attention to all factors promoting dehydration of gypsum and CO_2 adsorption. These include high mill temperatures, long residence times for fine gypsum particles in mills, low C_3S and C_3A contents, and exposure to excessive amounts of air or to any flue or exhaust gases during transport of the milled cement or subsequent storage.

If no plant changes can be made conveniently, improvement may be possible through a change in the source and type of gypsum used. This raw material varies to some extent in stability, as Wiedmann [9] has shown.

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Closure

W. C. Hansen

The written discussions of my paper give many new data and ideas that should be of great value in future studies pertaining to the overall problem of describing the mechanism of setting and hardening of cement pastes. It seems that many of these discussions require no comments, and, accordingly, I shall not attempt any extensive review of them. Instead, in this closure, some new data from our laboratories will be presented, and an attempt will be made to explain what happens when cements are aerated.

In the paper, I stated, "There is need for additional work to determine the exact mechanism by which aeration causes false set." Our work in this field was continued, and, with the results of that work, with a more thorough review of the literature, and with data and suggestions supplied by the written discussions, it appears that we can now explain what happens from the standpoint of stiffening when cements are aerated.

Portland cement clinkers vary with respect to the contents and compositions of the aluminoferrite phase and to the contents of C_3A, alkalies, and SO_3. Also, it seems that cements must vary widely with respect to the extent to which the gypsum has been dehydrated during grinding and storage. Because of these variations, one cannot be certain how any particular cement will respond under a given set of conditions, but it seems that we can now predict the general reactions of cements to aeration.

When speaking of false and flash or quick set, one is thinking of fast stiffening of a cement paste, either by itself or as a component of mortar or concrete, which occurs during the first 10 to 15 min after the paste comes in contact with water. It seems unquestionable that there are only two causes for this stiffening. One is the rapid reaction of C_3A and the aluminoferrite with water, and the other is the crystallization of gypsum. The first produces what is commonly known as flash or quick set and the other what is commonly known as false set. Normally, one associates the term flash or quick set with pastes that become relatively hot and unworkable. However, as pointed out in the paper, there should be all degrees of stiffening from mild to severe, caused by the reaction of C_3A with water. Hence, I propose using the expression "quick set" to indicate stiffening caused by C_3A and aluminoferrites. It seems that it is known beyond question that C_3S and C_2S cannot cause quick set.

It was pointed out in the paper that gypsum might crystallize from pastes made from cements that contained relatively large amounts of alkali sulfates. This, it seems, could be a cause of false set although the presence of dehydrated gypsum in cement appears undoubtedly to be the principal cause.

It seems that the general belief has been that quick set is caused only by C_3A. Professor Kondo, in his discussion, calls attention to work by Kondo, Tsukamato, and Yamauchi which showed that $C_{6.2}A_{2.2}F$ and C_4AF set about as rapidly as C_3A. Table 1 gives data by Yamaguchi, Takemoto, Uchikawa, and Takagi [1][1] obtained by X-ray quantitative analysis which show that C_4AF reacts rapidly with water. In the paper, I gave data obtained by Swayze with a cement that theoretically contained no C_3A which, it seems to me, show that the aluminoferrite phase in that cement caused quick set.

TABLE 1. *Data by Yamaguchi, Takemoto, Uchikawa, and Takagi* [1] *obtained by* X-ray *quantitative analyses of pastes*

Sample No.	Composition of sample—%				H_2O	Percent hydrated at 3 min		
	C_3S	C_3A	C_4AF	SO_3		C_3S	C_3A	C_4AF
					%			
S-3-0	-------	100	-------	-------	50	-------	27	-------
S-3-20	-------	100	-------	20	50	-------	28	-------
S-5-0	80	20	-------	-------	45	5	13	-------
S-5-5	80	20	-------	5	36	4	13	-------
S-4-0	-------	-------	100	-------	33. 6	-------	-------	7
S-4-20	-------	-------	100	20	25. 6	-------	-------	10
S-7-0	80	-------	20	0	50	3	-------	4
S-7-5	80	-------	20	5	50	5	-------	7

TABLE 2. *Data by Lerch* [4]

SO_3	Heat of hydration at hour indicated—cal/g				
	2	4	8	12	16
%					
1. 5	6. 6	9. 0	24. 8	28. 2	32. 4
1. 9	6. 3	9. 3	20. 9	35. 8	39. 7
2. 4	6. 1	9. 5	21. 5	31. 1	45. 9
3. 0	5. 9	9. 2	20. 9	28. 8	33. 7

Another general impression has been that calcium sulfate was the primary retarder of quick set in portland cement. Dr. Hattiangadi, in his discussion, states "Calcium hydroxide is the primary retarder of set in portland cement."

Roller [2] (in 1934) claimed that the role of calcium sulfate in cement was to react with alkali hydroxides to produce calcium hydroxide which was the retarding agent. He claimed that $Ca(OH)_2$ in solution combined directly with solid crystals of C_3A and coated them with hydrated C_4A which delayed their reaction with components of the solution.

The work of Bates [3] indicated that calcium sulfate was not an effective retarder in the absence of $Ca(OH)_2$ and C_3S. Heat-of-hydration studies by Lerch [4] (see table 2) showed that cement pastes developed what appeared to be a delayed quick set when most of the gypsum had combined with the aluminates. At that time, the solutions are primarily solutions of alkali hydroxides and contain very little calcium hydroxide.

The data of table 1 show that calcium sulfate did not retard the rates of hydration of C_3A and C_4AF. On the other hand, C_3S did retard the rates of hydration of these compounds, and cal-

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[1] Figures in brackets refer to the literature references at the end of this paper.

cium sulfate increased the retardation produced by C_3S.

This review of the literature seems to show very definitely that the aluminoferrites as well as C_3A can cause quick set and that high concentrations of $Ca(OH)_2$ in the solutions are required to prevent quick set by these compounds. It seems also that the principal purpose of calcium sulfate is to provide a high concentration of calcium ions in the solution.

As pointed out in the paper, Gilliland, Hansen, and Manabe have published data that show that the rate at which SO_3 combines with the aluminates is decreased by aeration of the cement. In his discussion, Manabe gives data that show that the rate of combination of SO_3 with the aluminates is only temporarily delayed by aeration.

Our data (shown in table 3) were obtained on a commercial cement ground with a blend of approximately 40 parts gypsum and 60 parts natural anhydrite. The grinding and storage conditions should have dehydrated all of the gypsum.

In this discussion, reference to extraction data will be to data obtained from slurries of 200 g of cement and 150 ml of water. These have a water-cement ratio of 0.75 whereas, in tests made with ASTM Method C359, this ratio is either 0.30 or 0.32. The compositions of the solutions in the slurry with $W/C=0.75$ and in the mortar with $W/C=0.30$ will not be identical. However, it is believed that conclusions from the former will apply to the latter.

The cement of table 3 showed slight stiffening in the false-set test, and the extraction data show that the solution, which, at equilibrium, should (on the basis of its Na_2O content) contain between 0.020 and 0.025 moles of SO_3, was saturated with respect to gypsum at 1 min but not at 3 min. These data show that, with about 40 percent of the SO_3 present as dehydrated gypsum, the calcium sulfate in this cement could not dissolve during the period between 1 and 3 min at a rate sufficient to maintain a saturated solution. Such a solution could not, of course, precipitate any gypsum to cause rapid stiffening. The drop in penetration from 50 to 37 mm during the 11-min period, it seems, may be classed as the result of what may be considered normal reactions in a cement with a satisfactory setting time. These reactions probably are mostly those that produce quick set when improperly controlled. Accordingly, one might visualize this cement as showing extremely mild quick-setting tendencies.

When the cement was aerated for 24 hr, it produced a slightly stiffer paste that showed very little stiffening during the 11-min period. The extraction data show that the solution in this paste was highly supersaturated with respect to gypsum at 1 and 3 min. These data show that the rate of combination of SO_3 was decreased by aeration. However, the drop from 0.052 to 0.040 moles/liter between 1 and 3 min shows that the rate of combination was still relatively high, and it appears that this rate was too high to permit much, if any, gypsum to crystallize in the paste.

Aeration for 48 hr produced a cement that stiffened relatively severely during the 11-min period. Tests on the clinker from which the cement was made showed that the rates at which it combined with chloride before and after aeration were as follows:

Sample and treatment	Grams Cl_2 reacted per 100 g of clinker for minutes indicated			
	1	5	15	30
As ground	0.22	0.28	0.34	0.36
Aerated 24 hr	.08	.14	.22	.24
Aerated 48 hr	.03	.11	.22	.26

These data indicate that the 48-hr aeration decreased the rate at which the aluminates reacted with SO_3 much more than did the 24-hr aeration. Hence, one would expect that gypsum could crystallize from this solution and produce false set.

Our first conclusion then is that, when the cements contain dehydrated gypsum, and possibly when they do not contain dehydrated gypsum but contain relatively large amounts of alkali sulfates, aeration can cause false set by decreasing the rates at which C_3A and aluminoferrites combine with SO_3 during the first few minutes of contact with water. Because of the wide variations in cements, it is not possible to give figures for the amounts of dehydrated gypsum and alkali sulfates required to produce this type of false set. Such figures would have to be determined for each cement.

Table 4 gives data for a cement ground with natural anhydrite at about 225 °F with 1 percent of water. The penetration data for the unaerated cement indicate no tendency toward rapid stiff-

TABLE 3. *Data for a commercial cement ground with a 40–60 blend of gypsum plus natural anhydrite*

Treatment	Penetration—mm (C359)				Minutes of shaking	Extract for $W/C=0.75$ Moles/liter			
	Init.	5 min	11 min	Remix		SO_3	$(OH)_2$	CaO	Na_2O
None	50+	45	37	50+	1	0.025	0.028	0.028	0.024
					3	.016	.043	.028	.031
Aerated 24 hr	47	47	46	50+	1	.052	.024	.059	.018
					3	.040	.024	.046	.018
Aerated 48 hr	46	27	10	50+	1	.053	.023	.063	.014
					3	.043	.023	.051	.015

Table 4. *Data for cement ground with natural anhydrite*

Cement	Penetration—mm					Minutes of sbaking	Moles/liter			
	Init.	5 min	8 min	11 min	Remix		SO_3 [b]	$(OH)_2$	CaO	Na_2O
As ground	50+	50+	50+	50+	50+	1	0.018	0.022	0.023	0.017
						3	.017	.023	.022	.018
Aerated 48 hr	50+	0	0	0	0	1	.009	.013	.007	.015
						3	.001	.020	.002	.019
Aerated+0.5% SO_3 [a]	50+	43	34	20	50+	1	.044	.014	.050	.009
						3	.042	.012	.042	.011
Aerated+1.0% SO_3	50+	47	15	6	50+	1	.043	.015	.049	.009
						3	.046	.012	.048	.010

[a] Hemihydrate.

[b] SO_3 at equilibrium, 0.015 to 0.018 mole/liter.

ening in this cement, and the extraction data show that the solution, which should contain about 0.018 moles of SO_3 per liter, was saturated with respect to SO_3 at the 1-min period and remained close to saturation during the 3-min period. In other words, the natural anhydrite in this cement dissolved at about the rate at which SO_3 combined with the cement.

Aeration gave a cement that generally would be classed as quick setting because it was not possible to get a workable mortar by reworking. An examination of the extraction data shows that the rate at which this cement combined with SO_3 was markedly increased by aeration. At 3 min, the solution was almost devoid of both SO_3 and CaO and contained primarily alkali hydroxides.

The results in this table indicate that aeration reduced the rate at which C_3S, and perhaps other cement minerals, released $Ca(OH)_2$ to the solution. They also indicate that this deficiency in the $Ca(OH)_2$ content of the solution permitted the aluminates to combine with SO_3 at a relatively high rate. It seems that these results support the conclusions by various authors which were stated earlier to the effect that $Ca(OH)_2$ is the primary retarding agent.

When 0.50 percent of SO_3 as hemihydrate was added to the aerated sample, quick set was eliminated, but the cement showed some false set. The extracts show that the solution was highly supersaturated with respect to gypsum at the 1- and 3-min periods and, accordingly, would be expected to precipitate gypsum. This addition of hemihydrate provided CaO to maintain a high concentration of $Ca(OH)_2$ in the solution.

There seems to be no reason to expect that aeration would decrease the rate of solution of natural anhydrite. Also, from the results of table 3 and the results reported by Dr. Manabe, there is good reason to believe that the rate at which SO_3 would combine in the aerated sample should have been reduced. Since it appears not to have been reduced, one has to search for a cause of the acceleration produced by aeration. The data indicate that this acceleration was caused by the lack of $Ca(OH)_2$ in the solution. These data appear to lend very strong support to the theory that $Ca(OH)_2$ is the material that retards the rate of reaction of the aluminates and that the real purpose of calcium sulfate is to supply Ca ions to react with alkali hydroxides and maintain the supply of $Ca(OH)_2$.

Our second conclusion is that aeration may produce quick set in cements when the cements contain relatively small amounts of dehydrated gypsum. Because of the variability in cements, it is not possible to predict the amounts of dehydrated gypsum required by different cements to prevent quick set.

Our third conclusion is that aeration decreases, by chemisorption of either or both CO_2 and H_2O from the air, the rates at which the cement minerals react with water. Data presented by Dr. Manabe indicate that CO_2 is required. However, it seems likely that CO_2 must be accompanied by water vapor. If the cement contains dehydrated gypsum, the decreased rate of reaction of aluminates will cause the cement to develop false-setting characteristics. If the cement contains very little or no dehydrated gypsum, the reduced rate at which C_3S releases $Ca(OH)_2$ to water will develop a tendency for the cement to become quick setting.

After reaching these conclusions, a study was made with a commercial cement ground in a short mill in closed circuit with an air separator. The cement from the separator was immediately cooled to about 120 °F before going to storage. The data for a sample of this cement after being in storage for a few days are given in table 5. X-ray diffraction data showed the presence of gypsum in this cement but gave no evidence for the presence of hemihydrate. Extraction data

Table 5. *Data for cement ground with gypsum and cooled to 120 °F*

Treatment	Penetrations—mm (C359)				
	Initial	5 min	8 min	11 min	Remix
A) As received	50+	50+	50+	50+	50+
B) 10 Weeks in a can	50+	45	38	22	50+
C) B+0.25% SO_3 [a]	50+	46	45	36	50+
D) B+0.50% $CaCl_2$	50+	50+	44	36	50+
E) B, aerated 24 hr	45	42	32	16	50+

[a] As hemihydrate.

indicated a slight supersaturation with respect to gypsum at 1 min and no supersaturation at 3 min.

The penetration data show that the rate of stiffening of the cement increased during storage for 10 weeks in a covered can and that aeration for 24 hr caused a further increase. Additions of either hemihydrate or calcium chloride decreased the rate of stiffening, which was to be expected if the increased rates of stiffening produced by storage and aeration were the result of more rapid reactions of the C_3A and aluminoferrites caused by decreased reactivity of C_3S. These data support the conclusion that aeration will tend to produce quick-setting characteristics in a cement that contains little or no dehydrated gypsum.

Several of the discussers have raised the question of alkali carbonates. I still feel that very little, if any, alkali carbonate will be formed during aeration. However, if it is formed and dissolves quickly when the cement comes in contact with water, it should precipitate $CaCO_3$. In this way, it would rob the solution of $Ca(OH)_2$ and tend to produce quick set. Any reagent added to cement that tended to form an insoluble calcium salt would tend to produce quick set. This might be the explanation for the results obtained by Dr. Manabe with lignosulfonates.

Messrs. Rio and Turriziani suggest that the ratio of dehydrated gypsum to gypsum in the original cement might be changed during aeration. Results of a recent study by Razouk, Salem, and Mikhail [5] indicate that this is unlikely. These investigators studied the sorption at different temperatures of water vapor by soluble anhydrite produced in vacuo. They found that this product quickly sorbed sufficient water at very low vapor pressures to form the hemihydrate. Only very minor amounts of additional water were sorbed as the vapor pressure increased until the relative humidity was very close to 100 percent. The sorption of water vapor to form gypsum from a saturated atmosphere was very slow compared to the sorption at lower vapor pressures to form hemihydrate. The authors concluded that the formation of gypsum took place "only in the presence of the saturated vapor of water".

It seems from this work that, if the conditions in a mill could produce soluble anhydrite, this compound would be converted almost instantaneously to hemihydrate when the cement was discharged from the mill and contacted the colder air which always carries some water vapor. It seems also that, except for exposures to air of extremely high humidities, hemihydrate in cements would never be converted to gypsum. The results of this work indicate that only three forms of calcium sulfate will be found in commercial cements. These are natural anhydrite, gypsum, and hemihydrate. In many cases, the gypsum used in cement plants contains small amounts of anhydrite and, in recent years, some cement plants have adopted the practice of using mixtures containing relatively large amounts of natural anhydrite.

Messrs. Gaskin and McGowan point out that mechanical as well as thermal action could destroy the structure of gypsum. They visualize that some particles of calcium sulfate in cements are composites of gypsum, hemihydrate, and soluble anhydrite and propose the term "cement gypsum" for the product. This condition seems entirely possible, but the action of such a composite probably is similar to the action of a blend of small particles of gypsum and small particles of hemihydrate. They state what everyone probably accepts, i.e., "prevention is better than cure where false set is concerned".

It seems from many of these discussions that it is well established that false set is caused by dehydrated gypsum and that a manufacturer who produces a cement containing dehydrated gypsum may have problems that differ somewhat from those of another manufacturer producing a similar cement because of differences in grinding circuits, differences in compositions of clinker, etc. It appears, however, that it would be difficult to prevent all dehydration of gypsum in commercial grinding circuits. It also appears that the presence of small amounts of dehydrated gypsum might be helpful in preventing quick set that might tend to develop in a cement containing largely gypsum or natural anhydrite or a mixture of the two.

Several discussers have suggested that, in cements which contain both gypsum and dehydrated gypsum, the former acts as nuclei to speed up the crystallization of gypsum in the cement pastes. This possibility was studied by grinding quartz sand with 2.0 percent of SO_3 as gypsum and as hemihydrate and blending the two to obtain powders with 2.0 percent of SO_3. Quartz was also ground with 1 percent of SO_3 as hemihydrate to provide a few blends with less than 2 percent of total SO_3.

The original powders and blends were tested with 32 percent of water by ASTM Method C359, and some were tested by modifications of this method in which mixing was stopped midway in the mixing period for either 1, 3, or 5 min. The mortar was then mixed for 1 min after this waiting period. The data are given in table 6.

The total period of mixing and molding in C359 is 3 min. It is seen from this table that 1.0 percent of SO_3 as hemihydrate produced rather severe stiffening. The stiffening was much less when the powder contained 1.0 percent of SO_3 as gypsum as well as 1.0 percent as hemihydrate. This supports the contention by Dr. Manabe and others that more crystallization of gypsum will occur in the mixing period if the cement contains some gypsum crystals to act as crystallization nuclei. The data also show that the 1-min waiting period was very effective in decreasing the stiffening in this mortar and that the longer periods were less effective than the 1-min period. This

TABLE 6. *Data for quartz with blends of gypsum and hemihydrate*

Percent SO_3 as		Waiting period—min [a]	Penetrations—mm (C359)			
Gypsum	Hemi-hydrate		Initial	5 min	11 min	Remix
2.00	None	No	50+	47	46	50+
None	2.00	No	2	2	1	17
None	1.00	No	30	23	16	35
1.00	1.00	No	50+	43	32	50+
1.00	1.00	1	50+	50+	43	50+
1.00	1.00	3	50+	46	41	47
1.00	1.00	5	50+	44	41	50+
0.25	1.75	No	11	10	4	15
.25	1.75	1	16	16	10	30
.25	1.75	3	34	20	13	39
.25	1.75	5	30	25	13	34

[a] Waiting period midway during mixing, followed by 1 min mixing.

result was to be expected because the mortar should tend to stiffen gradually with time.

The data show that 0.25 percent of SO_3 as gypsum was not very effective in decreasing the stiffening caused by 1.75 percent of SO_3 as hemihydrate, and that the 3- and 5-min waiting periods were more effective than the 1-min waiting period in decreasing the stiffening.

Mr. Laneuville gives data for two cements ground in a cold mill. One (cement B) made with a lightly burned clinker containing 2.50 percent of SO_3 was ground without added SO_3, and the other (a normally burned clinker) was ground with 4.0 percent of gypsum and had an SO_3 content of 2.30 percent. These cements contained alkalies equivalent to 0.78 percent of Na_2O. Pure gypsum has an SO_3 content of 46.6 percent. Therefore, about 1.9 percent of SO_3 was added as gypsum and about 0.4 percent existed in the clinker, probably as alkali sulfates.

The 0.78 percent of Na_2O could combine with 1.01 percent of SO_3. Hence, the SO_3 in cement B might have existed as 1.00 percent in alkali sulfates and 1.50 percent in natural anhydrite. It seems perfectly normal for these quantities of alkali sulfates and natural anhydrite to give a cement without quick-setting tendencies as ground. Heating should not in any way increase the rate of solution of this SO_3 and, accordingly, should not produce a false-setting cement. It appears that this cement contained sufficient readily soluble SO_3 in the form of alkali sulfates to prevent quick set upon aeration.

Cement A, ground with 1.9 percent of SO_3 as gypsum in a cold mill should not be false setting as ground, and it should develop false set upon heating to 293 °F. The fresh cement showed slight stiffening when aerated for 5 days and severe stiffening when aerated for 10 days. One would expect a cement ground with gypsum in a cold mill to show a tendency to become quick setting upon aeration. Also, one would expect that the cement when heated to 290 °F and aerated would show false set just as it did when heated and tested without aeration. The behaviors of these cements seem to fit into the hypothesis proposed for the development of false and quick set upon aeration.

The method for determining evaporable water described by Messrs. Seligmann and Greening and the X-ray method used by Mr. Ahlers should be be useful in studying a grinding operation to determine the degree to which the gypsum is dehydrated during grinding and the rate at which it dehydrates during storage. It appears that the rate at which C_3S reacts with CO_2 and water vapor as well as the rates at which the aluminates react with these materials should be investigated.

Professor Santarelli offers a new method of studying the setting characteristics of cements. The use of these newer methods might be a way of learning more about the nature of the reactions that occur during the setting of cements.

Mr. Swayze suggests a new approach to the study of these reactions and also that a more logical explanation of false set is needed. He suggests that stiffening of cement pastes is a flocculation of the grains of cement. Those who support the crystallization-of-gyspum theory feel that the cement paste is stiffened by the interlacing of the gypsum crystals. No one seems to have been very specific as to forces that produce a coherent mass of quick-setting paste. I have visualized the rapid reaction of water with C_3A and aluminoferrites as converting the surfaces of the crystals to more or less amorphous materials that cement the grains of cement together. The mechanism of setting and hardening certainly needs additional study, and it appears that the methods that have been devised to study false set will be useful in that study.

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Paper IV–3. Chemistry of Hydration of Portland Cement*

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Synopsis

The results of recent investigations have provided evidence for the presence of several aluminates and sulfoaluminates in hardened portland cement pastes. For some of these, little evidence for their presence had been obtained previously. Some indications have also been obtained as to the nature of the iron-bearing hydrates.

Information as to the water contents of the various hydrates formed can be obtained for certain drying conditions by statistical analysis of nonevaporable water data as a function of the composition parameters of the cement.

Along with X-ray and statistical results, free-lime data obtained by X-ray quantitative analysis can be combined with the oxide composition of a cement so that an estimated composition of a hydrated paste of that cement can be calculated. Most of our concepts about the rate of hydration of cement in pastes or concrete have been based on the rate of increase of strength, heat of hydration, and fixed water. Inferences concerning the rates of hydration of the individual components have been made from considerations of rate of change in heat of hydration, and in related physical and chemical properties of the hydration products. Direct measurement of these latter rates show that the inferences are not always true.

Recent data are presented on the heats of hydration of the different ASTM types of cements at ages from 3 days to 13 years at 0.40, 0.60, and 0.80 water-cement ratio. The significant influence of water-cement ratio on the rate of hydration of cement can be interpreted in terms of physical parameters of the hydrating paste. The effect of temperatures in the range of 4.4 to 110 °C on the rate of hydration of cement can be expressed by the Arrhenius equation.

As a first approximation, the intrinsic hydration characteristics of cements can be expressed in terms of the compositions of the cements, by least squares analyses of heat evolution and chemically combined water. Secondary changes of the hydrated calcium aluminate are indicated. Some aspects of the roles of gypsum, alkalies, glass content, and ignition loss of the original cement on heat evolution are considered.

Résumé

Les résultats de recherches récentes ont fourni des preuves de la présence de plusieurs aluminates et sulfoaluminates dans les pâtes de ciment portland durcies. Pour certaines d'entre elles, cette présence n'était jusqu'à présent que peu évidente. Des indications ont été également obtenues quant à la nature des hydrates ferrifères.

Pour certaines conditions de séchage, on peut obtenir des informations concernant les teneurs en eau des différents hydrates formés, au moyen d'une analyse statistique des données de l'eau non-évaporable en fonction des paramètres de la composition du ciment.

Avec les résultats des rayons X et statistiques, les données de chaux libre obtenues par analyse quantitative des rayons X peuvent être combinées aux compositions oxydes d'un ciment de façon telle que l'on peut calculer une composition estimée d'une pâte hydratée de ce ciment. La plupart de nos concepts sur la vitesse d'hydratation du ciment dans les pâtes ou dans le béton ont été basés sur la vitesse de l'augmentation de la résistance, la chaleur d'hydratation, et l'eau fixée. Des déductions concernant les vitesses d'hydratation des composants individuels ont été tirées à partir de considérations sur la vitesse de changement dans la chaleur d'hydratation, et dans les propriétés physiques et chimiques, s'y rapportant, des produits d'hydratation. La mesure directe de ces dernières vitesses indique que les déductions ne sont pas toujours vraies.

Présentation est faite de données récentes sur les chaleurs d'hydratation des différents types de ciments selon les normes ASTM à des âges allant de 3 jours à 13 ans à un rapport eau-ciment de 0.40, 0.60, et 0.80. L'influence significative du rapport eau-ciment sur la vitesse d'hydratation du ciment peut être interprétée en fonction de paramètres physiques de la pâte qui s'hydrate. L'équation Arrhenius peut exprimer l'effet des températures allant de 4.4 à 110 °C sur la vitesse d'hydratation du ciment.

Comme première approximation, on peut exprimer les caractéristiques intrinsèques d'hydratation des ciments en fonction des compositions des ciments, par analyses aux écarts moindres quadratiques de l'évolution de la chaleur et de l'eau chimiquement combinée. Les changements secondaires de l'aluminate de calcium hydraté sont indiqués. Certains aspects du rôle du gypse, des alcalis, de la teneur en verre, et de la perte au feu du ciment original sur l'évolution de la chaleur sont considérés.

Zusammenfassung

Die Ergebnisse der neuesten Forschung haben gezeigt, daß mehrere Aluminate und Sulfoaluminate in gehärteten Portlandzementmassen vorhanden sind. Einige dieser sind früher nicht identifiziert worden, und man hat auch schon etwas über den Charakter der eisenhaltigen Hydrate ausfindig machen können.

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Man kann den Wassergehalt der verschiedenen Hydrate für gewisse Trocknungsbedingungen mit Hilfe einer statistischen Analyse, bei der das nichtverdampfungsfähige Wasser als Funktion der Zusammensetzungsparameter des Zementes ausgedrückt wird, bestimmen.

Durch eine Kombination der Röntgenbeugungsmessungen, der statistischen Resultate und der Werte für freien Kalk, wie sie durch quantitative Röntgenstrukturbestimmungen erhalten werden, und auch der Oxydzusammensetzungen kann man eine schätzungsweise Zusammensetzung der hydratisierten Paste eines solchen Zements errechnen. Die meisten unserer Ideen über die Hydratationsgeschwindigkeit des Zements in Pasten oder in Beton wurden durch ein Studium der Geschwindigkeit der Festigkeitszunahmen, der Hydratationswärme und des gebundenen Wassers erhalten. Die Hydratationsgeschwindigkeiten der einzelnen Verbindungen wurden von Betrachtungen, die sich mit den Hydratationswärmeveränderungen befassen, und auch mit verwandten physikalischen und chemischen Eigenschaften der Hydratationsprodukte, inter- und extrapoliert. Aber direkte Messungen dieser Veranderungen haben gezeigt, daß solche Inter- und Extrapolierungen manchmal zu Irrtümern leiten können.

Die letzten Messungen der Hydratationswärmen der verschiedenen ASTM-Typen der Zemente, die zwischen 3 Tagen und 13 Jahren alt waren, und mit Wasser/Zementverhältnissen 0,40, 0,60 und 0,80 angemacht worden waren, werden erörtert. Der bedeutungsvolle Einfluß des Wasser/Zementverhältnisses auf die Hydratationsgeschwindigkeit des Zements kann mit Hilfe der physikalischen Parameter der hydratisierenden Masse ausgedrückt werden. Der Temperatureffekt kann zwischen 4,4 und 110 °C für die Zementhydratationsgeschwindigkeit vermittelst der Arrhenius Gleichung ausgedrückt werden.

In erster Annäherung kann die körpereigene Hydratatationskenngröße als Funktion der Zementzusammensetzungen ausgedruckt werden, wenn man die Methode der kleinsten Quadrate auf die Warmeentwicklung und das chemisch gebundene Wasser anwendet. Das hydratisierte Kalziumaluminat zeigt sekundäre Veränderungen, die besprochen werden. Die Einflüsse des Gipses, der Alkalien, des Glasgehalts und des Gewichtsverlusts bei Rotglut des ursprünglichen Zements auf die Wärmeentwicklung werden besprochen.

Foreword

The difficulties encountered in the study of the chemistry of hydration of portland cement have been discussed many times, and are known only too well by all who work in this field. In spite of these difficulties progress is being made, even though the path to understanding may meander a bit.

The past work on the pure compounds found in cement has provided a foundation for the study of the hydration of cement itself, and the constant improvement in experimental techniques has made it possible to begin the study of hydration products in hardened pastes of portland cement. The chemistry of hydration of cement in hardened pastes has been emphasized in this review; perhaps it has been overemphasized. Many of the conclusions presented here are based on good evidence; others are admittedly tentative, but they are included in order to establish a basis for further discussion.

The paper is divided into three main sections: In the first section the composition of the hydration products of portland cement is discussed. In the second section the rate of hydration of cement, and the rate of hydration of each of the four major phases in cement is reviewed. In the third section the most recent information on the energetics of hydration is presented.

I. The Stoichiometry of the Hydration of Portland Cement

D. L. Kantro and L. E. Copeland

Status of the Problem as of 1952

By 1952, it had been established [1] [1] that the silica-bearing phases in portland cement react with water to form calcium silicate hydrates of two possible types, designated CSH(I) and $C_2SH(II)$. These hydrates were observed and discussed by Taylor [2], many of his observations being in good agreement with earlier work. The similarity between CSH(I) and the natural mineral tobermorite was pointed out by Claringbull and Hey [3] and discussed in detail by Bernal [1]. The $C_2SH(II)$, while not in the tobermorite composition range, showed many similar properties. The X-ray diffraction diagrams of these two calcium silicate hydrates are so much alike that to distinguish between them is quite difficult. Hence it could not be ascertained at the time of the 1952 London Symposium whether either or both of these calcium silicate hydrates occurred in hydrated portland cement.

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[1] Figures in brackets indicate the literature references at the end of this paper.

It had been surmised by a number of investigators that the 3:2 calcium silicate hydrate of the tobermorite series, that is, CSH(I), was the more likely product formed in the hydration of portland cements. That this is the case arises from the fact that it is this composition of solid which is in equilibrium with a saturated $Ca(OH)_2$ solution [4]. If $C_2SH(II)$ were to form, it would presumably be a metastable product. As far back as 1938, the 3:2 calcium silicate hydrate was considered to be the product of the hydration of the silicate phases of portland cement. For example, Bessey [5] arrived at this conclusion on the basis of free calcium hydroxide determinations on hydrated pastes.

Steinour, in his 1952 review [4], points out that the most probable reaction product of tricalcium aluminate, at least initially, is the tetracalcium aluminate hydrate, C_4AH_{13}. The cubic calcium aluminate, C_3AH_6, if it forms at all, forms only slowly. He points out also that the hexagonal hydrate that forms has at times been reported as an intergrowth of a dicalcium aluminate hydrate and the tetracalcium aluminate hydrate, such that the overall $CaO:Al_2O_3$ ratio of the phase is 3.0.

In their discussion of Steinour's paper, Nurse and Taylor [6] cite evidence from X-ray diffraction for the presence of C_4AH_{13}. They also cite X-ray evidence for the cubic C_3AH_6, but inasmuch as their observations were on a 22-year-old specimen, they concluded that the cubic hydrate was the result of a slow conversion of the tetracalcium aluminate hydrate.

There have been a number of investigations of calcium aluminoferrites and ferrites, and calcium ferrite hydrates have been prepared which are analogous to some of the calcium aluminate hydrates. The calcium ferrite hydrates form solid solutions with the corresponding calcium aluminate hydrates, but little experimental data had been found that these solid solutions occur in hydrated portland cement pastes.

One problem that has received a great amount of attention for many years from cement chemists is that of the sulfoaluminates, and, to a lesser extent, sulfoferrites. These complex compounds arise from the interaction of the appropriate component of clinker with gypsum, added as a retarder. In general, either of two calcium sulfoaluminates may form, these being the calcium monosulfoaluminate, $C_3A \cdot CaSO_4 \cdot 12H_2O$, and ettringite, $C_3A \cdot 3CaSO_4 \cdot 31H_2O$. These compounds are also known as the low sulfate and high sulfate sulfoaluminate, respectively. As was pointed out by Steinour [4], equilibrium studies such as those made by Jones [7] indicate that ettringite forms during the early stages of reaction, but as further hydration of C_3A takes place, the low sulfate sulfoaluminate will form at the expense of the ettringite. Once all of the SO_3 has been used for this reaction, further hydration of aluminate should lead to a solid solution of tetracalcium aluminate hydrate and calcium monosulfoaluminate. However, at the time of Steinour's review, no direct observation of either sulfoaluminate in cement pastes had been made, and any conclusions drawn were strictly by inference. The ettringite observed in cracks and pores in old concrete or hardened paste was considered to be formed by secondary reaction due to exposure. More recently similar observations were made on old mortar exposed to air [8].

The calcium sulfoferrites corresponding to the low-sulfate and high-sulfate sulfoaluminates have been prepared individually [9]. The analogy of the sulfoferrites to the sulfoaluminates both in constitution and behavior has been pointed out. However, no identification of either of the sulfoferrites as a reaction product of cement, gypsum, and water under ordinary conditions of hydration could be made.

Methods of Investigation of the Chemical Reactions Occurring During the Hydration of Portland Cement

The qualitative and quantitative information concerning the hydration processes of portland cement have been obtained in several different ways. In general, however, regardless of what technique is being used, the cement paste may be treated in either of two ways. The observations may be made on the paste as a whole or the paste may be broken down into fractions such that one or more of these fractions may be enriched with respect to certain of the hydration products.

Nurse and Taylor [6] describe a method whereby the paste is ground to a powder and then ground in a suitable liquid such that a suspension of finest particles is formed. The suspension is removed from the coarse fraction and centrifuged to recover the fine fraction.

Differences in specific gravity of various constituents have also been used to effect separation. Taylor [10] separated several fractions from finely ground pastes by centrifuging the material in bromoform and bromoform-benzene mixtures. Turriziani [11] used a sedimentation apparatus in which the suspending agent was amyl alcohol. Several fractions of different finenesses were obtained and division of these into subfractions by the specific gravity technique using bromoform-benzene mixtures was then performed.

The separation methods have certain difficulties associated with them. It has not yet been possible to separate a fraction consisting of a single hydration product, nor has it been possible to separate a fraction which contained all of a given substance that occurs in the paste, e.g., if a given fraction is shown to be enriched with respect to the iron-bearing component, it still will not contain all of the iron-bearing phases in the original paste. Finally, there is the distinct possibility that the products of hydration may be altered by the separation process. Nurse and Taylor found C_3AH_6 in some of their fractions, but attach little importance to the result since the sample was heated at one stage of the procedure.

Perhaps the most fruitful investigations made of hydrated cement pastes, either whole or divided, are those using X-ray diffraction techniques. Most of the X-ray examinations of cement pastes made up to the present time have been by the Debye-Scherrer film technique. However, the recent development of the diffractometer now permits greater resolution and reveals important details heretofore unknown. It was with apparatus of this type that Kantro, Copeland, and Anderson [12] examined a group of well-hydrated portland cement pastes of various compositions. Although portions of these pastes were ground and dried, no treatment was given them to cause any unknown phase alteration. Fully hydrated pastes were used so that clinker lines would not interfere with the lines of the various hydrates. The hydrated pastes were examined both in saturated condition and in dried condition. The saturated specimens were small rectangular slices removed from the centers of the paste cylinders and polished smooth. The surfaces obtained contained no holes due to air bubbles inasmuch as the pastes were prepared by a vacuum-mixing technique [13] so that no air was entrained. Provisions were made to keep the specimen saturated during the entire X-ray observation. The remainder of the paste was ground to pass a 200-mesh sieve and dried either over $Mg(ClO_4)_2 \cdot 2\text{-}4H_2O$ or over ice at −78 °C (see below). These dried powders were packed in small sample holders and their diffraction patterns observed in the usual manner. Some dry powder specimens were brought to equilibrium at other relative humidities prior to X-ray examination. This was accomplished by placing the sample in a desiccator over an appropriate saturated salt solution, evacuating the desiccator, and allowing the sample to stand under these conditions for at least 2 weeks.

One of the difficulties encountered by many investigators attempting to identify the hydration products of portland cement by X-ray diffraction techniques is the alteration or decomposition of certain of the hydration products as the result of drying.

Lines of some substances disappear and others shift to new positions. In view of this type of behavior, observations of both wet and dry samples produce more useful information than either type of observation alone. The assignment of a diffraction line to a particular material is often complicated by the presence of a second substance having a line in the same vicinity. However, when the water content of the paste is changed, such that some of the lines may shift while others do not, the identification of a particular hydrate in portland cement paste may be made not only on the basis of the presence of lines at certain *d*-spacings, but also on the basis of the shifts the lines have when the paste is wetted or dried. Likewise, the lack of a line shift serves as a useful identifying feature in some cases.

Thermogravimetric and differential thermal analysis techniques have been applied to hydrated portland cement pastes. Taylor [10] used thermogravimetric analysis to show the relationship of the weight loss-temperature curve of a portland cement paste to those of various substances which may be hydration products. However, no definite conclusions may be drawn from the cement paste data, although they do indicate the type of result to be expected.

Recently Turriziani [11] used differential thermal analysis (DTA) in an investigation of the hydration products of portland cement. This method, however, like thermogravimetric analysis, in its present state of development suffers from certain shortcomings. Primary among these is that a number of possible cement hydration products have endotherms so close to the same position that, as Turriziani points out, ". . . the characterization of the individual components of the mixture is practically impossible." However, by observing samples under reproducible conditions, one can often derive information from the relative amplitudes of certain peaks.

Until recently, most of the investigations carried out with the electron microscope have been limited to the study of hydration products formed in a large excess of water. Such studies are subject to the "difficulties in verifying the indications relative to cement paste" mentioned by Steinour [4]. Surface replica techniques are now being used to study the structure of hardened pastes, and methods of sample preparation are being developed that may permit one to study the substances produced when cement hydrates as a paste. Selected area electron diffraction in conjunction with electron microscopy promises to be a most useful tool. Its greatest disadvantage is the inability to control the orientation of the extremely small crystallites found. Eventually electron diffraction patterns of crystals with known compositions will provide the information necessary to make certain the identification of the products of hydration of cement.

Although electron-optical investigations of the stoichiometry of portland cement hydration fall within the realm of this discussion, they have, for the most part, been omitted, inasmuch as the entire field of electron-optical investigations in cement chemistry is discussed elsewhere in this symposium.

Chemical analysis has and always will provide a great deal of necessary information in the study of cement hydration products. One of the techniques of chemical analysis widely used is the determination of free calcium hydroxide. The quantitative analysis for free calcium hydroxide by means of X-rays [14] provides an excellent means for determining the amount of crystalline calcium hydroxide present in a given paste. If amorphous calcium hydroxide is also present [15], needless to say, it is not detected by the method.

All free calcium hydroxide, both crystalline and amorphous, may be determined by solvent extraction techniques. The Franke method [16] using a mixture of isobutyl alcohol and ethyl acetoacetate as the extraction solvent has been modified recently [17, 18] so that the total calcium hydroxide extracted may be corrected for the amount of calcium oxide removed from other substances in the mixture, provided this decomposition has proceeded slowly relative to the rate of solution of free calcium hydroxide. If the decomposition is rapid, however, no such correction can be made, and it is impossible to distinguish between extractable and free calcium hydroxide by this technique alone.

It therefore is quite advantageous to compare results of X-ray and solvent extraction calcium hydroxide determinations in order to obtain useful information about the hydrated cement paste system. Some results obtained by this method will be discussed in a later section.

The interpretation of the data obtained by the methods described above in quantitative or semiquantitative terms requires that other chemical data be available. Among these are the oxide composition of the original cement, the compound composition of the original cement and the bound water content of the hydrated paste.

The oxide analyses may be obtained by conventional analytical techniques. The potential compound composition of the cement may then be calculated according to the method of Bogue [19]. The determination of the actual composition of the cement may be carried out by means of X-ray quantitative analysis [20, 21]. This again, like the X-ray free lime determination, is an internal standard method.

The bound water content or nonevaporable water content of hydrated cement paste is a somewhat arbitrary value, depending upon the equilibrium water vapor pressure to which the material was dried. Although many methods of drying have been devised in the past only two will be considered in the ensuing discussions and these will be described here. The two methods differ mainly in the desiccant used, and hence in the equilibrium vapor pressure. One of the desiccants is a mixture of magnesium perchlorate dihydrate and tetrahydrate, which produces an equilibrium vapor pressure of 8 μ. The other is ice at the temperature of dry ice having an equilibrium vapor pressure of $\frac{1}{2}$ μ. The method of vacuum drying specimens to the $\frac{1}{2}$ μ level has been described in detail by Copeland and Hayes [22].

The Hydration Products of Portland Cement

The Calcium Silicate Hydrate

The results obtained from patterns of both wet and dry cement pastes [12] indicate that a calcium silicate hydrate of the tobermorite type is present, in agreement with the results reported by Taylor [10]. Only three diffraction maxima are observed for this substance. Bernal, Jeffery, and Taylor [23] report only two lines for the products of hydration of C_3S at room temperature. These were at 3.07 and 1.83 A. More recently, Brunauer, Copeland, and Bragg [24] reported lines at 3.03, 2.82, and 1.83 A from the products of the hydration of C_3S as paste at room temperature. It is possible that the 2.82 A line was missed in the older work because it is a peak superimposed on the broad high angle shoulder of the 3.03 A line, and as a result, would be difficultly detectable by a Debye-Scherrer technique. Brunauer, Kantro, and Copeland [15] have found that the calcium silicate hydrate produced by the hydration of C_2S as well as that by C_3S shows the same three diffraction lines.

The X-ray diffraction patterns of hydrated portland cement pastes have certain characteristics in common with those of hydrated C_3S and C_2S. The same three lines ascribable to calcium silicate hydrate in the pastes of the pure silicate compounds also appear in cement paste patterns. The characteristics of these lines in cement paste patterns are much the same as in the calcium silicate paste pattern. There is a broad hump with a maximum in the vicinity of 3.05 A. This peak is quite asymmetric, just as in the cases of C_3S and C_2S, falling off relatively sharply on the low angle side and much more gradually on the high angle side. In the wet slab patterns, the principal calcite line, at 3.03 A [25], is superimposed on this peak.

The line found at 2.82 A in calcium silicate hydrate patterns appears shifted to 2.78 A in cement paste patterns. This shift is due to the presence of lines from other hydration products at about the same spacing. Among the substances contributing to the 2.78 A peak is ettringite, with a line at 2.77 A [26]. This line, however, would not be present in dry powder patterns. Although the ettringite pattern disappears when the sample is dried, the 2.78 A line does not shift back to 2.82 A. The low sulfate sulfoaluminate has a line in the vicinity of 2.78 A [27, 28, 29]. Thus, the persistence, on drying, of the 2.78 A line in substances showing no low sulfate sulfoaluminate, but only ettringite, as well as in substances showing the simultaneous presence of both indicates that sulfoaluminates are not solely responsible for the shift.

The 2.78 A line in cement pastes appears to be somewhat stronger than that of the 2.82 A line in pastes of hydrated calcium silicates. The shape is also somewhat different and is that shape to be expected if a line from a well-crystallized hydrate were superimposed upon the 2.82 A tobermorite line.

The 1.82 A tobermorite line is easily distinguishable. The line appearing here is far too strong to be accounted for as the low sulfate sulfoaluminate line found by Midgley [27, 28] at 1.82 A, while Fratini, Schippa, and Turriziani [29] do not report a low sulfate sulfoaluminate line at this spacing. No known hydration product other than tobermorite can give a line strong enough to account for the 1.82 A spacing observed.

It can be seen from the above discussion that the same calcium silicate hydrate lines appearing in patterns of hydrated pastes of C_3S and C_2S are found in the patterns of hydrated portland cement pastes. Although these lines tend to characterize this hydrate as a tobermorite type, they constitute a set of data too meager in themselves to give any information as to the composition of this phase.

There are indications from other techniques as well that the calcium silicate hydrate in portland cement pastes is of the tobermorite type, e.g., the thermogravimetric curves of Taylor [10] and the differential thermal data of a number of investigators, most recent among these being Turriziani [11]. Finally, Gaze and Robertson [30] have identified tobermorite crystals as the product of hydration of a foamed mixture of portland cement and asbestos, using an electron microscope. The presence of tobermorite in this latter example is not conclusive that it is the product of ordinary paste hydration, however.

The calcium silicate hydrate which forms in portland cement pastes probably contains small amounts of impurities, primarily alumina. It was shown by Kalousek [31] that aluminum can be substituted for silicon in the tobermorite lattice without the substance losing its original identity. Compositions containing as much as 4 to 5 percent Al_2O_3 were prepared hydrothermally. A similar situation may exist in portland cement pastes during hydration at room temperature. Other substances such as alkali may also enter into the silicate structure [32].

The Calcium Sulfoaluminates

In the preceding paragraphs, several references were made concerning the presence of either the low sulfate calcium sulfoaluminate, the high sulfate calcium sulfoaluminate, or both. X-ray diffraction lines of both substances have been observed in hydrated pastes, sometimes separately and sometimes simultaneously. Table 1 lists the X-ray diffraction *d*-spacings observed with wet slabs of several cement pastes. Table 2 lists *d*-spacings observed with dried ground cement pastes.

The two strongest ettringite lines, at 9.73 and 5.61 A [26] occur in positions not interfered with by other possible products of cement hydration. It can be seen in table 1 that whenever the 9.73 A line appears in a hydrated cement, the 5.61 A line also appears. In most cement pastes where they appear, these lines are weak and the other ettringite lines are proportionately weaker so as to be obscured by normal background variation. However, in those patterns where the 9.73 A line is more intense, some of the weaker lines such as 4.69 and 3.48 A can be distinguished. The rather strong line occurring at 3.88 A is somewhat obscured by a calcite line. However, as this calcite line is weak relative to the principal calcite line, at 3.03 A, the 3.88 A line found in all cement paste patterns showing 9.73 and 5.61 A lines is easily seen to be too strong to be accounted for only as calcite.

As can be seen from table 1, the ettringite lines are found in pastes which have been cured for long periods of time. Thus the data for 10-year-old pastes made from cements of various compositions indicate the presence of a significant quantity of ettringite, except for those pastes made from cements high in C_3A. However, in pastes of one high C_3A cement, 15754, samples of which have been prepared under a variety of conditions, no ettringite is found except in the youngest paste observed, one which was hydrated for only 6 months. Thus it would appear that this cement behaves in the manner described by Taylor [10], in that ettringite forms at early ages, and then disappears. Taylor suggested that the disappearance of ettringite may be due to the formation of the low sulfate sulfoaluminate, which then dissolved in the C_4AH_{13} phase to form a solid solution.

On the other hand, ettringite has been observed in some cements, such as those mentioned above, even after long periods of curing. This type of behavior is in agreement with that observed by Turriziani [11], who found this material in pastes made from four different cement compositions, and hydrated at two different water-cement ratios, at ages from 7 days to 6 yr.

Considerably less success has been had in years past in identifying the low sulfate sulfoaluminate in portland cement pastes by X-ray diffraction techniques. Turriziani [11] was unable to find evidence for monosulfoaluminate in any of his specimens over the whole range of compositions, water-cement ratios, and times investigated. He concluded that if this material does form, it does so only at a very slow rate. Diffraction patterns for the compound $C_3A \cdot CaSO_4 \cdot 12H_2O$ have been reported by Midgley [27, 28] and Fratini, Schippa, and Turriziani [29]. The results are in reasonably good agreement. The principal diffraction peaks for this material are at 8.9 and 4.45 A. The 8.9 A line has been observed in certain of the wet slab patterns, the data for which are given in table 1. The 4.45 A line appears in every one of these as well, but in addition, in patterns in which the 8.9 A line does not appear. As will be seen later, this arises from the fact that a strong line from another phase also appears at 4.4 A. The other lines of the calcium monosulfoaluminate are either too weak to be detectable in view of the difficultly distinguishable 8.9 A line, or else other substances have lines appearing in the same locations, such

Table 1. *X-ray d-spacings—hydrated cement wet slab and rewetted sample data*

Specimen	C-88	C-54	C-87	C-75	C-75 [c]	C-66-K	C-66-O	C-61-C	C-33-1	C-33-1 [c]	C-31-1	C-32-1
Cement	15754	15754	15754	15754	15754	15754	15754	LTS-17	15622	15622	15497	15669B
Type	I	I	I	I	I	I	I	I	II	II	III	IV
Nominal W/C	.40	.55	.40	.65	.65	.70	.57	.70	.60	.60	.60	.60
Age	11 yr	11 yr	7 yr	7 yr	7 yr	11 mo	6 mo	1 yr	10 yr	10 yr	10 yr	10 yr
Spacings, A	----	----	----	----	----	----	9.7	9.8	9.8	9.8	9.7	9.8
	----	8.9	----	8.9	9.0	9.0	----	9.0	----	8.8	9.0	----
	----	----	----	----	----	----	8.7	8.6	----	----	8.3	----
	7.8	7.8	7.8	7.7	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
	----	----	----	----	----	----	----	7.4	7.4	7.4	----	----
	----	----	----	----	----	----	5.66	5.68	5.64	5.66	5.64	5.64
	5.09	5.06	5.09	5.09	(b)	5.09	5.11	[a] 5.08	[a] 5.06	(b)	5.08	----
	4.94	4.92	4.93	4.93	4.93	4.94	4.92	4.94	4.93	4.94	4.92	4.92
	----	----	----	----	----	----	----	----	4.72	4.72	4.72	4.72
	----	----	----	4.49	4.48	----	----	4.48	----	----	----	----
	4.41	4.38	4.43	4.39	4.40	4.41	4.39	4.41	4.39	4.40	4.41	----
	----	4.27	4.27	----	4.28	----	4.27	----	4.26	----	4.26	4.29
	4.00	4.00	4.03	4.02	4.02	----	----	4.02	4.04	----	4.02	4.02
	3.88	3.86	3.86	3.87	3.86	3.88	3.88	3.88	3.88	3.88	3.88	3.88
	3.79	3.78	3.77	3.77	----	3.78	----	3.81	----	----	3.81	----
	----	----	----	----	3.67	----	----	----	3.67	3.67	----	3.69
	----	----	----	----	----	3.50	----	3.50	3.48	3.48	3.49	3.49
	----	3.43	----	3.45	3.42	----	3.45	----	----	----	----	----
	3.35	3.35	3.34	3.35	----	----	3.34	3.36	3.35	3.38	3.35	3.36
	3.31	3.30	----	3.31	3.32	3.32	----	3.31	----	3.32	3.31	----
	----	----	----	----	----	----	----	----	----	----	----	3.26
	3.12	3.11	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12
	3.05	3.04	3.05	3.05	3.04	3.05	3.05	3.05	3.05	3.05	3.05	3.05
	----	2.97	----	----	2.97	----	2.98	----	----	----	----	----
	2.88	2.88	2.88	2.88	2.89	2.89	2.88	2.89	----	----	2.89	----
	----	----	----	2.84	----	2.83	----	----	----	----	----	2.84
	2.78	2.77	2.78	2.78	2.78	2.78	2.79	2.78	2.78	2.78	2.77	2.78
	----	----	----	----	----	2.69	2.69	----	2.67	2.69	2.70	----
	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63
	2.60	2.58	2.59	2.59	2.58	2.59	2.59	2.59	2.57	2.58	2.56	2.56
	2.53	2.52	2.54	2.53	2.54	----	2.54	2.54	2.54	2.53	2.53	----
	2.50	2.50	2.50	2.49	----	2.49	2.49	----	2.51	----	2.50	2.51
	2.47	2.45	2.46	2.47	2.46	----	2.46	2.46	2.46	----	2.45	2.45
	2.43	2.42	2.43	2.43	2.42	2.43	2.43	2.43	2.42	2.44	2.43	2.41
	2.37	----	2.37	2.36	2.36	----	2.36	2.37	----	2.35	2.36	----
	----	2.31	2.31	----	----	----	----	----	----	----	----	----
	2.29	2.29	2.29	2.29	2.29	2.29	2.29	2.30	2.29	2.29	2.29	2.29
	2.27	2.26	2.27	2.27	2.26	2.27	2.26	2.27	2.27	2.27	2.26	----
	----	----	2.19	2.19	2.20	2.19	2.20	2.20	2.21	2.21	2.21	2.21
	2.14	----	----	2.14	2.14	2.14	2.14	2.14	2.15	2.16	2.14	2.16
	2.10	2.10	2.10	2.10	2.10	2.11	2.10	2.10	2.09	2.10	2.10	2.10
	2.07	2.06	2.06	----	2.07	2.07	----	2.04	2.06	2.06	2.06	2.06
	2.01	2.01	2.02	2.01	2.01	2.01	2.02	2.01	2.01	2.01	2.01	2.01
	1.96	1.96	1.97	----	1.96	1.96	1.96	1.96	----	----	1.96	1.97
	1.932	1.929	1.931	1.931	1.930	1.932	1.930	1.931	1.930	1.931	1.930	1.932
	1.912	1.912	1.912	1.912	----	----	1.912	----	1.912	----	1.912	1.912
	1.881	1.875	1.879	1.879	1.875	----	1.879	1.881	1.879	----	1.875	1.879
	1.826	1.819	1.824	1.824	1.823	1.827	1.823	1.828	1.823	1.824	1.823	1.826
	1.799	1.796	1.799	1.799	1.798	1.799	1.798	1.799	1.797	1.798	1.797	1.801
	1.722	1.714	1.723	1.719	1.717	1.719	1.723	1.723	1.722	1.720	1.717	----
	1.690	1.688	1.689	1.690	1.688	1.690	1.688	1.690	1.689	1.689	1.688	1.689
	----	----	1.665	----	----	----	1.662	----	----	1.663	1.667	1.665
	1.660	1.658	1.660	1.660	1.658	1.662	1.652	1.661	1.657	1.656	1.654	----
	1.639	1.635	1.638	1.638	1.638	1.635	1.638	1.639	1.636	1.638	1.638	1.634
	----	----	1.609	----	----	----	1.607	----	----	----	----	----

[a] Shoulder on strong peak. Exact d-spacing not certain.
[b] Badly obscured by strong peak. Spacing cannot be estimated.
[c] Dried sample, rewetted in a saturated atmosphere.

that assignment of the diffraction maximum to a particular substance would be questionable.

However, the low sulfate sulfoaluminate lines do not behave in the same way as ettringite, when the material is dried. Instead, the basal reflections shift to lower *d*-spacings, while the other lines show no significant change. Roberts [33] points out that upon drying over anhydrous $CaCl_2$, the low sulfate sulfoaluminate basal spacing contracts from 8.9 to 8.2 A. When this material is dried in CO_2-free air at 115° or *in vacuo* at room temperature to the half-micron level, the 8.9 A line, assigned 001 by Fratini, Schippa, and Turriziani [29], contracts to 8.2 A, and the line at 4.45 A, assigned 002, contracts to 4.1 A [34]. The 8.2 A line appears in the patterns of those pastes for which the wet slab pattern showed the 8.9 A line. In the past, the 8.2 A line has been attributed to the tetracalcium aluminate hydrate [10], but the fact that it appears only in patterns of material which, when dry, shows the low sulfate sulfoaluminate line, indicates that it is this substance which is responsible for the line. Likewise, the 4.15 A line in dried powder patterns appears only when the 8.2 A line does. That the 4.4 A line does not disappear in dry powder patterns is due to the fact that another material, not affected by drying, contributes to it.

The lines of low sulfate sulfoaluminate appearing in dry powder patterns are strong and sharp, indicating that a significant amount of the material is present in the paste. This is true even for those pastes whose wet slab patterns gave low sulfate sulfoaluminate lines which were very weak. The weakness of the lines in wet pastes is due to the effect of carbonation.

Dried specimens of several of the pastes included in tables 1 and 2 were brought to equilibrium with various relative humidities. No significant changes were observed at humidities below 28 percent. However, in patterns of low sulfate sulfoaluminate-bearing samples, equilibrated at higher humidities,

Table 2. *X-ray d-spacings—hydrated cement dried powder data*

Specimen	C-75	C-49	C-61-C	C-33-1	C-33	C-33-1	C-31	C-32-1	C-32
Cement	15754	15754	LTS-17	15622	15622	15497	15497	15669B	15669B
Type	I	I	I	II	II	III	III	IV	IV
Nominal W/C	.65	.65	.70	.60	.60	.60	.60	.60	.60
Age	7 yr	5 yr	1 yr	10 yr	7 yr	10 yr	7 yr	10 yr	7 yr
Spacings, A	8.2	8.2	8.2	------	------	8.2	8.2	------	------
	7.7	7.9	7.7	7.8	7.8	7.7	------	------	------
	------	------	7.3	7.4	7.3	------	------	------	------
	5.47	5.48	5.45	5.47	5.43	5.45	------	5.47	5.48
	[a] 5.06	(b)	(b)	[a] 5.06	5.06	5.07	[a] 5.06	(b)	(b)
	4.92	4.95	4.91	4.92	4.92	4.92	4.92	4.92	4.92
	4.41	4.41	4.41	4.41	4.39	4.39	4.39	4.40	4.39
	4.09	4.10	4.07	------	------	4.08	4.08	------	------
	------	------	------	------	4.00	------	------	------	------
	3.89	3.92	------	3.86	3.89	3.86	------	------	3.92
	3.62	------	------	------	3.66	------	------	------	------
	3.31	3.32	3.31	3.32	3.35	3.31	3.30	------	3.30
	------	------	------	------	------	------	3.21	------	3.18
	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.11
	3.04	3.05	3.03	3.05	3.04	3.04	3.05	3.03	3.03
	2.92	------	------	------	------	2.92	------	------	------
	2.88	2.88	2.88	------	------	2.86	2.86	------	2.87
	2.78	2.78	2.78	2.78	2.77	2.77	2.76	2.79	2.78
	------	2.70	2.71	[a] 2.67	2.68	------	------	------	------
	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63
	------	[a] 2.60	2.59	2.60	2.58	2.55	2.58	------	------
	2.53	2.53	2.53	2.53	2.53	2.53	2.53	2.53	------
	2.49	------	2.48	------	------	------	------	------	------
	2.46	2.46	------	2.46	2.45	2.46	2.47	------	2.45
	2.43	2.43	2.43	2.44	------	2.43	2.42	------	------
	2.35	2.35	2.35	------	------	2.35	2.35	------	------
	2.31	2.30	------	2.30	------	------	2.30	2.30	------
	2.26	2.26	2.26	2.26	2.26	2.26	2.28	------	------
	2.08	2.10	------	------	------	------	2.08	------	------
	------	2.05	------	2.06	2.05	------	------	------	2.05
	2.01	2.01	2.01	2.01	2.01	2.01	2.00	2.01	2.02
	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93
	1.88	1.89	------	------	------	------	------	------	1.89
	1.82	1.82	1.83	1.82	1.82	1.82	1.82	1.82	1.82
	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
	1.72	1.72	1.72	1.72	1.72	1.72	1.71	------	1.71
	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69
	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.66
	1.64	1.64	1.64	1.64	1.64	1.64	1.64	------	1.64
	1.61	1.60	------	------	1.62	------	------	------	------

[a] Shoulder on strong peak. Exact d-spacing not certain.

(b) Bably obscured by strong peak. Spacing cannot be estimated.

the 8.9 A line appeared. It showed only as a shoulder on the 8.2 A peak at 28.8 percent relative humidity, was about equal in intensity with the shrinking 8.2 A peak at 33 percent relative humidity, and at 42 percent relative humidity, the 8.2 A peak was a small shoulder on the 8.9 A peak. These features are illustrated in figure 1. At higher humidities, the patterns appeared quite like the wet slab patterns, except that no significant amount of carbonation had occurred. As a result, the low sulfate sulfoaluminate lines were of intensities comparable to those of the lines in the dried powder patterns. That is, they were strong and sharp. Because of this, it was easy to distinguish the 4.45 A sulfoaluminate line from a 4.40 A line due to another phase (see below). This resolution is illustrated in figure 1. Furthermore, it can be seen from results in tables 1 and 2 and in figure 1 that while the 4.1 A line in the dry material shifts to 4.45 A in the wet material, the line at 4.0 A reappears as well when the sample is rewetted. This corresponds to the line reported at 3.99 A by Midgley [27, 28] and at 4.02 A by Fratini, Schippa, and Turriziani [29].

Thus in figure 1, idealized patterns in the 9 A and 4 A regions are shown for pastes containing the dry form of low sulfate sulfoaluminate, the wet form, and an intermediate case (33 percent humidity) in which both forms appear simultaneously. The differences between wet slab and rewetted powder patterns show that low sulfate sulfoaluminate reacts with CO_2 just as does $Ca(OH)_2$.

The ettringite lines appearing in wet slab patterns at 9.8 and 5.6 A are absent in the dried powder patterns of these pastes. Rewetting these pastes at humidities up to 47 percent has no significant effect on the diffraction pattern. Rewetting at 100 percent relative humidity causes the ettringite lines to return. No significant amount of carbonation occurred with these rewetted samples, and yet the ettringite lines were of comparable intensities to those in the original wet slab patterns wherein considerably more carbonation occurred. Thus, if CO_2 reacts with ettringite, it does so sufficiently slowly so as not to affect the X-ray observations.

The low sulfate sulfoaluminate is found in pastes made from cements high in C_3A, but not in those made from cements low in C_3A. On the other hand, ettringite is the only sulfoaluminate found in pastes made from cements low in C_3A, while little if any of it is found in pastes of cements high in C_3A.

One of the cements low in C_3A discussed above is of especial interest in one respect, however. If the low sulfate sulfoaluminate were to have formed instead of ettringite, not enough Al_2O_3 would be present in the cement to react with all the SO_3. Under these circumstances, it is possible that a sulfoferrite might form. Malquori and Cirilli [35] have prepared calcium sulfoferrites analogous to

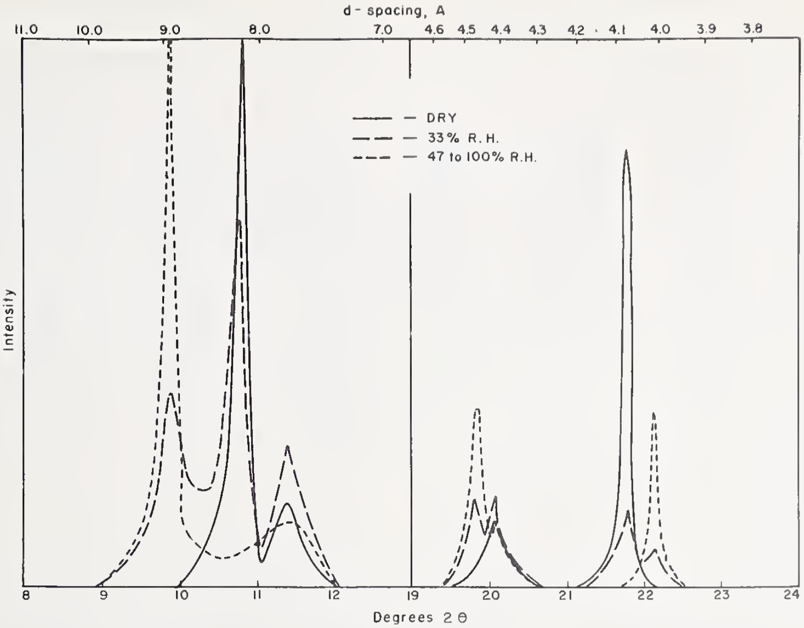

Figure 1. *Calcium monosulfoaluminate lines in X-ray patterns of portland cement paste at different relative humidities.*

the calcium sulfoaluminates which are found in hydrated portland cement pastes. The X-ray diffraction patterns of these sulfoferrites are, in general, very much like those of their sulfoaluminate analogs. As a result, the sulfoferrite compounds, were they present in portland cement pastes, would not be readily distinguishable from their aluminate counterparts. However, there is evidence that the iron-bearing phase in cement hydrates in a unique manner not involving SO_3. This will be discussed in the next section.

The Calcium Aluminate and Calcium Ferrite Hydrates

The calcium aluminate and calcium ferrite hydrates have been reported as existing in hydrated cements in two different forms: cubic and hexagonal. The cubic hydrates are represented by the compounds C_3AH_6 and C_3FH_6; the hexagonal hydrates are represented by the compounds C_4AH_{13} and C_4FH_{13}. It was shown by earlier investigators such as Wells, Clarke, and McMurdie [36] that C_3AH_6 is the stable calcium aluminate hydrate in contact with solutions saturated with respect to calcium hydroxide. On the other hand, in none of the discussions of the stoichiometry of the hydration of portland cement is much evidence given for the presence of the cubic tricalcium aluminate hydrate. On the basis of evidence available at the time, Steinour [4] stated that ". . . initial formation of C_4AH_{13} in clinker and water paste seems much more probable than formation of cubic C_3AH_6. . . . It is not impossible, however, that the cubic hexahydrate might form later." In recent X-ray investigations of portland cement pastes, Taylor [10] and later Turriziani [11] report only the hexagonal tetracalcium aluminate hydrate, C_4AH_{13}; they observed no cubic tricalcium aluminate hydrate in the pastes.

In the discussion to follow we shall review evidence that both cubic and hexagonal hydrates are present in hardened pastes and that the cubic phase at least is a solid solution of several substances. We shall discuss first the cubic and then the hexagonal hydrates.

It can be seen from the data in tables 1 and 2 that a group of lines appears distinctly in patterns of all cement pastes except the Type IV cement, which is quite low both in Al_2O_3 and in Fe_2O_3, and even in patterns of this cement paste there is evidence of these lines. This group of lines appears at 5.07, 4.40, 3.32, 2.26, 2.01, and 1.72 A, corresponding to six relatively strong C_3AH_6 lines reported at 5.14, 4.45, 3.37, 2.30, 2.04, and 1.75 A by Midgley [27, 28], and at 5.13, 4.45, 3.36, 2.30, 2.04, and 1.75 A by Burdese and Gallo [37]. The lines for the analogous iron compound, C_3FH_6, are reported at 5.20, 4.54, 3.40, 2.33, 2.07, and 1.77 A by Flint, McMurdie, and Wells [38] and at 5.18, 4.50, 3.41, 2.33, 2.07, and 1.77 A by Burdese and Gallo [37]. More complete *d*-spacing data for these materials are given in table 3. The reported C_3AH_6 lines are all higher than those observed in the hydrated cement pastes, and the C_3FH_6 lines are farther removed from the observed lines. The spacings observed in cement pastes would not be those expected from C_3AH_6, C_3FH_6, or a solid solution of the two.

Burdese and Gallo [37] also report spacings for a partially dehydrated cubic tricalcium ferrite, C_3FH_2. These spacings are 5.07, 4.38, 3.32, 3.10, 2.78, 2.53, 2.27, 2.01, and 1.72 A in very good agreement with those observed in cement pastes,

TABLE 3. *d-spacings reported for tricalcium aluminate and ferrite hydrates and corresponding spacings in some representative hydrated cement pastes*

hkl [38] [a]	C_3AH_6 [38]	C_3AH_6 [27, 28]	C_3AH_6 [37]	$C_3AH_{3.75}$ [44]	C_3FH_6 [38]	C_3FH_6 [37]	C_3FH_2 [37]	C–75	C–33–1
211	5.16(VS)	5.14(S)	5.13(MS)	5.03(VW)	5.20(M)	5.18(MS)	5.07(M)	5.09	5.06
220	4.47(M)	4.45(M)	4.45(M)	4.39(VW)	4.54(S)	4.50(S)	4.38(MW)	4.39	4.39
321	3.37(M)	3.37(M)	3.36(MW)	3.30(VW)	3.40(W)	3.41(MW)	3.32(W)	3.31	3.32
400	3.15(M)	3.15(M)	3.15(W)	3.09(VW)	3.19(S)	3.19(MS)	3.10(MS)	(b)	(b)
420	2.81(M)	2.82(MS)	2.81(MS)	2.77(VW)	2.85(S)	2.85(MS)	2.78(MS)	(b)	(b)
332	---	---	2.68(VW)	---	2.72(VW)	2.72(VW)	---	---	---
422	2.56(VW)	2.57(W)	2.55(W)	---	2.60(M)	2.61(MW)	2.53(M)	2.53	2.53
431	2.46(W)	2.47(MW)	2.47(W)	---	2.50(VW)	2.51(W)	2.44(WW)	2.43	2.44
521	2.30(VS)	2.30(VS)	2.30(MS)	2.26(VW)	2.33(M)	2.33(MS)	2.27(W)	2.27	2.27
440	2.22(VW)	2.23(VW)	2.23(W)	---	---	2.26(W)	---	---	---
611, 532	2.04(S)	2.04(S)	2.04(S)	2.01(VW)	2.07(M)	2.07(S)	2.01(S)	2.01	2.01
620	1.99(VW)	1.99(VW)	1.99(VW)	---	1.99(W)	2.02(W)	1.96(W)	1.96	---
444	1.81(VW)	1.82(VW)	1.82(VW)	---	---	1.84(WW)	1.79(VW)	(b)	(b)
640	1.74(W)	1.75(MW)	1.75(MS)	1.72(VW)	1.77(M)	1.77(M)	1.72(M)	1.72	1.72
633, 552, 721	1.71(W)	1.71(W)	1.71(W)	---	1.73(W)	1.74(VW)	1.70(VW)	---	---
642	1.68(M)	1.68(M)	1.68(S)	1.66(VW)	1.70(VS)	1.71(VS)	1.66(VS)	1.66	1.66
651, 732	1.60(VW)	1.60(M)	---	---	1.62(VW)	---	---	---	---
800	1.57(W)	1.57(VW)	1.57(W)	---	1.59(W)	1.60(W)	1.55(W)	---	---
840	1.40(W)	1.41(MS)	---	---	1.43(M)	---	---	---	---

[a] Numbers in brackets refer to literature cited at end of text.

[b] Probably present, but overlapped by line from some other component.

as can be seen in table 3. The lines at 3.10 and 2.78, of course, are overlapped by strong lines of $Ca(OH)_2$ [39] and the calcium silicate hydrate, respectively. (It is to be pointed out here again that the strength of the 2.78 A line is far too great to be accounted for on the basis of any aluminate or ferrite.) The compound C_3FH_2, however, is obtained by dehydration of C_3FH_6 at 250 °C [40]. It is difficult to imagine that a species normally formed by dehydration at relatively high temperatures should form at room temperature in a saturated aqueous system, unless some other substance were dissolved in it to stabilize it. Stabilization of solid phases under conditions far removed from equilibrium is not an unusual phenomenon, especially in cement chemistry; one merely need consider the case of β-C_2S. However, the more usual examples, such as β-C_2S, do not involve an aqueous solution phase.

From the kinetic data presented in another section of this discussion, it would appear that the ferrite phase in portland cement hydrates with no significant change in A/F ratio of the remaining unhydrated material. Hence, one might assume that the product of hydration may be a solid solution of a ferrite and an aluminate such that the A/F ratio of the solid solution is the same as it was in the original ferrite phase. Thus, if the original ferrite phase had an A/F ratio of unity, then the hydration product in question would presumably be an equimolar solid solution of a C_3F hydrate and a C_3A hydrate, the phase having the overall composition C_6AFH_x. On the basis of a statistical analysis of nonevaporable water data as a linear function of the composition parameters of a group of 27 cements (the water data being obtained from a group of well-hydrated cement pastes), the water content of such a phase is calculated to be 6 moles per mole of C_6AF; that is, the phase has the composition C_6AFH_6. This work, and the calculations leading to this result, will be discussed in detail in a later section. However, it is interesting to note that the water results obtained are such as to indicate that no pure ferrite phase can form, and that solid solution with an aluminate is probably necessary.

The composition C_6AFH_6 can be considered to correspond to a solid solution of C_3FH_2 with an aluminate of composition C_3AH_4. The lattice of C_3AH_6 shrinks in a regular manner as water is removed [41, 42, 43] but the lattice remains cubic as long as the H/A ratio is greater than 1.5. One might expect a composition C_3AH_4 to have almost exactly the same lattice parameter as C_3FH_2. Indeed, this appears to be the case, since Burdese and Gallo report the lattice constant of C_3FH_2 to be 12.39 A, and Köberich [44] gives the lattice constant of $C_3AH_{3.75}$ as 12.37 A. The X-ray *d*-spacings reported for this material are in reasonably good agreement with those of C_3FH_2 and those found in patterns of hydrated pastes as can be seen in table 3.

The estimation of the composition of this ferrite-aluminate solid solution phase is still a first approximation. The material is more likely to be a silica-containing member of the hydrogarnet series. The estimated water content would be expected to be low because it is replaced by silica as was described by Flint, McMurdie, and Wells [38]. Thus, if the estimated lattice spacing of 12.38 A is taken into consideration, and it is still assumed that the A/F ratio of the material is 1.0, then the material corresponds to a hydrogarnet having a composition in the vicinity of $C_6AFS_2H_8$.

The lines ascribed to the proposed solid solution phase appear in wet slab as well as dry powder patterns, as is indicated by the data in tables 1 and 2. However, in almost all patterns, wet or dry, the 5.07 A line is partly obscured by the 4.90 A calcium hydroxide line [39]. In many cases a shoulder appears sufficiently distinctly so that a reasonable estimate of the *d*-spacing at 5.07 A can be made. In a few other cases, however, the shoulder is not as distinct, and about all that can be said for such cases is that there is a line present, though fairly well hidden by the

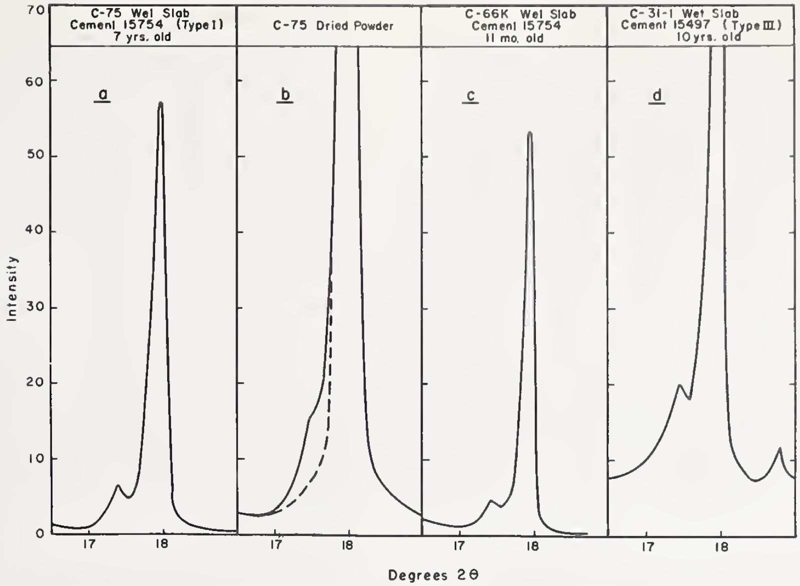

FIGURE 2. *The appearance of the 5.07 and 4.40 A lines in portland cement paste X-ray patterns.*

calcium hydroxide line. Examples of these types are given in figure 2.

The X-ray pattern of this solid solution phase obtained from a sample of a well-hydrated paste of cement 15754 from which most of the calcium hydroxide had been extracted by means of water was somewhat more distinct. The 5.07 A peak was almost completely undisturbed by the 4.90 A calcium hydroxide line. The 3.11 A line was too large to be accounted for by the remaining calcium hydroxide, and although little evidence for other substances containing aluminum or iron was found, the 2.78 A peak was still too large to be caused only by the calcium silicate hydrate phase.

There is little evidence to show either a growth or decrease of the solid solution hydrate lines as a function of time. The lines appear in the pastes of cement 15754 at all ages reported in table 1. Hence, there is no indication that this hydrate would only be a product of hydration of the C_4AF phase after long periods of time. On the contrary, whatever amount of this hydrate is found would appear to have been formed at some early age, and to have remained unchanged thereafter.

In his DTA investigation Turriziani [11] was unable to detect any cubic phase, either C_3AH_6, C_3FH_6, or a hydrogarnet. He observed decomposition temperatures in the vicinity of 375 °C for C_3AH_6 and two members of the solid solution series C_3AH_6-C_3AS_3. However, if the hydrogarnet had an A/F ratio of 1.0, then the decomposition temperature ought to be in the vicinity of 240 °C [38]. An endotherm at this temperature may be difficult to detect when an endotherm also appears at 220 °C due to the presence of tetracalcium aluminate hydrate.

Many investigators in the past have reported the presence of a hexagonal tricalcium aluminate hydrate. Schippa and Turriziani [45] state that it is impossible to form such a compound under conditions such as those that exist in a hydrating cement paste, and that the substance observed is actually calcium monocarboaluminate. All of the wet slab patterns show a line at 7.8 A, corresponding to the principal line of calcium monocarboaluminate [46]. Much of this carboaluminate may have resulted from the carbonation of the wet slabs during handling. However, the pastes of cements high in C_3A have a 7.8 A line with a pronounced asymmetry on the low-angle side, indicating the presence of another, weaker line at a higher *d*-spacing. In some high C_3A cement paste patterns, this asymmetry has developed into a shoulder such that the *d*-spacing of the peak causing it may be estimated. The value obtained, 8.3 A, is very close to the position of the strongest line of tetracalcium aluminate hydrate, C_4AH_{13}, reported by Schippa and Turriziani [45] as 8.4 A, and by Roberts [33] as 8.2 A. In the wet slab patterns, this line is sufficiently weak that it is not expected that any of the other C_4AH_{13} lines, all of which are weaker than the 8.4 A line, would be detectable. In some dried powder patterns, other lines are seen.

The principal peak of the iron analog of this aluminate, that is, C_4FH_{13}, occurs at 8.2 A [47]. Thus, a solid solution of this material with the corresponding aluminate could produce a line at 8.3 A. However, the determination of *d*-spacing from a shoulder of the type described is far too inaccurate to warrant any conclusion regarding the composition of the hexagonal phase.

In the dried powder patterns, the 7.8 A line is much weaker, since very little if any carbonation has occurred during handling. The fact that no shift is observed in this line when the specimen is dried is in agreement with results obtained on a sample of pure calcium monocarboaluminate which was dried to the half-micron level. The pattern of the dried pure compound showed no appreciable shift in line positions from those in the wet sample pattern [34], and was in reasonably good agreement with the spacings reported by Turriziani and Schippa [45, 46] and by Buttler, Dent Glasser, and Taylor [48]. The carboaluminate line in dried samples, and in rewetted samples as well, is weak, indicating that not much of the material is present. That little, if any, CO_2 has entered the dried pastes is indicated by the fact that the principal calcite line is not observable.

Buttler, Dent Glasser, and Taylor present diagrams of patterns of C_4AH_{13} after various drying treatments. These patterns indicate a shift in the basal reflection in the same way as was found for the monosulfoaluminate. When heated to 105 °C, the C_4AH_{13} line at 8 A shifted to 7.8 A. Drying at 105 °C is roughly equivalent to the vacuum drying condition described by Copeland and Hayes [22]. However, when C_4AH_{13} is dried *in vacuo* at room temperature [34], the basal line shifts from 8.4 A, the wet state position [45], to 7.8 A over a relatively short period of time. Continued drying for a much longer period of time (21 days) led to only a small weight loss relative to that in the first 3 days, but the basal reflection shifted to 7.4 A, in agreement with the value reported by Roberts [33]. X-ray patterns of this material revealed only the 7.8 A line unless special precautions were taken to eliminate all traces of water vapor, this being done by passing a dry nitrogen stream over the sample while the pattern was being obtained. Hence, it appears that very little water need be taken up by the well-dried C_4AH_{13} before the basal reflection shifts from 7.4 A to 7.8 A, so that in many cases, the line observed at 7.8 A may represent either carboaluminate, C_4AH_{13}, or both. The reversibility of the hydration-dehydration process in C_4A hydrate was also noted by Roberts. However, there is always a small amount of CO_2 in any paste, most of which was present in the cement prior to hydration. If all this CO_2 were in the form of carboaluminate, there would, in most cases, not be enough present such that all of the tetracalcium aluminate hydrate potentially in the paste would be in the form of carboaluminate.

The diffraction maximum observed at 7.8 A is not a strong, sharp peak, but rather a low, broad hump. This spacing is the basal reflection of the pseudohexagonal crystal [48], regardless of which of the two compounds it represents. The fact that this reflection is poorly developed indicates that the crystals may be quite small and disordered, a condition somewhat akin to that of the CSH(I) produced by reaction of CaO and SiO_2 at room temperature. (The calcium silicate hydrate produced by the hydration of C_3S, of course, shows no basal reflection whatever [15, 24].)

There is some evidence that tetracalcium ferrite hydrate may also have a diffraction line at 7.8 A. Various investigators have reported different basal reflections for C_4FH_x, presumably because each investigated material with a different moisture content. Greening and Seligmann [47] found the basal spacing to be 8.2 A for material in the saturated state. Watanabe and Iwai [49] report a value of 7.96 A for somewhat drier material. Taylor [50] has X-ray data for a hydrate of the composition C_4FH_{10} which includes a basal reflection of 7.8 A. However, even this material would presumably lose water on further drying to the $\frac{1}{2}$-μ level, and as a result, undergo further layer contraction. This would result in a downward shift of the basal reflection toward the 7.4 A value reported for dried tetracalcium aluminate hydrate. There is no information available at present as to how rapidly this dried ferrite hydrate would pick up moisture.

In some of the dried powder patterns, other lines of the hexagonal calcium aluminate hydrate are seen. The most important among these is at 3.9 A, the 002 reflection. The carboaluminate has no line at 3.9 A, but rather, one at 3.8 A. This latter spacing appears in many wet slab patterns, along with a line at 3.9 A caused by the presence of calcite. In the dry powder patterns, no calcite lines appear, and no line at 3.8 A. However, a small line at 3.9 A is found indicating that the hydrated aluminate is primarily C_4AH_{13}. The spacing at 3.9 A is also one found with C_4FH_{10} [50]. Lines appear at 2.46 and 2.10 A in the dried powder patterns, but these also contain contributions from other compounds, such as calcium monosulfoaluminate. The similarity of the pattern of this latter compound with that of tetracalcium aluminate hydrate is quite marked, with the exception of the locations of the basal reflections.

There remains the distinct possibility that the cement paste pattern lines attributed to monosulfoaluminate are in truth those of a solid solution of this material with the tetracalcium aluminate hydrate, but this would not obviate the fact that the evidence obtained indicates the presence of this latter material by itself.

The Dependence of Water Content on Cement Composition

Nonevaporable water data have been obtained on a group of cements hydrated for times up to 13 yr [51, 52]. The cements used were those prepared for use in the "Long Time Study" project at the Portland Cement Association Research and Development Laboratories. The oxide compositions and the potential compound compositions of these cements were published by Lerch and Ford [53].

It was assumed that both nonevaporable water and surface area were dependent on linear functions of the cement composition parameters. Thus:

$$w_n/c=k_1(\text{alite})+k_2(\text{belite})+k_3(C_3A)+k_4(F_{ss})+k_5(CaSO_4) \qquad (1)$$

where the k_t are constants and w_n/c is the nonevaporable water content in grams of water per per gram of cement. The quantities (alite) and (belite) refer to the C_3S and C_2S phases as they occur in portland cement, each containing minor quantities of other oxides, primarily Al_2O_3, as has been discussed by Jeffery (in the case of alite) [54], and in some recent publications on the quantitative analysis of portland cements by means of X-rays [20, 21]. The symbol F_{ss} represents the ferrite solid solution phase. All cement compound quantities may be expressed in grams per gram of cement.

It was shown in the quantitative cement analysis work that the compositions obtained from X-ray analysis did not differ significantly from those obtained from the potential compound calculation devised by Bogue [19] except in the case of C_3A. The C_3A values were lower in the X-ray determination because of the Al_2O_3 in the alite and belite phases; the alite phase was correspondingly higher because of this Al_2O_3. Inasmuch as the ferrite solid solutions had A/F ratios near unity for the most part, the X-ray and potential values were in good agreement.

For the purposes of the calculations, it proved expedient to use potential rather than X-ray values because X-ray values were not available for all of the cements. Since the Al_2O_3 in the alite and belite phases probably behaves during the hydration process in much the same manner as the Al_2O_3 in C_3A, it is likely that no significant error is introduced by the use of potential data. Expressed in terms of the potential compound compositions, eq (1) becomes

$$w_n/c=a_1(C_3S)+a_2(C_2S)+a_3(C_3A)+a_4(C_4AF)+a_5(CaSO_4) \qquad (2)$$

where the a_t are again constants in the equation.

Since the quantity w_n/c in eq (2) is a linear function of the potential compound quantities, which, in turn, are linear functions of the oxides [19], it follows that w_n/c is also a linear function of the oxides. Thus

$$w_n/c=b_1(CaO)+b_2(SiO_2)+b_3(Al_2O_3)+b_4(Fe_2O_3)+b_5(SO_3). \qquad (3)$$

The coefficients in eq (2) have been evaluated by the method of least squares from data obtained from the "Long Time Study" (LTS) cements hydrated for 1, 6½, and 13 yr, at water:cement ratios of 0.4, 0.6, and 0.8, and dried to approximate equilibrium with the vapor pressure of water over a mixture of $Mg(ClO_4)_2 \cdot 2H_2O$ and $Mg(ClO_4)_2 \cdot 4H_2O$ (8 μ), or that of water over ice at −78.5 °C (½ μ). The parameters of eq (2) were evaluated including the $CaSO_4$ term (5-parameter system) or omitting this term (4-parameter system). The results are shown in table 4. In this table, the age of the specimen is given in column 1, the water:cement ratio and method of drying in column 2, the number of parameters evaluated in column 3, the number of cements in the data set in column 4, the values of the parameters in columns 5, 7, 9, 11, and 13, and the standard errors of these parameters in columns 6, 8, 10, 12, and 14.

Investigations of the stoichiometry of the hydration of C_3S and C_2S [15, 24] have shown that the hydration reactions may be represented by the equations

$$2C_3S+5H=C_3S_2H_2+3CH \qquad (4)$$

$$2C_2S+3H=C_3S_2H_2+CH \qquad (5)$$

the composition of the calcium silicate hydrate being given as that of the half-micron material. From these equations, it is seen that each gram of C_3S reacts with 0.197 g of water, and each gram of C_2S with 0.157 g of water. The constants, a_1, in eq (2), obtained from the least squares treatment of the various sets of half-micron sample data, range from 0.199 to 0.208. It would therefore appear that in 6.5-year-old pastes, hydrated at relatively high water:cement ratios, for which these values were obtained, the C_3S is completely hydrated.

The constants, a_2, obtained from these same data, range from 0.147 to 0.152. The fraction of C_2S hydrated, estimated as the ratio of the calculated value of a_2 to the theoretical value based on eq (5) is 0.951, on the average, for a

TABLE 4. *Least squares coefficients from nonevaporable water data*

Age	w_0/c & drying [a]	No. of parameters	No. of cements	a_1	σ_1	a_2	σ_2	a_3	σ_3	a_4	σ_4	a_5	σ_5
13 yr	0.4(P)	5	27	0.226	0.017	0.194	0.014	0.510	0.066	0.097	0.065	0.149	0.312
"	"	4	27	.230	.015	.196	.013	.522	.060	.109	.058	----------	----------
6½ yr	0.8(P)	5	23	.228	.022	.193	.020	.478	.097	.151	.097	0.317	0.460
"	"	4	23	.234	.020	.197	.018	.509	.085	.184	.083	----------	----------
"	0.8(D)	5	23	.201	.020	.154	.017	.571	.086	.190	.086	−0.120	0.410
"	"	4	23	.199	.018	.152	.016	.561	.075	.178	.073	----------	----------
6½ yr	0.6(P)	5	24	.228	.020	.188	.018	.412	.090	.091	.079	0.607	0.409
"	"	4	24	.238	.020	.198	.017	.477	.081	.142	.074	----------	----------
"	0.6(D)	5	24	.204	.019	.147	.016	.470	.083	.129	.074	0.243	0.380
"	"	4	24	.208	.017	.151	.015	.496	.072	.149	.065	----------	----------
6½ yr	0.4(P)	5	27	.223	.018	.170	.015	.463	.070	.117	.069	0.503	0.333
"	"	4	27	.234	.017	.178	.015	.504	.066	.158	.065	----------	----------
1 yr	0.4(P)	5	27	.212	.020	.155	.016	.363	.076	.067	075	0.786	0.360
"	"	4	27	.228	.019	.168	.016	.429	.074	.132	.073	----------	----------

[a] (P)—dried at 8μ vapor pressure; (D)—dried at ½μ vapor pressure.

6.5-year-old paste hydrated at a water:cement ratio of 0.6, and 0.974 for pastes of the same age hydrated at a water:cement ratio of 0.8. These latter values, however, must be considered as maximum values, inasmuch as there is usually somewhat more water in the calcium silicate hydrate phase than the two moles per mole of SiO_2 indicated by the two eqs (4) and (5), [15].

For 8-μ dried C_3S and C_2S pastes, the stoichiometric equations are [15]:

$$2C_3S+5.8H=C_3S_2H_{2.8}+3CH \quad (6)$$
$$2C_2S+3.8H=C_3S_2H_{2.8}+CH. \quad (7)$$

These equations predict the values of a_1 and a_2 to be 0.229 and 0.199, respectively. The values obtained indicate that for pastes hydrated at water:cement ratios of 0.4, after 1 yr, the C_3S is over 95 percent hydrated and after 6½ yr, it is completely hydrated. The C_2S is not so well hydrated, however, being, on the average, 81.4, 87.6, and 98.2 percent hydrated at 1, 6½, and 13 yr, respectively.

Inasmuch as the cements used in the least squares analysis are of widely different compositions, it must be pointed out that such a treatment is valid only for relatively well-hydrated pastes, wherein the effect of dependence of hydration rate on cement composition is no longer important.

Interpretation of the aluminate, ferrite, and sulfate nonevaporable water results is more difficult. In the first place, there are several possible products of hydration, and as has been shown, evidence has been obtained for the presence of some of them. Others may be present for which no evidence has as yet been obtained. As can be seen from the standard errors, the least squares parameters for the ferrite and sulfate are far less certain than are the C_3S and C_2S parameters. Furthermore, while there is no significant difference between the 4- and 5-parameter C_3S and C_2S results, the other parameters are strongly affected. The contribution of the sulfate in the 5-parameter calculation is absorbed primarily by the aluminate and ferrite parameters in the 4-parameter calculation.

The least squares results may be expressed in terms of oxides, according to eq (3). The parameters may then be converted to moles of water per mole of oxide. When this is done, the results for half-micron dried samples at a water:cement ratio of 0.8, rounded to whole numbers (except in the case of SiO_2) are $H/C=1$, $H/S=-0.5$, $H/A=5$, $H/F=-5$, and $H/SO_3=-2$. These values may be used to predict the water contents of the various possible products of hydration. For instance, a calcium silicate hydrate with a C/S ratio of 3/2 would have the composition $C_3S_2H_2$, just as was indicated from the potential compound parameters and the stoichiometric equations for the hydration of the pure silicates. Tetracalcium aluminate hydrate would have the composition C_4AH_9, which is to be compared with the compositions reported by Roberts [33] for tetracalcium aluminate hydrates dried under various conditions. Roberts gives H/A values of 11 for material dried over solid NaOH or anhydrous $CaCl_2$, and values of 7 for material dried over P_2O_5 or at 120 °C.

The calcium ferrite hydrate case is not so simple. A tetracalcium ferrite hydrate would have a negative water content, which is, of course, absurd. However, if the aluminates and ferrites were in solid solution, physically possible, and not unreasonable, water contents are predicted.

The predicted water contents of the sulfoaluminates are, as was pointed out above, quite uncertain. The water-to-oxide ratios given above lead to the compositions $C_3A{\cdot}CaSO_4{\cdot}7H$ and $C_3A{\cdot}3CaSO_4{\cdot}5H$. Lerch, Ashton, and Bogue [55] found water contents for these materials, dried at 110 °C, to be 6H and 7H, respectively. Roberts' recent work [33] indicates a value for the low sulfate sulfoaluminate of about 8H. If the least squares H/SO_3 value were -1 instead of -2, the predicted compositions of the sulfoaluminates would be $C_3A{\cdot}CaSO_4{\cdot}8H$ and $C_3A{\cdot}3CaSO_4{\cdot}8H$. Thus, on the basis of experimental evidence, it appears that the H/SO_3 ratio should be somewhere between -1 and -2. Both these values fall well within the uncertainty limits determined statistically.

The evidence from the least squares calculations combined with the evidence obtained from the X-ray diffraction studies provides a strong indication that the alumina in C_3A reacts in a different manner from that in the ferrite phase. The cements low in C_3A shown in tables 1 and 2 both contain ettringite. On the other hand, those cements high in C_3A when hydrated contained the low sulfate sulfoaluminate. Thus, it appears that only when the A/F ratio in the cement is relatively high, does the low sulfate sulfoaluminate form. Steinour points out, in his recent discussion of the setting of portland cement [56], that when the molar A/F ratio in a cement is less than 1.0, no retarder is needed. He also attributes flash set to the formation of a hexagonal calcium aluminate. Under the conditions obtained with the use of the high C_3A cements whose compositions are given in table 5, the presence of gypsum

TABLE 5. *Oxide compositions of four portland cements*

Cement type	15754 I	15622 II	15497 III	15669 IV
	Percent	*Percent*	*Percent*	*Percent*
SiO_2	20.67	22.44	19.83	27.51
CaO	63.03	63.81	63.41	63.73
Al_2O_3	6.13	3.88	5.21	1.95
Fe_2O_3	[a] 2.20	4.20	[a] 2.59	1.92
MgO	2.05	1.36	1.28	1.64
SO_3	2.37	1.59	1.82	1.82
Total	96.45	97.28	94.14	98.57
Free CaO	0.93	0.49	3.14	0.15
Na_2O	.17	.05	0.30	.05
K_2O	.16	.17	.40	.22

[a] The total Fe_2O_3 includes a small amount of FeO expressed as Fe_2O_3.

prevents the formation of the hexagonal aluminate (presumably tetracalcium aluminate hydrate) by the formation of the sulfoaluminate. The first sulfoaluminate to form is ettringite, apparently, since of the X-ray patterns of pastes from cement 15754, only that of the youngest observed, a 6-month old specimen, showed ettringite. Taylor [10], too, studying a normal portland cement, observed initial formation of ettringite, with subsequent disappearance. It is interesting to note that a hexagonal phase ultimately does form, this however being the low sulfate sulfoaluminate. The molar A/F ratios in the two cements, 15754 and 15497, in which the monosulfoaluminate does form are 4.37 and 3.15, respectively.

On the other hand, the low sulfate sulfoaluminate does not form in cements 15622 and 15669 in which no significant amount of C_3A is present. The molar A/F ratios in these two cements are 1.45 and 1.59, respectively, or, when corrected for the alumina in the silicate phases, 0.81 and 1.34. It would appear from these results that no significant amount of alumina from the ferrite phase enters into a sulfoaluminate as long as enough alumina is available from other sources to combine with all of the SO_3 present to form at least the high sulfate sulfoaluminate.

Flint and Wells [57] observed that while C_3AH_6 was susceptible to attack by sulfate, hydrogarnets containing either iron or silica were quite resistant. It would appear from these considerations that the molar ratio of nonferrite alumina to SO_3 in a given cement would serve as an indication as to which sulfoaluminate forms ultimately. Thus, the high C_3A cements, which contain the low sulfate sulfoaluminate for the most part have SO_3 to nonferrite Al_2O_3 ratios of 0.7 and 0.6, respectively, while the low C_3A cements, which contain the high form for the most part have ratios 1.2 and 3.9.

It is therefore also likely that no sulfoferrites form in portland cement pastes, at least of cements within the wide composition range covered by those whose X-ray data are given in tables 1 and 2, and whose compositions are given in table 5. Furthermore, the least squares coefficients discussed above also indicate that there is no sulfoferrite, in that such a compound, either high form or low form, could not have a negative calculated water content, physically absurd. Of course, a solid solution of sulfoaluminate and sulfoferrite is possible as far as the least squares considerations go just as in the case of aluminates and ferrites.

II. Kinetics of the Hydration of Portland Cement

L. E. Copeland and D. L. Kantro

Introduction

The purpose of this section of the paper is to review our knowledge of the kinetics of hydration. Mechanisms of hydration may at times be mentioned but a discussion of mechanisms is not a principal objective.

The first kinetic studies of the hydration of portland cement were concerned with determining the strength of concrete and mortars as a function of time of curing. Useful information can be obtained from such studies, but their value for theoretical purposes is limited because the development of strength in concrete and mortar is influenced by many factors other than the rate of hydration of the cement in the mix. Knowledge of the rates of hydration of cement is just one step toward understanding the mechanism of hydration and the development of strength, but it is an important one.

Three general methods have been used in studying the kinetics of hydration of portland cement: (1) microscopic examination of hardened neat cement pastes after known curing times, (2) observations of changes in the physical and chemical properties of hardened pastes as a function of time, and (3) X-ray diffraction analysis of unhydrated cement in hardened pastes.

In general, the microscopic studies can be, and in some cases have been, interpreted to support Michaelis' theory of the hardening of portland cement in that the unhydrated clinker particles are found embedded in a gel which has no structure visible in the light microscope. The presence of all four major phases has been observed in these particles—even after 20 yr.

The measurement of several physical and chemical properties of pastes as a function of curing times has been made. In some cases inferences concerning the rates of hydration of the individual components of cement have been drawn from these measurements. It will become evident that some of these inferences are not justified.

In recent years new techniques have been developed. One of these, X-ray diffraction, offers about our best tool for measuring directly the rates of hydration of the individual phases in portland cement. At the present time the experimental error is large when compared with the experimental error of standard chemical methods of analysis, but significant results can be obtained. Further experience with the method will bring improved results. Perhaps other new techniques can also be applied to the problems.

Direct Microscopic Observations

Most of the microscopic examinations have been made on polished sections, or sometimes upon thin sections, of hardened pastes. But Anderegg and Hubbell [58] chose to develop a different technique for their work. They first passed cement through an air separator to obtain several fractions of cement with particles with a narrow size range. They then prepared pastes of these sized fractions, $w_o/c=0.4$, and cured them in contact with a small quantity of water. At each of several selected ages a small fragment was broken from each paste and dried in an oven to stop the hydration reactions by removing the water. Each fragment was then ground until microscopic evidence showed the material to be subdivided into small and uniformly sized particles. Specimens for microscopic examinations were prepared by placing these particles on a microscope slide in an oil with a refractive index of 1.67. Thus it was possible for them to tell whether or not a particle was hydrated by its refractive index, for if it is hydrated its refractive index is lower than that of the oil and vice versa. They counted thousands of particles (weighting the count by the size of the particles) and determined the volume fraction of hydrated cement from the number of hydrated particles relative to the total number of particles. They obtained the weight fraction hydrated by using the densities of the unhydrated cement and of the completely hydrated cement.

To check their results they determined the fraction of cement hydrated in samples prepared by mixing completely hydrated cement with unhydrated cement in known proportions. They reported results accurate to about 2.5 percent.

They proceeded then to calculate the depth of penetration of the water into cement particles. To do this they assumed that the shape of the original cement particles was the same as that of the unhydrated particles remaining in the paste, and made microscopic measurements to determine the size and shape of a great many cement particles. Typical results, given in table 6, were estimated for a cement with a known particle size distribution using their results on depth of penetration of water in sized fractions of clinker particles. They noted that their Type III cement appeared to hydrate no more rapidly than did their Type I cement.

These experiments were repeated [59] using pure compounds and mixtures of pure compounds. Pure C_2S hydrated much more slowly than did pure C_3S, which hydrated much more slowly than did pure C_3A. The addition of 10 percent C_4AF to either C_3S or C_2S caused the mixture to hydrate much more rapidly than either component of the mixture would hydrate when pure.

Brownmiller [60] examined polished sections of neat cement pastes cured for various times. From this examination he estimated that about ⅓ of the cement remained unhydrated at the end of the first day. He compared the sizes of the particles visible in the polished sections with the sizes of the particles of original cement and estimated that a 60μ particle decreased in size to about 45μ during the first day, that the depth of penetration was about $7\frac{1}{2}\mu$. At 7 days approximately 80 percent of the cement had hydrated, and at 28 days about 85 percent. Cements that were high in C_3S and C_3A were almost completely hydrated at the end of 7 days. He concluded that as hydration proceeds there is a uniform decrease in the size of the cement particles, and stated, "There is no microscopic evidence of the channeling of water into the interior of cement particles to selectively hydrate any single major constituent."

Table 6. *Depth of penetration of water in clinker particles and the degree of hydration of a typical portland cement*

Time (days)	Depth of penetration (μ)	Percent hydrated
1	10	24
7	47.2	42
28	78.1	51
90	---------------	60

However, he did observe that different phases at the boundary of a particle did not hydrate at the same rates: e.g., C_3S hydrates more rapidly than C_2S, and some interstitial material hydrates very slowly indeed.

Rexford [61] used thin sections. He pointed out that accurate rates of hydration from such microscopic examination were very difficult to obtain; one needs to examine many fields and measure accurately with a Wentworth micrometer stage. He confirmed Brownmiller's conclusions that hydration proceeded from the boundaries of cement particles inwards towards the center at a comparatively uniform overall rate, which affected all the constituents of that particle more or less simultaneously. He stated further, "No indication of completed hydration of any one compound was ever observed although incipient selectivity was often visible around the periphery of a cement particle." His conclusions were based upon the examination of hardened pastes cured up to 6 months, and upon examination of concrete up to 20 yrs old.

Ward [62] examined thin sections and came to somewhat different conclusions. He described two kinds of gel, one of which he called a "ground mass" gel that was interrupted by unhydrated clinker grains, calcium hydroxide crystals, and by small channels, and pores. Small crystalline particles of low birefringence were scattered throughout this gel. As the paste aged, a clear gel appeared to exude from the ground mass or to precipitate in the voids and channels.

He observed that C_2S and C_4AF were slow to hydrate and that many cement grains were shattered during the hydration. He identified the fragments as C_2S. He concluded that each clinker grain does not hydrate in such a manner as to develop an individual coating of hydrate with subsequent uniting of these coatings.

The overall rate of hydration of cement observed in these microscopic studies agrees qualitatively with expectations based upon the rate of strength development. Anderegg and Hubbell tacitly assumed a mechanism of hydration that was supported later by the independent observations of Brownmiller and of Rexford. In answering a criticism of their paper, Anderegg and Hubbell show that they were aware that this assumption was not universally accepted, but argued that it is true. Actually, it is supported by the theory of hardening advanced by Michaelis, just as Brownmiller interprets his results to support Michaelis' theory.

There is a small difference between the compositions of the finely ground part and the coarser part of a cement, but if hydration proceeds by a more or less uniform diminution in the size of the cement grains, then the finer fraction would disappear first—probably during the first day. After that time the composition of the unhydrated residue should change only slowly if at all.

Ward criticized the above views. He wrote of an apparent increase in the amount of C_2S in the hardened pastes and suggested that the individual phases react separately, then at a favorable concentration a general precipitation of gel occurs. But both concepts can be correct. The mechanism proposed by Ward could account for the initial setting of cement but by far the greatest amount of cement could be hydrated as Brownmiller and Rexford have described it. It is certainly true that if cement grains were "shattered" by hydration, this must have occurred before the paste hardened.

Ward observed shattering of C_2S grains in observing the hydration of the pure compound under the microscope. He noted that his pure C_2S showed a tendency to dust and suggested that perhaps the shattering was the result of the $\beta \rightarrow \gamma$ conversion. Is it possible that water could leach a soluble stabilizing agent out of the C_2S phase in portland cement, causing the same conversion with shattering of the cement grain?

Kinetics From Changes in Physical and Chemical Properties

Heat of Hydration

Many workers have determined the heat of hydration of portland cement as a function of time of curing. Woods, Steinour, and Starke [63, 64] were able to correlate such heats of hydration with the development of strength in mortars, and also found a good correlation between the rate of development of strength and the composition of the cement. Their primary motive was development of low heat cement, and therefore it was essential to their purpose to find a relationship between heat of hydration and composition of cement. For this they employed the method of least squares, assuming that at any given age each percent of each cement compound makes a fixed contribution to the heat evolution independent of the proportion of the compound in the cement. They were successful in accomplishing their objective. Other workers have generally followed their example. Davis, Carlson, Troxell, and Kelly [65] made similar studies of heats of hydration, and Verbeck and Foster [51] published initial results of an extensive investigation which is continuing. The latter authors included the effects of gypsum and both gypsum and glass in their computations.

By comparing the magnitudes of the respective "contributions" of each of the components to the heat of hydration, it can be inferred that the rates of hydration of the major components have the order C_3A, C_4AF, C_3S, C_2S. This order agrees with that obtained by comparing the rates of hydration of the pure components. The contribution of each component to the heat of hydration of completely hydrated cement paste is, within experimental error, the heat of hydration of the pure component.

Apparently no one working with heats of hydration has done more than draw qualitative conclusions concerning rates of hydration of the individual components from his data. If the assumption made tacitly in applying the principle of least squares to heat of hydration data is valid, the rates of hydration of the individual phases can be estimated. It will be instructive to consider this assumption.

Consider k cement pastes, each made with a cement different in composition from all the others. Let H_i be the heat of hydration of the paste made from 1 g of the ith cement and cured t days. Let X_{ij} be the weight fraction of component j in the ith cement, and $w_{ij}(t)$ be the weight of component j per gram of cement that has hydrated in t days. Let h_j be the heat of hydration of 1 g of component j. The heat of hydration of the paste can now be written:

$$H_i(t)=\sum_j w_{ij}(t)h_j. \tag{8}$$

The $w_{ij}(t)$ are unknown. In the application of the least squares principle to the k pastes, each hydrated t days, it is assumed that H_i can be written:

$$H_i(t)=\sum_j a_j(t)X_{ij}. \tag{9}$$

The coefficients $a_j(t)$ are called the contributions of the major components j to the heat of hydration. Eq (8) can be put into the form of eq (9) by multiplying and dividing each term on the right of eq (8) by X_{ij}, that is,

$$H_i(t)=\sum_j \frac{w_{ij}(t)}{X_{ij}} h_j X_{ij}. \tag{10}$$

Equations (9) and (10) are consistent if

$$a_j(t) = \frac{w_{ij}(t)}{X_{ij}} h_j. \qquad (11)$$

In applying the method of least squares to eq (9), it must be assumed that the $a_j(t)$ are independent of the compositions of the cements; consequently, $\frac{w_{ij}}{X_{ij}}$, the degree of hydration of component j, must be the same in all cement pastes at the time t. Also, the time derivative of the degree of hydration, which we shall call the fractional rate of hydration, must be independent of the composition of the cement used in making the paste. A mechanism could be devised to account for this behavior, but the validity of the assumption must be shown by evidence independent of heats of hydration.

Heats of hydration have been used in other ways to obtain information concerning rates of hydration. Steinherz [66] has recently noted that Anderegg and Hubbell [58] oversimplified their calculations on the depth of penetration of water in cement grains by their assumption concerning the shape of their particles. He presents a different approach based upon the measurement of a mean volume and weighted mean diameter of the particles and the assumption that the shape of the particles corresponds more closely to flattened cylinders than to spheres. He used the heat of hydration of the fraction of clinker grains he studied to estimate the amount of cement hydrated, and calculated a depth of penetration. He obtained results similar to those of Anderegg and Hubbell.

The effect to be expected of assuming that the components hydrate at equal fractional rates in cement has been shown by zur Strassen [67]. He considers two different conditions: (1) the rate of diffusion of water through the gel layer is so high that sufficient water is always present in the reaction zone to bring about conversion, or (2) that the reaction is impeded by the rate at which water can diffuse through the gel film being formed. He assumed that the particle size distribution of the original cement could be represented by a Rosen-Rammler size distribution with exponent 1.05. Using Verbeck and Foster's heats of hydration as a measure of the amount of cement hydrated, he calculated the depth of penetration of water into the cement particles and found that the rate followed the diffusion law at times up to 28 days for Type I cement, and times up to 7 days for Type III cements. Thereafter the rate became slower.

He also used the data of Schwiete and Knoblauch [68] on the heats of hydration of pure C_2S and pure C_3S and concluded that for C_2S the rate of reaction is constant up to about 80 percent conversion. For C_3S, after a short period when the rate is linear, the rate follows the diffusion law. He suggests that in cement the expected initial retardation of the hydration of β-C_2S is so little reflected in the $\frac{V_m}{w_n}$ and $\frac{\Delta H}{w_n}$ ratios that the impression of a fully uniform rate of hydration is given. (V_m is the weight of water required to form an adsorbed layer one molecule thick.)

Nonevaporable Water

The nonevaporable water content (or any other good measure of fixed water) is a measure of the extent of hydration of cement in pastes, just as is the heat of hydration. As yet no extensive analysis concerning kinetics of nonevaporable water data has been made as has been done for heats of hydration. Actually there is little need to do so for it has been shown [51, 69] that there is a linear relationship between the two quantities. Least squares calculations based upon the same model as was used for heats of hydration would certainly give the same results.

The effect of the original water-cement ratio, w_o/c, upon the rate of hydration of cement can be seen by comparing nonevaporable water contents of pastes made from the same cement and cured under the same conditions, except for variations in w_o/c. Unpublished data from this laboratory show that w_o/c has little effect upon the rate of hydration during the first 3 or 4 days. After that, the smaller is w_o/c, the more rapidly the rate of hydration decreases. This effect is consistent with the widely accepted view that the rate of hydration is controlled in some manner by the rate of diffusion of reacting species through the gel.

Recently Taplin [70] has published similar, but more complete data, covering w_o/c ratios from 0.157 to 0.80. These data, figure 3, show the same effects when w_o/c is over 0.5, but in pastes where w_o/c is low, the rate of hydration for a short time is higher than in pastes where w_o/c is high. The slightly greater rate of hydration can probably be accounted for by the temperature of the pastes. The temperature of fresh pastes cast in molds and stored in a constant temperature room will rise several degrees above room temperature during the first 24 hr. The smaller the mass of the paste per gram of cement the greater will be this temperature rise, and the greater will be the effect upon the rate of hydration.

The effect of availability of water immediately after hardening is shown graphically in figure 4. The upper curve shows w_n/c for a paste with $w_o/c = 0.6$ cured in contact with water at all times. The lower curve represents two samples of a paste made from the same cement with the same initial w_o/c, but cured under different conditions [71]. The pastes were placed under a bell jar for 48 hr after mixing. After that time, half of the paste was transferred to a sealed jar for the remaining curing time. The other half was wrapped with filter paper and placed in a covered tray in contact with a small amount of water. These two samples continued to hydrate at the same rate even though the total water content per gram of cement w_t/c, of the sample in contact with

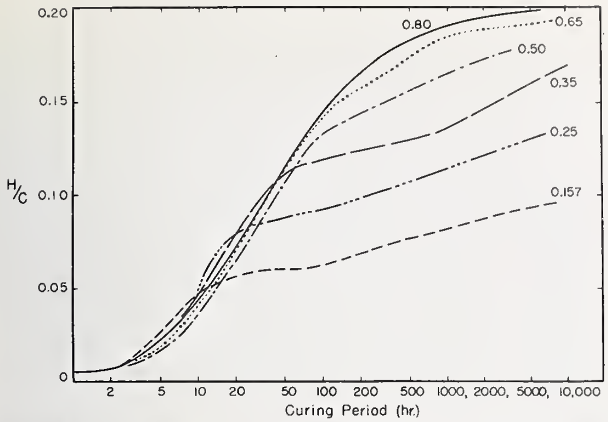

FIGURE 3. *Effect of* w$_o$/c *upon rate of increase of combined water in portland cement pastes.*

water increased to 0.64 at 200 days. The total water content of a sample cured continuously moist to the same nonevaporable water content, $w_n/c=0.20$, should be 0.652 [72]. The nonevaporable water content of 0.20 was attained in less than 28 days in the sample cured continuously moist.

The effect of the lack of an adequate supply of water during the first 2 days upon the rate of hydration was so great that the effect of w_o/c was almost eliminated. Pastes with $w_o/c=0.6$ hydrated only slightly more rapidly than pastes with $w_o/c=0.44$. It is important that the fresh paste has an adequate supply of water continuously if the maximum rate of hydration is to be maintained. Copeland and Bragg observed very little effect due to self-desiccation after the first 2 days, but their curing conditions missed the large effect shown in figure 4.

Specific Surface of Hardened Paste

In their study of the physical properties of hardened portland cement paste, Powers and Brownyard [73] observed that the specific surface of hardened paste was a linear function of the nonevaporable water content. The data were not quite precise enough to show that the line definitely passed through the origin, but if there is an intercept, it must be small. Further data, obtained later, confirmed the linear relationship for pastes made from cement with normal composition. In pastes made from cements with high C_2S contents, V_m did not appear to be exactly proportional to w_n.

Rate of Formation of Calcium Hydroxide

A part of the nonevaporable water of hardened pastes is in the calcium hydroxide. Pressler, Brunauer, Kantro, and Weise [18] determined calcium hydroxide in a number of hardened pastes. One series of pastes was made from a cement low in C_2S; another series was made from a cement high in C_2S. Pastes in each of these series were cured for intervals of time ranging from 1 day to several years. In the series made from the low-C_2S cement, the calcium hydroxide produced in hydration was found to be a linear function of the nonevaporable water content. The relationship between the calcium hydroxide and nonevaporable water formed by hydrating the high-C_2S cement was decidedly curvilinear.

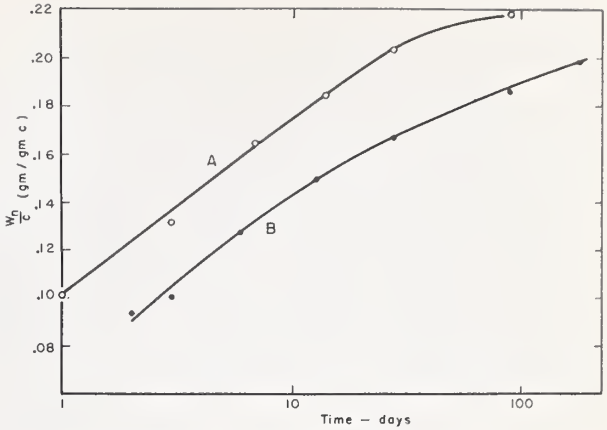

FIGURE 4. *Effect of self-desiccation of portland cement pastes upon rate of hydration of the cement.*

A—cured continuously moist, B—self-desiccated.

Discussion of Rates of Change of Physical Properties

Powers and Brownyard [73] pointed out that if V_m is proportional to w_n, then the ratio of colloidal to noncolloidal products should be the same at all stages of hydration. To simplify the handling of their data, they assumed that V_m/w_n was constant. The linear relationship [51] between the heat of hydration and nonevaporable water, and also V_m, seemed to confirm the idea that the same kinds of hydration products were being formed at all stages of hydration. One of the authors (Copeland) pointed out that these linear relationships would be observed if the components in cement hydrated at the same fractional rates. It was recognized that this assumption could not be true during the initial stages of the reaction, but it might be true after the first 24 hr.

Brunauer [74], after a careful examination of heat of hydration data, observed that the heat of hydration of cements high in C_2S was not a linear function of the nonevaporable water. It was pointed out above that V_m/w_n is probably not constant in pastes made from these same cements, so if the assumption is true at all, it is limited to cements comparatively low in C_2S.

The assumption of equal fractional rates of hydration of the components in cement is different from the assumption made in applying the principle of least squares to heat of hydration data. In the latter case it is assumed that the fractional rate of hydration of each component is independent of the composition of the cement. The results of the least squares calculation show that the fractional rates of hydration are not equal to each other, so one or both of these assumptions is incorrect.

The heat of hydration studies exemplify the difficulty of inferring rates of hydration from the rate of change in physical and chemical properties. Different assumptions have been made and rates calculated from the same data: (a) The interpretation of least squares coefficients as the contribution to the heat of hydration by that component requires that the fraction of a component hydrated in a given interval of time be always the same and independent of the composition of the cements and accordingly the composition of the gel. This assumption seems to require that all cements become completely hydrated in the same period of time—that time required by the component with the lowest fractional rate of hydration. (b) The assumption of a uniform depth of penetration of water in cement grains can also fit the data as has been shown by Steinherz [66] and by zur Strassen [67]. The concept of a uniform depth of penetration is consistent with the assumption that the components hydrate at equal fractional rates. It is not supported in detail by direct microscopic examination, for as pointed out above [60, 61], C_2S and some interstitial material hydrate more slowly than C_3S and C_3A. But it is just this effect of the slower hydrating components covering C_3S and C_3A regions and preventing water from getting to them that could account for equal fractional rates of hydration for all components.

X-Ray Diffraction Analysis

The rates of change in physical and chemical properties of portland cement pastes depend upon the rates of hydration of the components in cement, but the dependence is complex. The rates deduced from observing changes in properties depend upon the assumptions that are made in interpreting the data. The desire to find a method of measuring the rates directly prompted us to make our first attempts at X-ray analysis.

The first published attempt to use X-ray analysis to estimate rates of hydration directly is that of H. F. W. Taylor [10]. He prepared pastes of portland cement and hydrated them for periods of time up to 300 days. An attempt to separate the hydration products from the unhydrated cement with a dense liquid was not completely successful. Nevertheless, he examined Debye-Scherrer patterns of the fractions and concluded that C_3S hydrates much more rapidly in cement pastes than does C_2S, as is shown by his estimates of the weight fraction of C_3S in the silicates in table 7. He estimated that after 14 days curing, at least 50 percent of the cement had hydrated. The ignition loss indicated 61 percent hydration.

Table 7. *Weight fraction of C_3S in silicates of the unhydrated residue of cement in pastes*

Days	0	1	4	7	14	44	300
$\frac{C_3S}{C_3S+\beta\text{-}C_2S}$	60	50	30	25	20	<10	<5

At the same time attempts were being made in this laboratory to use X-rays to analyze portland cement pastes; but only recently has acceptable precision in cement analysis been attained [21]. The method has been applied [75] to the analysis of two series of pastes made from different cements, the first, a cement of average composition, 15754, the second a cement low in C_2S and C_3A, 15669.

The same method of analysis was used for analyzing these pastes as is used for analyzing cements with one exception: the 511 line for silicon (the internal standard) was used instead of the 111 line used in analyzing the cements. The advantage of using this line at smaller spacing in pastes is twofold: (1) there are no interfering lines from either the cement or the hydration products for this line, whereas the 111 line is affected to some extent by the broad 3.06 A line from the tobermorite and the adjacent 100 line from $Ca(OH)_2$; (2) after the pastes have hydrated a few days, the weaker 511 line matches better the strengths of the lines from the cement components. The intensity of this line relative to the 111 line of silicon is given as 0.17 by Swanson and Fuyat [25] and found by us to be 0.171 ± 0.002 for our sample of silicon.

The cement pastes were prepared with $w_o/c=$ 0.4 and cured for intervals of time ranging from 2 hr to 6 months. The analyses of the four major phases unhydrated in each paste is given in table 8. The values reported are referred to the original weight of cement in the paste. Nonevaporable water contents are also given.

The degree of hydration of each component in the two series of pastes are compared in figure 5. Time is plotted on a log scale for convenience. Equal fractional rates of hydration for the components of a cement will be shown by coincidence of these curves. A cursory examination of the figures shows that the components of cement do not hydrate at the same fractional rate in either cement.

The degree of hydration of alite is plotted in figure 5(a). The alite in the normal portland cement does not hydrate at the same fractional rate as that in cement 15669, although probably this condition is realized within experimental error after about 28 days.

The degree of hydration of alite in cement 15669 increases more rapidly than in cement 15754, but the actual rate of hydration of alite in cement 15754 is more rapid than in cement 15669, as is shown in figure 6(a).

The results for belite are plotted in figures 5(b) and 6(b). The degree of hydration of belite at any time in cement 15754 is greater than in cement 15669, but again the actual rate of hydration is higher in the cement containing the more belite. The relatively large error in determining the amount of belite in the pastes made from cement 15669 makes the conclusion that the fractional rates are not equal somewhat less certain than for the case of alite.

Table 8. *Composition of unhydrated residue in portland cement pastes (g component/g cement)*

	Type I cement					Type IV cement				
Time hydrated	Alite	Belite	C_3A	F_{ss}	$\left(\frac{W_n}{c}\right)_{\frac{1}{2}}$	Alite	Belite	C_3A	F_{ss}	$\left(\frac{W_n}{c}\right)_{\frac{1}{2}}$
0	.531	.259	.069	.097	----------	.262	.627	.010	.058	----------
2 hr	.538	.248	.054	.064	.0108	.253	.605	.009	.068	.0000
6 hr	.416	.242	.060	.082	.0258	.194	.553	.007	.084	.0118
1 day	.308	.226	.025	.082	.0881	.105	.618	.003	.060	.0426
2 days	.222	.196	.021	.053	.1145	.063	.515	.004	.051	.0570
3 days	.179	.198	.016	.052	.1204	.052	.600	.005	.051	.0619
4 days	.150	.170	.012	.044	.1276	.054	.536	.007	.053	.0674
7 days	.119	.152	.013	.038	.1438	.041	.477	.009	.052	.0763
14 days	.079	.118	.008	.024	.1614	.031	.518	.001	.056	.0818
28 days	.059	.136	.001	.021	.1748	.025	.282	.000	.036	.1048
3 months	.023	.034	.001	.010	.1890	.006	.220	.000	.024	.1305
6 months	.008	.020	.000	.010	.1947	.004	.185	.000	.004	.1394

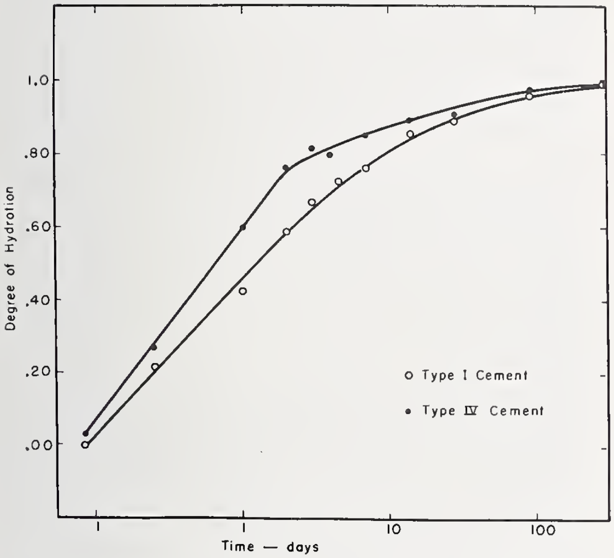

Figure 5a. *Degree of hydration of alite in the two series of pastes.*

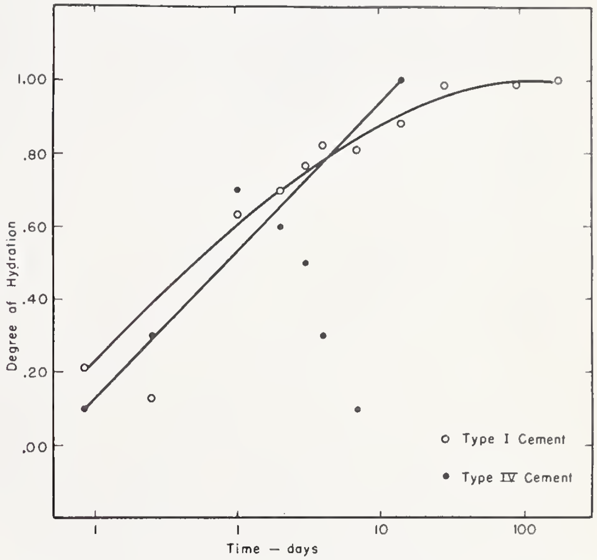

Figure 5c. *Degree of hydration of tricalcium aluminate in the two series of pastes.*

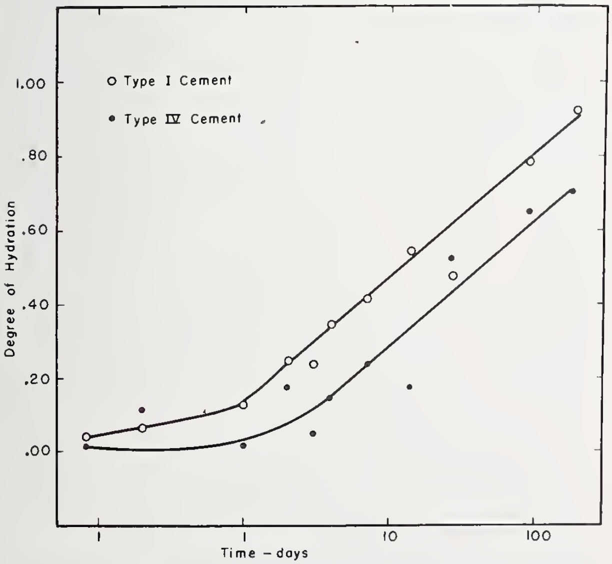

Figure 5b. *Degree of hydration of belite in the two series of pastes.*

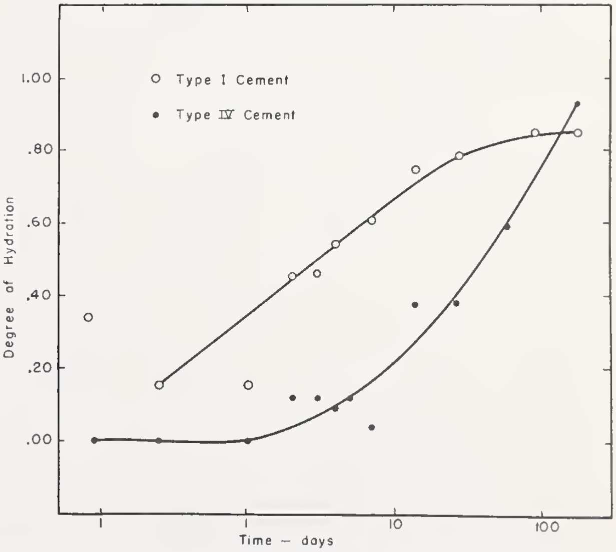

Figure 5d. *Degree of hydration of ferrite solid solution phase in the two series of pastes.*

The degrees of hydration of C_3A in the two cements are the same within experimental error, figure 5(c). There is only 1 percent C_3A in cement 15669, and this small quantity is difficult to determine precisely. The C_3A results for cement 15754 present a consistent trend, and most of the C_3A results on cement 15669 agree with the same trend. The screening of C_3A from water may be responsible for the fact that its absolute rate of hydration, figure 6(c), is so much lower than the rate of hydration of C_3S.

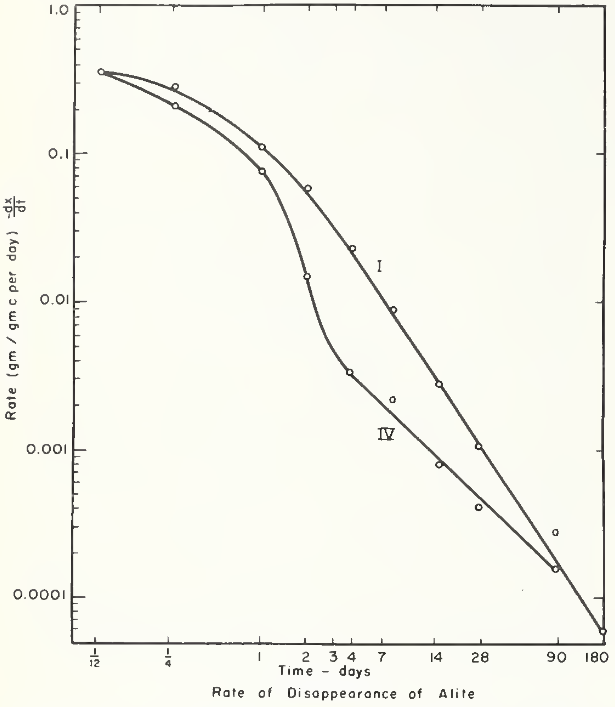

FIGURE 6a. *Rates of hydration of alite in Type I and IV cements.*

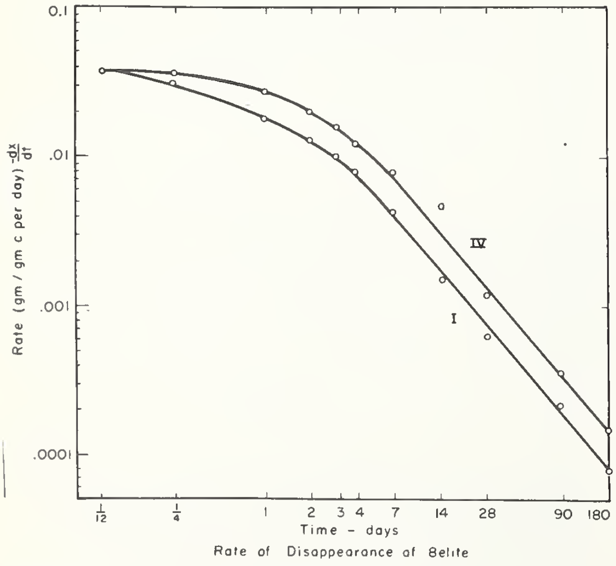

FIGURE 6b. *Rates of hydration of belite in Type I and IV cements.*

The greatest difference in the fractional rate of hydration of a component in these two cements is shown by the ferrite solid solution phases, figure 5(d). Perhaps a difference in the composition of the phase is partially responsible, although there is, as yet, no way of knowing how the composition of the ferrite phase affects its rate of hydration in cement. The A/F ratio of the F_{ss} phase in cement 15754 is 1.44. That in cement 15669 is 1.22. It was observed that the strongest ferrite line did not shift in position as hydration progressed; consequently, the composition of the unhydrated residue is the same as that of the original component. The absolute rate of hydration of the ferrite solid solution phase, as well as its fractional rate, is lower than that of any other component.

The X-ray analyses are certainly not as precise as one would like, and probably not as precise as will be obtained in subsequent studies. They are precise enough to show without question that the major phases in portland cement do not hydrate at equal fractional rates; but in the discussion to follow it will be seen that the observed rates of hydration are consistent with the empirical relations that formed the basis for the assumption of equal fractional rates of hydration for all the components.

One of these empirical relations was the proportionality between V_m and w_n, and another the proportionality between the heat of hydration and w_n. Powers and Brownyard [73] recognized that V_m might not be strictly proportional to w_n, but assumed proportionality to simplify the treatment of their data. The best straight line through the data does not pass through the origin, but has a small positive intercept on the w_n axis. This

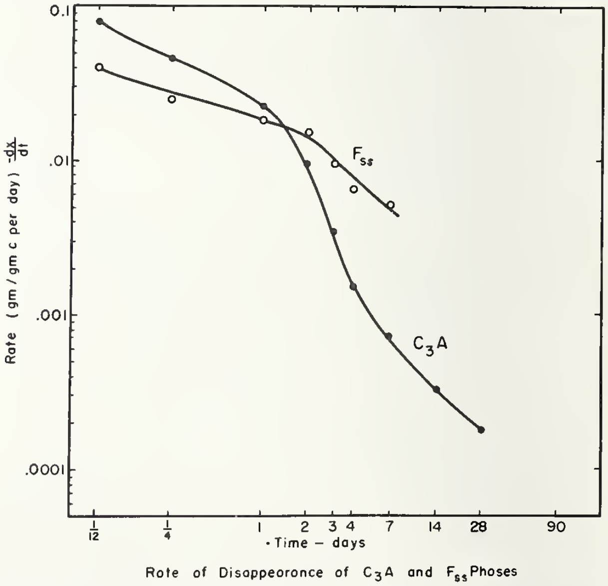

FIGURE 6c. *Rates of hydration of tricalcium aluminate and calcium aluminoferrite solid solution in Type I cement.*

relationship is discussed in detail in another paper in this symposium.

Calculations were made to compare the X-ray results with the data of Verbeck and Foster [51]. To do this, the least squares coefficients for the heat of hydration of cement at 6½ years were used with amounts of each component that had hydrated in each paste as determined from the X-ray analysis. Similarly, the nonevaporable water and the amount of water adsorbed at 36 percent relative humidity in pastes dried over $Mg(ClO_4)_2{\cdot}2H_2O$ were calculated from the respective least squares coefficients for fully hydrated pastes and the X-ray analyses. The data are plotted in figure 7. The two lines are the lines drawn by Verbeck and Foster in their figures 6–7. The calculated heats of hydration agree very well with the heat of hydration line for Type I cement. The calculated adsorptions are slightly below the line drawn by Verbeck and Foster, but well within the range for Type I and Type III cements as determined by them.

There is no equation relating V_m of a paste to the composition of the cement used in making the paste. Instead of calculating V_m, the water adsorbed at 36 percent relative humidity was calculated and is plotted as a function of the nonevaporable water for pastes dried at the vapor pressure of water at −78 °C in figure 8. The data fall on a line with a slight curvature, but if the observed values of w_n had been used, the scatter would have been great enough to obliterate the curvature. A straight line through the origin gives a pretty good fit to the points. The slope of the straight line has the value 0.42. This is a reasonable value since for this cement $V_m/w_n = 0.31$. The best straight line through the data would not pass through the origin, but would give a small positive intercept on the w_n/c axis, as is observed experimentally.

The rates of hydration give satisfactory agreement with the empirical relationships between properties of hardened pastes. Since the major phases hydrate at fractional rates different from each other, one may question the significance of the expression "degree of hydration" as applied to cement and the meaning of terms such as "maturity factor" for pastes, mortars, or concrete. These concepts are important practically, even though they may not be precisely defined theoretically.

The ratio of the heat of hydration of a cement paste to the heat of hydration of a fully hydrated paste from that cement has been used as a measure of the "degree of hydration" of the cement in the paste. The ratio of the nonevaporable water to the maximum nonevaporable water has been used for the same purpose in our laboratories.

The "degree of hydration" of the cement in each of the pastes used in this investigation was calculated by adding together the amounts that had hydrated of the four major phases and dividing by the original cement content of the paste. In figure 9, the values are plotted as a function of the ratio of the observed w_n/c divided by the maximum w_n/c for the cement. The function is not quite linear, but the ratios give a fairly

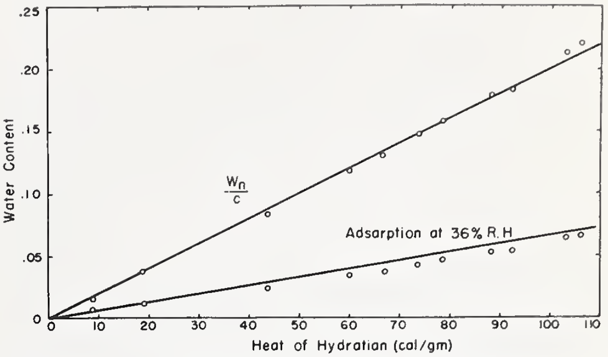

FIGURE 7. *Relationship between heat of hydration, nonevaporable water, and water sorption at 36 percent relative humidity.*

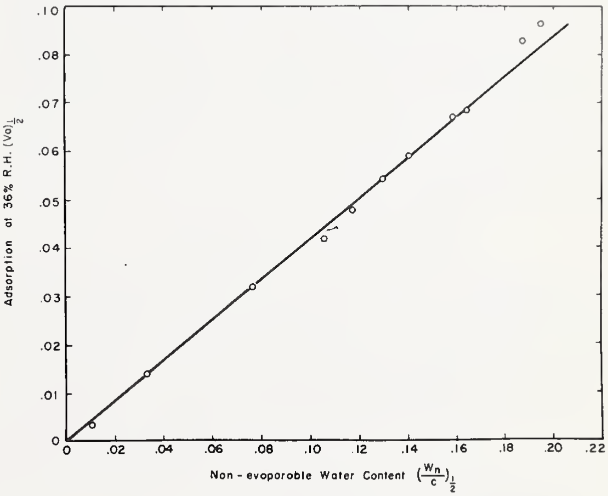

FIGURE 8. *Relationship between* $\left(\frac{W_n}{c}\right)_{1/2}$ *and water sorption at 36 percent relative humidity.*

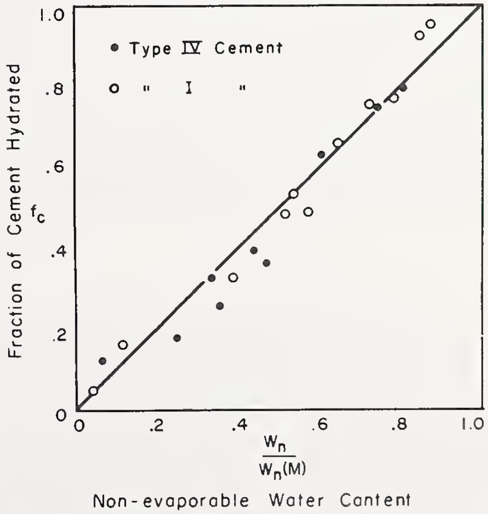

FIGURE 9. *Relationship between the degree of hydration of cement and* $\left(\frac{W_n}{c}\right)_{1/2}$ *in hardened pastes.*

reliable estimate of the degree of hydration, particularly when the cement is over 50 percent hydrated.

Because of near linearity between w_n and the heat of hydration, and also w_n and the surface area, any of these may be used as estimates of the degree of hydration of cement.

Analysis of pastes with X-ray diffraction promises to be a most useful tool for investigating rates of hydration of the individual constituents of cement. The preliminary work shows that the fractional rates of hydration of the four major compounds are not equal to each other. Further, the fractional rate of hydration of any chosen component, except possibly C_3A, is not the same, for all cements, but does depend upon the composition of the cement. The reliability of the X-ray analysis has been shown by calculating the heat of hydration, nonevaporable water, and the amount of water adsorbed at 36 percent relative humidity. The relationships between these calculated quantities were the same as has been observed from measurements of these properties on hardened pastes. Although these relationships are probably not exactly linear, they are sufficiently close to being linear that any of them may be used to estimate the "degree of hydration" of the cement in a paste.

Effect of Temperature

The study of the effect of temperature upon the rate of hydration of cement has been limited, for the most part, to the study of the effect of temperature upon either the heat of hydration or the development of strength in concrete. As a result of these studies, several functions have been proposed with which one may estimate the maturity of concrete after curing under prescribed conditions of time and temperature.

Saul [76] defined the maturity of concrete "as its age multiplied by the average temperature above freezing it has maintained," and concluded that concretes of the same mix will have approximately the same strength at the same maturity, whatever combination of time and temperature produce that maturity. Bergstrom [77] concluded that the base temperature should be −10 °C instead of the freezing point. Thus the maturity should be calculated from the temperature, θ, and the time, t, by the equation

$$M=\int_0^t (\theta+10)dt \qquad (12)$$

Plowman [78] found that concrete hydrated slowly at −10 °C, but that hydration ceased at −11.7 °C, and recommended this latter temperature as the base temperature.

Rastrup [79, 80, 81] examined heat of hydration data and assumed that the hydration of cement proceeded very much as most chemical reactions proceed. He concluded that the heat of hydration of a variable temperature process could be compared with the heat of hydration determined at a predetermined constant temperature, θ_a, by use of the time-temperature function

$$\tau_a=\int_0^t 2^{\left(\frac{\theta-\theta_a}{10}\right)}dt \qquad (13)$$

The Saul-Bergstrom function corresponding to Rastrup's use of a time-temperature function is

$$\tau_a=\int_0^t \left(\frac{\theta+10}{\theta_a+10}\right)dt \qquad (14)$$

Nykänen [82, 83] performed an extensive series of tests to determine a time-temperature function. He observed that a sharp decrease in the rate of hydration of concrete occurred as the temperature dropped below 0 °C, and that the composition of the cement affected the time-temperature function. He modified Bergstrom's function to

$$M=\Sigma k(\theta-\theta_b)\Delta t \qquad (15)$$

where θ_b is the base temperature at which hydration ceases, and k is a factor the value of which depends upon the temperature of the concrete and the composition of the cement.

For temperatures above 0 °C, $k=1$; for temperatures below 0 °C, $k=0.2$ to 0.4, depending upon the composition of the cement. The base temperature, θ_b, ranged between −10 and −15 °C, depending upon the composition of the cement.

These time-temperature functions serve for approximate calculations and are probably good enough for practical purposes. McIntosh [84] points out some of the shortcomings of these functions; when they are applied to concrete cured continuously at low temperatures, an estimate based on maturity calculated from −10 °C leads to an overestimate at low maturities and an underestimate at high maturities. The error at low maturities can be partly alleviated by calculating maturity from the time the concrete starts to gain strength instead of from the time of mixing. But the time-temperature functions cannot account for the fact that concrete cured initially at low temperature and later at normal temperature can develop a higher compressive strength than concrete cured continuously at a normal temperature. Bernhardt [85] shows that the maximum strength developed in a concrete is not independent of its temperature during curing.

Danielsson [86] points out that if a time-temperature function exists, the composition and morphology of the hydration products of cement must be independent of the temperature at which they were formed, but depend only upon the state of hydration or, what amounts to the same thing, upon the value of the heat of hydration, H. The value of dH/dt would depend upon θ and H alone, and would not depend upon the temperature-time path by which H was reached. Also, values of dH/dt for two different temperatures would have a fixed ratio for the same H. He found, experimentally, that at low H this last condition was approximately true, but that at high H the condition did not hold. Consequently, a time-temperature function should not be more than an approximation. He also found that dH/dt was not independent of the time-temperature path by which H was reached. This indicates that the composition and properties of the hydration products depend upon the temperature of the hydration process as do the findings of McIntosh and Bernhardt mentioned above.

III. Energetics of the Hydration of Portland Cement

George Verbeck

Introduction

Numerous studies have been made of the heat evolved when cement reacts with water and various methods of measurement of heat liberation have been used, depending upon the purpose of each investigation.

Where the primary interest is in temperature rise of concrete for use in massive structures, large adiabatic calorimeters have been used, thereby obtaining directly the information desired without assumptions as to the heat capacity of the paste and aggregate components of the concrete or the effect of temperature history of the concrete on the heat actually evolved. However, most studies of the energetics of cement hydration have involved measurements directly on cement paste.

For the study of the early stages of hydration, conduction calorimeters can be used most advantageously. Such devices permit the continuous and accurate recording of the rate of heat liberation from an age of about ½ hr to perhaps 3 days of hydration; this technique is usually supplemented by a simple "bottle" calorimeter for measurements prior to ½ hr. The magnitude, number, and times of appearance of the heat liberation "peaks" that are observed during this early period assist in the understanding of the various chemical reactions taking place and of the influence of various factors, such as hydration temperature, gypsum content, and accelerators and retarders on the properties of pastes and concrete at both early and later ages.

After the first few days of hydration, the rate of heat liberation becomes very low and direct measurement of heat evolution is difficult. The heat of solution method developed by Woods, Steinour, and Starke [63] is most useful for heat of hydration measurements for hydration periods from about 3 days to any desired age.

It is not the present purpose of this paper to consider studies of the heat evolution during the initial reactions. The discussion to follow will concern the various aspects of cement hydration as revealed by the heat of solution technique for hydration periods from 3 days to 13 yr.

Heat of Hydration at Ages of 3 Days to 13 Years

The data previously published by Verbeck and Foster [51] have been substantially augmented in a continuing study of the heat of hydration characteristics of cements. Data are now available for the heat of hydration characteristics of 27 plant-produced portland cements corresponding to ASTM Types I, II, III, IV, and V cements for hydration periods up to 13 yrs and at 0.40 0.60, and 0.80 water-cement ratios by weight. For the immediate purpose only the average results obtained for each of the different ASTM types of portland cement will be considered.

Data on the average heats of hydration of the different types of cement for ages from 3 days to 13 yr are presented in table 9 and figure 10. The cement pastes used in these tests were prepared at an initial water-cement ratio of 0.40 by weight and were hydrated in sealed vials until tested. In general, only small increments of heat were evolved between the 6½ and 13 year test ages. For the Type III cements very little, if any, heat was evolved during this period, the −0.1 cal/g observed being well within expected experimental error.

Table 9. *Average heats of hydration of the different ASTM types of cements*

0.40 water-cement ratio; cured at 21° C.

ASTM cement type	No. of cements averaged	Heat of hydration at age indicated, cal/g						
		3 days	7 days	28 days	3 mo.	1 yr	6½ yr	13 yr
I	8	60.9	79.2	95.6	103.8	108.6	116.8	118.2
II	5	46.9	60.9	79.6	88.1	95.4	98.4	100.7
III	3	75.9	90.6	101.6	106.8	114.2	120.6	120.5
IV	4	40.9	50.1	65.6	74.4	80.6	85.3	87.3

It should be noted that the average heat of hydration characteristics of the different ASTM types of cement are in keeping with the purposes for which each was designed. At early ages, the average heat of hydration of the Type III cements (high early strength) were significantly greater than the Type I cements (normal) although at 13 yr the heats of hydration are comparable. At all ages through 13 yr, the average heat of hydration of the Type IV cements (low heat) is significantly below the average of the Type II cements (moderate heat) which in turn evolves less heat at all ages than the Type I (normal) cements.

It should be emphasized that the particular plant-produced cements in this study were specifically selected to include cements possessing a wide range of characteristics within each ASTM type classification. The individual cements within each of the different ASTM types therefore show differences in heat evolution characteristics. The data shown in figure 11 represent the maximum, minimum, and average heats of hydration of the different ASTM types of cement at the various ages. These results show that each cement type has a reasonably separate and distinct range in heat of hydration at the various ages and that, in general, only moderate overlapping occurs between the various types The greatest range among the cements of any type occurs among the Type I cements, presumably in part because of the greater number of cements included in this classification and in part because the specifications for Type I cement (normal or general purpose portland cement) are purposefully less restrictive than for the other types of cements designed for more specific purposes.

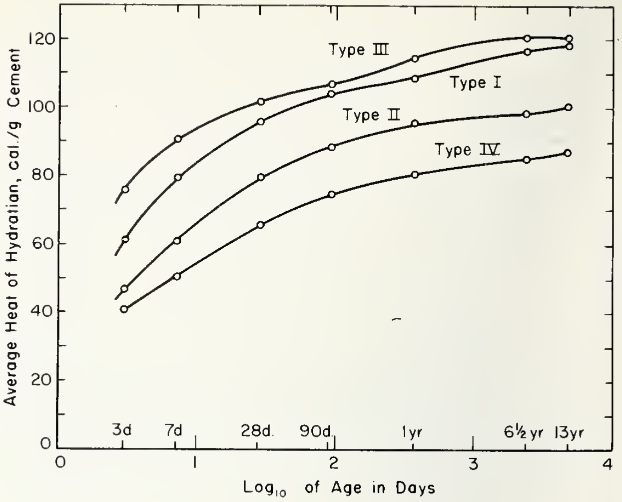

FIGURE 10. *Average heats of hydration of different ASTM types of cement at various ages.*

(0.40 water-cement ratio; cured at 21 °C.)

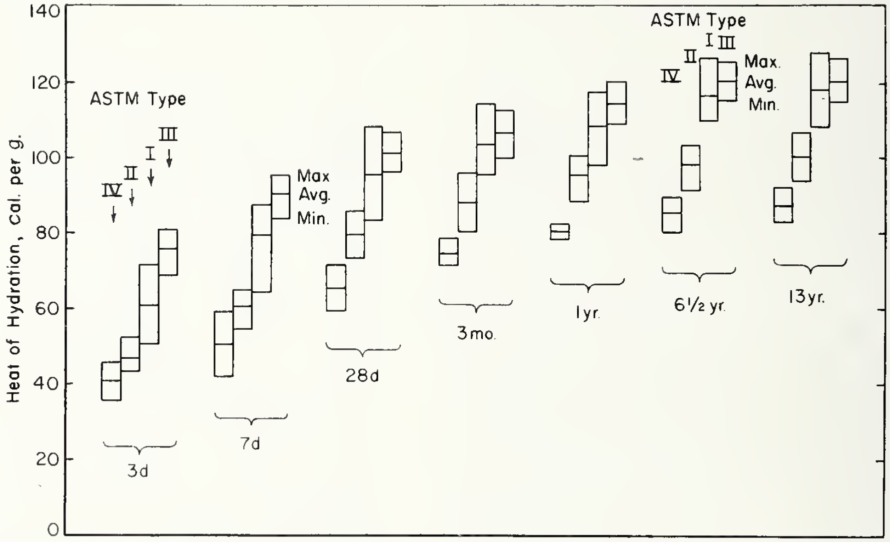

FIGURE 11. *Comparison of ranges in heats of hydration of the different ASTM types of cement.*

(0.40 water-cement ratio; cured at 21 °C.)

Effect of Water-Cement Ratio

The hydration of cement is accompanied by an increase in the volume of solids within the hydrating paste, the volume of the hydration product being greater than the volume of cement from which it was produced. The hydration product steadily increases in volume and fills the capillary void space within the paste, the initial volume of which is established by the original water-cement ratio of the paste. If the capillary void space originally present is small (low water-cement ratio) this space can become completely filled with hydration products and hydration will cease even though a substantial fraction of the cement remains unhydrated.

Some published information on the influence of water-cement ratio on heat evolution is available in the data of Carlson and Forbrich [87]. These data were limited to a single cement for ages ranging from 3 days to only 28 days. Their data indicate that the original water-cement ratio has a great influence on the heat of hydration of the cement as shown in table 10. An increase in water-cement ratio from 0.30 to 0.50 increased the heat of hydration by 14 percent at 3 days and 23 percent at 28 days.

The effect of water-cement ratio on heat of hydration might be expected to vary among cements having different hydration characteristics and compositions and in addition to become most pronounced at the later ages when the hydration of cement is more nearly complete. Because of the reported magnitude of the influence of water-cement ratio on heat of hydration and the practical and theoretical significance of such effects, the heat of hydration studies at 0.40 water-cement ratio presented in table 9 were extended to include measurements of pastes having water-cement ratios of 0.60 and 0.80 by weight.

In order to prepare hardened paste specimens having these high water-cement ratios it was necessary to prevent the segregation (bleeding) of water from the pastes while still plastic by slowly rotating the sealed vials containing the paste until setting occurred. To determine whether rotation of the fresh paste altered hydration of the cement as suggested by Carlson and Forbrich, redeterminations were made of the heat evolutions of five different cements at 0.40 water-cement ratio using this rotation technique for comparison with the previously obtained "static" results.

Such comparisons have since been made for hydration periods from 3 days to 6½ yr. The initially rotated vials were hydrated at 23 °C as compared to 21 °C for the earlier static vial tests. The average difference between results obtained by these two methods was ±2.8 cal/g when comparing each cement at each age and averaged −0.2 cal/g for all cements at all test ages. This is considered to be a satisfactory agreement. The rotated vial tests were initiated several years after the static vial tests. Because of this lapse of time, the five cements were resampled and their heats of solution and ignition losses redetermined when the rotated vial tests were begun. The average deviations of the heats of solution and ignition losses of the cements were ±2.1 cal/g and ±0.06 percent respectively. Thus it may be concluded that rotation of the specimen vials and hydration at the slightly elevated temperature did not significantly affect the heat evolutions of the cements. The differences that were observed in heats of hydration can be considered to be due to experimental errors and to differences in the heats of solution of the unhydrated cements caused by differences in the ignition losses of the two samples of each cement used.

Table 10. *Effect of water-cement ratio on heat of hydration*

Carlson and Forbrich [87]

Water-cement ratio, wt.	Heat of hydration at age indicated cal/g		
	3 days	7 days	28 days
0.30	45.7	58.3	74.3
.40	49.2	61.8	82.9
.50	52.3	69.8	91.4

Comparisons will now be made of the effect of water-cement ratio on the heat of hydration of cements representing different ASTM types at ages up to 6½ yr. Such data are shown in table 11.

It is readily apparent from the data that heat evolution is significantly influenced by water-cement ratio. During the early stages of hydration, an increase in water-cement ratio from 0.4 to 0.8 had only a slight effect on hydration and heat liberation of the Type IV cements, but produced a significant effect, an increase of 14 percent, in the heat of hydration of the Type III cements at 3 days. The greatest differences in heat of hydration occur at intermediate hydration ages, the exact age for the maximum difference depending upon the type of cement and occurring at earlier ages for the more rapidly hydrating cements. The increase in heat of hydration resulting from an increase in water-cement ratio from 0.4 to 0.8 was a maximum of 19.5 cal/g for the Type III cements at 90 days, and was a maximum of 14.2 cal/g for the Type IV cements at 1 yr, a very substantial effect which should be considered when evaluating cements for mass concrete. These increases in heat evolution exceeded the heat yet to be evolved from those ages to the 13-yr test age for the 0.4 water-cement ratio pastes.

Table 11. *Effect of water-cement ratio on average heats of hydration of different ASTM types of cements cured at 21 °C*

ASTM cement type	No. of cements averaged	Water-cement ratio	Heat of hydration at age indicated, cal/g						
			3 days	7 days	28 days	90 days	1 yr.	6½ yr.	13 yr.
I	8	0.40	60.9	79.2	95.6	103.8	108.6	116.8	118.2
		.60	65.8	87.7	107.1	114.7	120.0	123.1	----
		.80	66.3	89.4	111.6	119.5	122.2	125.0	----
II	5	.40	46.9	60.9	79.6	88.1	95.4	98.4	100.7
		.60	49.6	61.3	83.5	94.8	102.1	104.6	----
		.80	49.3	64.3	84.7	99.2	106.8	106.1	----
III	3	.40	75.9	90.6	101.6	106.8	114.2	120.6	120.5
		.60	86.1	103.6	119.9	124.4	127.3	127.2	----
		.80	86.7	105.0	121.0	126.3	130.0	130.6	----
IV	4	.40	40.9	50.1	65.6	74.4	80.6	85.3	87.3
		.60	43.2	53.5	66.6	78.7	90.4	92.5	----
		.80	41.7	52.8	69.8	82.5	94.8	96.4	----
All	20	.40	55.65	70.52	86.50	94.44	100.54	106.47	107.99
		.60	60.28	76.64	95.02	103.98	110.70	112.97	----
		.80	60.19	78.14	97.92	108.20	114.04	115.40	----

Although at the 6½-yr test age the average heat of hydration of all cements at 0.8 water-cement ratio was 8 percent greater than at 0.4 water-cement ratio, it should be noted that the rate at which heat was evolved at the later ages was greatest for the low water-cement ratio pastes; between the 1- and 6½-yr test ages, the 0.4 water-cement ratio pastes on the average liberated 5.9 cal/g while the 0.8 water-cement ratio pastes liberated only 1.4 cal/g. These differences indicate that the major effect of water-cement ratio in the range of 0.4 to 0.8, is not primarily to limit the maximum degree of hydration and hence heat liberation, but rather to influence the rate of hydration.

Interesting comparisons of the effect of the different water-cement ratios on the corresponding rates of hydration can be made if it is assumed: (1) that the heat of hydration observed at 6½ yr for the 0.8 water-cement ratio paste represents complete hydration of the cement, a very reasonable assumption and, (2) that the rate or degree of hydration of the 0.8 water-cement ratio pastes at the various ages represents hydration of cement as unimpeded by surrounding reaction products as can be expected at rational water-cement ratios. With these assumptions, at each of the test ages and water-cement ratios, the amount of unhydrated cement present can be estimated from the difference between the heat of complete hydration and the heat of hydration at each test age. The fraction of this unhydrated cement which was actually hydrated during the subsequent test interval can be calculated from the increment of heat evolved during the subsequent test interval. Such fractions when compared to the fraction of hydration for the 0.8 water-cement ratio paste for the corresponding age increment yield the relative rate of hydration during the various test age intervals of the 0.4 and 0.6 water-cement ratio pastes compared to the assumed ideal at 0.8 water-cement ratio.

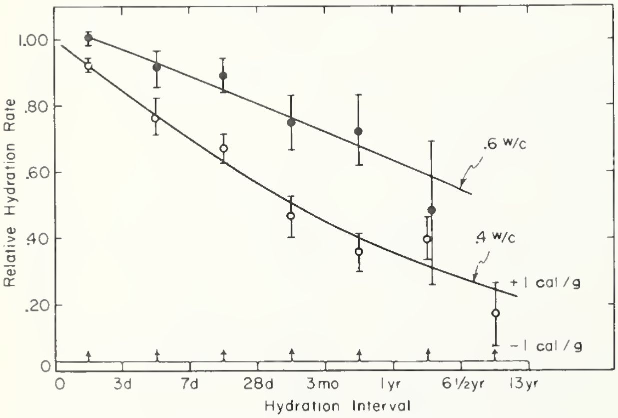

FIGURE 12. *Average effect of water-cement ratio on rate of hydration at various ages.*

Such comparisons for the average of all 20 cements are made in figure 12 for the various test periods. For presentation an arbitrary time scale has been used and the essentially linear nature of the relationships that appears with the use of this scale is not significant. The influence of a calorimetric error of ±1.0 cal/g in heat of hydration on the comparisons at the various ages is shown and emphasizes the sensitivity of the calculated relative hydration rate, particularly at the later ages.

It is apparent that the water-cement ratio significantly affects the inherent rate of hydration of the cements. The 0.6 water-cement ratio pastes hydrated more slowly than the 0.8 water-cement ratio pastes and this retardation became more pronounced at the later test ages. During the 1- to 6½-yr test interval to 0.6 water-cement ratio pastes hydrated only 50 to 60 percent as fast as the 0.8 water-cement ratio pastes. The 0.4 water-cement ratio pastes were retarded at all ages to an even greater extent and during the 6½- to 13-yr test interval, hydrated only about 25 percent of the remaining unhydrated cement, whereas in the 0.8 water-cement ratio pastes any unhydrated cement would have been completely hydrated.

The influence of water-cement ratio on rate of hydration appears readily interpretable. The hydration of cement requires the diffusion of water through the hydration products to the surface of the unhydrated cement and the diffusion of reacted material away from the reaction site. The hydration product which is laid down in the liquid surrounding the unhydrated cement serves to retard the diffusion of these materials and hence retard the hydration of the cement. At a particular water-cement ratio the ratardation of hydration should increase as hydration proceeds due to the increasing amounts (concentrations) of hydration product present. Such effects can be seen in figure 12. As the original water-cement ratio of the paste is reduced, the concentration of hydration product is increased; this increased concentration further retards the hydration of the cement.

The effects of progressive hydration and of water-cement ratio can be combined to express this concept of retardation due to increasing concentrations of hydration product in a manner similar to the "gel-space" ratio used by Powers [88]. The relative rates of hydration of cement at 0.4 and 0.6 water-cement ratio previously shown in figure 12 at the various test intervals are compared in figure 13 with their corresponding average gel-space ratios. It can be seen that this concept approximately expresses the retarding effects observed. A second approximation to the relationship could be made by a correction for the moderate retardation that must have occurred at the later stages of hydration of the 0.8 water-cement ratio pastes for which a maximum gel-space ratio of 0.59 is calculated.

It should be kept in mind that although the gel-space ratio may approximately express the concentration of hydration gel for any particular cement or average of cements, it would not be expected to quantitatively express the gel concentrations when comparing different cements since the amount of gel produced per unit of heat evolved depends to some degree on the composition of the cement. Additional empirical correlations between the relative hydration rates and other fundamental parameters of the hydrated paste can also be obtained.

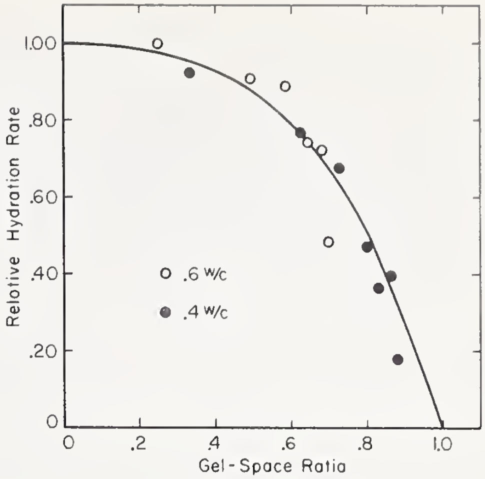

Figure 13. *Average effect of gel-space ratio on rate of hydration of pastes of different water-cement ratios and ages from 3 days to 13 yr.*

Effect of Temperature

The information available on the influence of temperature on degree and rate of hydration is not as extensive as desired, particularly as regards the higher water-cement ratios for extended hydration periods. However, the available data very satisfactorily reveal the effect of a wide range of temperatures on hydration rate of pastes of 0.4 water-cement ratio.

Heat of hydration data obtained by Carlson and Forbrich [87] using a "standard" cement at 0.4 water-cement ratio cured at temperatures of 4.4, 23.3, and 40 °C for ages from 3 to 90 days are shown in figure 14. The large increase in heat evolution during the early stages of hydration produced by increase in temperature is evident. It would appear from these data, for pastes of 0.4 water-cement ratio, that the temperature affects only the rate of hydration, the results obtained at the 28 and 90 day test periods suggesting equal ultimate heats of hydration at some later age.

It is interesting to quantitatively compare the early rates of hydration at the different temperatures; these rates may be taken as relative to the heat of hydration at one day and estimated from the curves in figure 14. For most chemical reactions the dependence of the kinetic reaction rate, K, upon reaction temperature $T°_K$, is expressed by the Arrhenius equation, $\ln K = -\frac{E}{RT} + \text{const.}$, in which E represents the "activation energy" and R is the gas constant. As may be noted in figure 14, the observed relationship between log K and $1/T$ is essentially linear and hence the relative reaction rates observed at the different temperatures are related in the manner required by the Arrhenius equation.

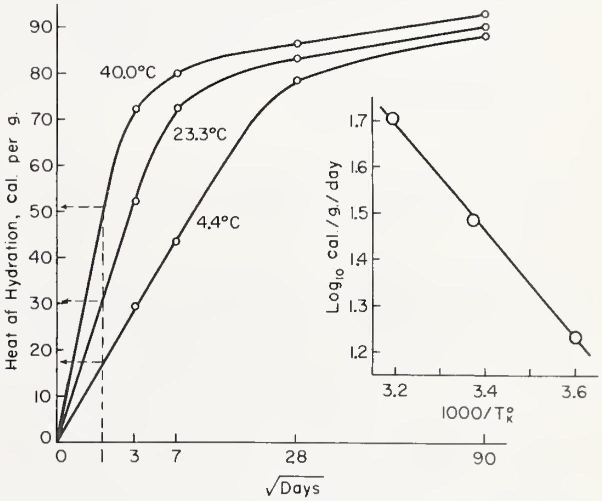

Figure 14. *Effect of temperature on hydration of cement*

Data from Carlson and Forbrich [87].

Additional information of a somewhat different nature is available from the studies in this laboratory [52] over the temperature range of 4.4 to 110 °C. Two different cements, ASTM Type I and Type IV, were hydrated at the preselected temperatures for the lengths of time required to produce approximately the same degree of hydration in the pastes of each cement, as estimated from heat of hydration and nonevaporable water measurements. The relative rates of hydration at the different temperatures are inversely related to the time required at each temperature to reach the equivalent degree of hydration. Such data are shown in table 12. Although the degrees of hydration attained for the various tests of each cement are not identical, they are believed to be sufficiently alike to permit the direct calculation of rate of hydration as shown in the table. Evaluation of these results on the basis of the Arrhenius equation is shown in figure 15. It may be observed that an acceptably linear relationship is obtained for each cement over this wide temperature range. The relationship for the Carlson and Forbrich data shown in figure 14 is reproduced in figure 15. It is important to note that all three of the linear relationships obtained are essentially parallel, indicating that these cements do have the same "activation energy" although they have a very wide range in calculated potential compositions and inherent rates of heat liberation.

TABLE 12. *Effect of temperature, on rate of hydration, of cement.*

0.40 water-cement ratio.

ASTM cement type	Hydration temp. °C	Hydration period, days	Heat of hydration cal/g	Hydration rate cal/g/day	Log_{10} hydration rate	$\frac{1}{T^{\circ}_{K}}$
I	110.0	1	92.35	92.35	1.965	0.00261
	71.0	2	98.02	49.01	1.690	.00290
	43.4	3	93.05	31.02	1.492	.00316
	21.0	9	96.43	10.71	1.030	.00340
	4.4	11	83.22	7.57	0.879	.00360
IV	110.0	1	56.51	56.51	1.752	0.00261
	71.0	2	56.49	28.24	1.451	.00290
	43.4	3	49.44	16.46	1.216	.00316
	21.0	8	47.48	5.93	0.773	.00340
	4.4	11	41.89	3.81	0.581	.00360

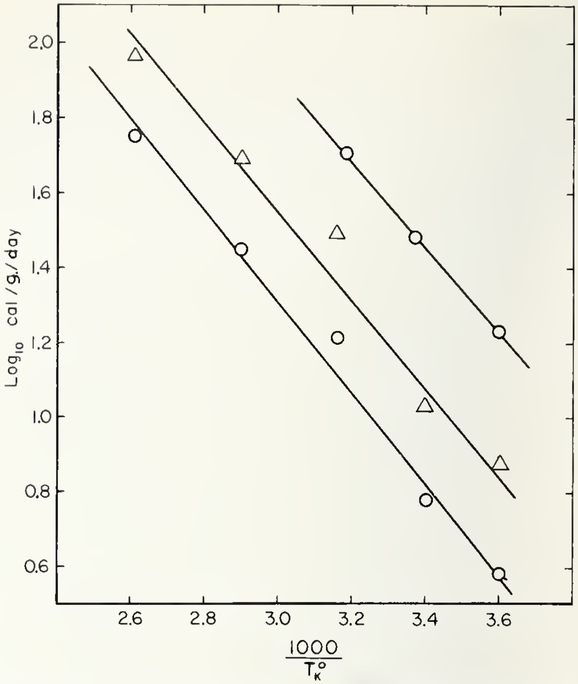

FIGURE 15. *Relationship of log "reaction rate" and* $1/T^{\circ}_{K}$ *for cements over temperature range from 4.4 to 100° C.*

Effect of Moisture Content—Heats of Adsorption and Wetting

The heat of hydration of a cement, as normally measured, represents the total heat evolution that is usually of direct practical interest. However, this heat consists of two separate factors representing the energy change due to chemical reactions and the heat of the simultaneous adsorption of water on the colloidal hydration product. For a well hydrated cement, perhaps 80 percent of the energy released is due directly to the chemical reactions, i.e., the formation of "hydrates," while 20 percent of the energy represents the "wetting" of the large surface area of this colloidal product, this "wetting," of course, being necessary for the continuation of hydration. The relative amounts of these energies depend to some degree upon the chemical composition of the cement. The heat of adsorption of the hydration product is of considerable practical and theoretical interest.

In its most practical aspect, it appeared possible that unevaluated heat of adsorption effects could influence the heat of hydration measurements of cement with resulting errors in estimation of the degree of hydration of the cement from such data. Copeland and Bragg [71] have shown that hydrating past specimens, sealed to prevent uptake of water, become "self desiccated," the relative humidity within such pastes decreasing as the cement hydrates, with the decrease being most pronounced for pastes of low water-cement ratio. The lowest relative humidity they observed was 94 percent in a paste of 0.44 water-cement ratio at 1 yr. It would appear probable that pastes of 0.40 water-cement ratio cured 6½ or 13 yr might have relative humidities significantly below this value. In addition to self desiccation, a cement paste can lose further increments of moisture during the crushing, grinding, screening, and weighing procedures required in the preparation of paste samples for heat of solution measurements. These considerations suggest that the relative humidity of 0.40 water-cement ratio pastes at the later test ages, such as shown in table 9, might be as low as 80 or 90 percent. The heat of solution of a paste at 80 percent relative humidity is greater than that of a more nearly saturated paste, the additional increment representing the heat of wetting of the surface from perhaps 80 to 100 percent relative humidity. This greater heat of solution of the hydrated but partially dried paste reduces the apparent heat of hydration of the paste. Powers and Brownyard [69] report the heat of wetting of paste equilibrated by adsorption to 80 percent relative humidity to be as great as about 6 to 7 cal/g cement. An "error" of this magnitude in determination of the heat of hydration of low water-cement ratio pastes at later ages if neglected could introduce a significant error in estimation of degree of hydration of the cement from such data.

The heat of wetting was determined at the 13-yr test age for all pastes of 0.40 water-cement ratio reported in table 9. In addition to the customary determination of the heat of solution of the partially desiccated paste, a sample of the paste was wetted and equilibrated and then introduced into the calorimeter using a specially designed capsule for heat of solution measurements. For the cements of 0.40 water-cement ratio at the 13-yr test age, the average heat of wetting was determined to be only 0.9 cal/g cement. Since even smaller heats of wetting could be anticipated in tests at higher water-cement ratio and earlier ages further use of this special technique was not considered necessary.

In addition, the heats of adsorption and desorption of hydrated cement paste are of considerable theoretical interest. Unfortunately, only a modest amount of information is available on the heat of adsorption. The data obtained by Powers and Brownyard [69] regarding heat of adsorption of hydrated pastes is most instructive and also serves to reveal the need for additional information.

These data, shown in figure 16, were obtained by the heat of solution method for pastes dried to the nonevaporable water state (magnesium perchlorate) and then equilibrated at various relative vapor pressures. It can be observed that the relationships obtained for these two cements are similar and that each relationship appears to consist of two discrete portions each of which is a linear function of water content. These data imply that two different classes of water are sorbed on hydrated paste, the types of water having distinctly different "heats of adsorption" but yet each type having a constant differential heat of adsorption over the entire range of water contents in which it operates. In addition, there appears to be a rather abrupt discontinuity in the relationships observed, which would not be anticipated if only simple surface adsorption were involved. It should be further noted that the total heat of adsorption, taken as the difference between the heat of solution of the pastes at the nonevaporable water state and the heat of solution extrapolated from the observed relationships to the total water content at 100 percent relative humidity, is approximately 30.4 cal/g for cement 16186 and 30.8 and 30.9 cal/g for cement 16189, A, B, and C rounds respectively. This apparent equality in the total heat of adsorption of these pastes is of considerable significance since the degrees of hydration of the two pastes were materially different; the original water-cement ratios of the pastes being the same.

These observations of the "heat of adsorption," are analogous to recent observations in this laboratory of the drying shrinkage of cement pastes in the absence of carbonation. These shrinkage studies of hydrated pastes yield similar implications; the shrinkage-moisture content relationships of pastes between 100 and 0 percent relative humidity consistently demonstrated that there are two distinctly different types of water desorbed, each type of water having a constant shrinkage-water loss ratio over its operative range.

It is well established that various hydrated compounds in cement, the calcium aluminates and calcium sulfoaluminates, at least, will dehydrate and lose chemically combined water in this general range of relative vapor pressures. These results indicate the importance of the energy changes which accompany adsorption and desorption, particularly in their contribution to a full understanding of the volume changes of cement paste.

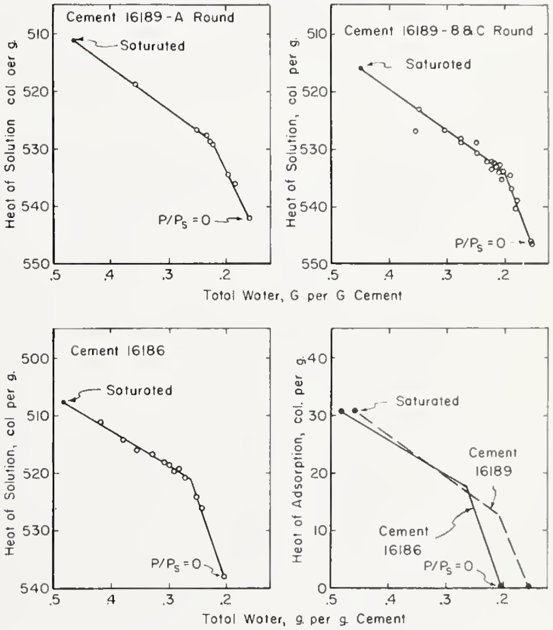

FIGURE 16. *Heats of solution and adsorption of pastes containing various amounts of adsorbed water.*

Data from Powers and Brownyard [69].

Intrinsic Characteristics of Cement

It is apparent from the data presented in figures 10 and 11, and from numerous other studies of the heat of hydration of cement, that cements differ significantly in heat evolution characteristics, both as to total ultimate heat evolution and the rate at which this heat is liberated. It is believed that the causes of these different heat evolution characteristics in cements are understood, at least to a semiquantitative degree. Factors causing these differences include the composition of the cement, the fineness of the cement, partial prehydration of cement, glass content, and alkali and gypsum contents. The influence of some of these factors will now be discussed.

Cement Composition

As a first approximation it is apparent that the heat liberated by a cement during complete hydration is approximately the sum of the heats of com-

Table 13. *Heats of complete hydration of individual compounds*

Anhydrous compound	Product	Heat of hydration, cal/g anhydrous compounds	
C_3S	C_3S+3H_2O	120	Lerch & Bogue [89]
C_2S	C_2S+2H_2O	62	Lerch & Bogue [89]
C_3A	$C_3A{\cdot}6H_2O$	207	Lerch & Bogue [89]
C_3A	$C_3A{\cdot}6H_2O$	214	Thorvaldson, Brown & Peaker [94]
C_3A	$C_3A{\cdot}8H_2O$	235	“ “ “ “
C_3A	$C_3A{\cdot}10{\cdot}2H_2O$	251	“ “ “ “
C_3A	$C_3A{\cdot}11{\cdot}6H_2O$	261	“ “ “ “
C_3A	$C_3A{\cdot}3CaSO_4{\cdot}32H_2O$	347	Lerch & Bogue [89]
C_4AF		100	Lerch & Bogue [89]
CaO	$Ca(OH)_2$	278.9	Thorvaldson, Brown & Peaker [95]

plete hydration of the individual compounds present or calculated to be present in the cement. The individual chemical compounds have significantly different heats of complete hydration as is shown in table 13. The heat evolved by C_2S is only 62 cal/g whereas the heat of hydration of C_3A is at least 207 cal/g, with C_3S and C_4AF having intermediate values. Cements having high C_3A (and C_3S) contents have significantly higher heats of complete hydration than cements low in these constituents and high in C_2S content.

The various compounds differ not only in heat of complete hydration but also in rate at which they hydrate; it has been generally observed that those compounds with high heats of complete hydration, C_3A and C_3S, also hydrate much more rapidly than C_2S, which has a low heat of hydration.

It is of interest to interpret the observed heats of hydration of different cements at various periods of hydration in terms of the composition of the cements. Various investigators [63, 65, 51] have used the method of least squares for this purpose. The coefficients obtained by such least squares analyses need to be interpreted with considerable care because of the several assumptions that are involved. Least squares analyses can be performed on the basis either of calculated compound composition or of oxide analysis. Since the calculated compound composition can be expressed by linear relationships with the oxide composition, least squares analyses on both bases are mathematically equivalent. Therefore, a least squares analysis in terms of calculated compound composition that produces heat coefficients that correspond to the heats of hydration of the individual compounds, and that collectively will closely reproduce the heats of hydration of the cements, does not require that the assumed or calculated compounds in reality exist. In addition, the least squares method assumes that the various compounds hydrate independently as has been discussed in the second main section of this paper.

Since it is not expected that the inherent hydration characteristics for any particular compound or phase would be identical in the various cements because of differences in actual composition and grain size of that phase among the different cements, the coefficients obtained for the various compounds will represent only the average coefficient for that compound among the different cements.

The results of least squares analyses of heat of hydration results at various ages obtained by Woods, Steinour, and Starke [63] with laboratory prepared cements are shown in table 14 and are compared with the heats of complete hydration for the pure compounds as reported by Lerch and Bogue [89]. The coefficients obtained for the compounds at the later ages acceptably correspond to the heats of complete hydration of the individual compounds. In addition, the coefficients obtained at the early ages conform qualitatively, at least, to the intrinsic reactivity of the individual compounds in that C_3S and C_3A react rapidly whereas C_2S reacts slowly. Therefore, the heat of hydration coefficients obtained by least squares analyses appear to have a real significance in relation to both the rate of hydration and the total heat evolutions of the individual compounds. These cements were laboratory ground with a constant amount of gypsum from laboratory prepared clinker having a very low alkali content.

Table 14. *Results of least squares analysis of heats of hydration of cements*

From Woods, Steinour, and Starke [63, 64]

Compound	Least squares coefficients. Heats of hydration, cal/g compound						Heats of complete hydration, (Lerch & Bogue [89]) cal/g compound
	3 days	7 days	28 days	3 mo	6 mo	1 yr	
C_3S	98	110	114	122	121	136	120
C_2S	19	18	44	55	53	62	62
C_3A	170	188	202	188	218	200	207
C_4AF	29	43	48	47	73	30	100

The least squares analyses previously reported by Verbeck and Foster [51] for commercially prepared cements at 0.40 water-cement ratio hydrated up to 6½ yr have now been extended to include analyses of results obtained after 13 yr of hydration and new results obtained for pastes of 0.60 and 0.80 water-cement ratio. Results obtained at 0.40 water-cement ratio are shown in table 15 and are compared with the data of Lerch and Bogue [89] for the heats of complete hydration of the pure compounds. The heat coefficients obtained for C_3S, C_2S, and C_4AF with these commercial cements are in close agreement with the reported heats for complete hydration. However, the coefficient obtained for C_3A is considerably

Table 15. *Results of least squares analysis of heats of hydration of cements*

Compound	Least squares coefficients, heat of hydration at water-cement ratio and age indicated							Heats of complete hydration (Lerch & Bogue [89]) cal/g compound
	cal/g compound—0.40 W/C and 21 °C.							
	3 day	7 day	28 day	90 day	1 yr.	6½ yr.	13 yr.	
C_3S	58	53	30	104	117	117	122	120
C_2S	12	10	25	42	54	53	59	62
C_3A	212	372	329	311	279	328	324	207
C_4AF	69	118	118	98	90	111	102	100

greater than that obtained for the formation of C_3AH_6, 207 cal/g, but approximates the heat of hydration of C_3A, 347 cal/g of C_3A, to form $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$, as reported by Lerch and Bogue.

Analyses by least squares can be based on various models and many have been evaluated. The coefficients shown in table 15 were derived on the following assumption:

(1) $H_t = a\ (\%\ C_3S) + b\ (\%\ C_2S) + c\ (\%\ C_3A) + d\ (\%\ C_4AF)$

in which H_t=heat of hydration at a given age.

However, and particularly in view of the high coefficient that was obtained for C_3A, additional postulations were made as follows:

(2) Formation of $C_3A{\cdot}CaSO_4{\cdot}12H_2O$
$H_t = a\ (\%\ C_3S) + b\ (\%\ C_2S) + c\ (\%\ C_3A - 1.125\%\,SO_3) + d\ (\%\ C_4AF) + e\ (\%\,SO_3)$ and

(3) Formation of $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$
$H_t = a\ (\%\ C_3S) + b\ (\%\ C_2S) + c\ (\%\ C_3A - 3.375\%\ SO_3) + d\ (\%\ C_4AF) + e\ (\%\ SO_3)$

The results of such analyses are shown in table 16,

Table 16. *Results of least squares analyses of heat of hydration data including the formation of calcium sulfoaluminates*

Compound	Least squares coefficients—cal/g compound, 0.8 W/C—1 yr		
	eq (1)	eq (2)	eq (3)
C_3S	124	128	125
C_2S	76	91	81
C_3A	325	396	384
SO_3	----------	−602	672
C_4AF	95	152	121

where it may be noted that these additional assumptions did not assist in revealing further details of the nature of the hydration reactions and the accompanying heat evolutions.

Of the various assumptions evaluated, perhaps the most instructive concerned the role of clinker alkalies on heat evolution. Newkirk [90] has reported that K_2O and Na_2O in portland cement clinker form the compounds $KC_{23}S_{12}$ and NC_8A_3. Least squares analysis based on calculated potential compound compositions, including the formation of these alkali substituted compounds produced the coefficients shown in table 17.

Table 17. *Comparison of least squares coefficients for alkali substituted compounds at early and late ages*

Compound	Least squares coefficients, cal/g compound, 0.8 W/C—16 cements		
	3 days	1 yr	6½ yr
C_3S	92	130	134
C_2S	22	73	76
$KC_{23}S_{12}$	57	62	74
C_3A	127	310	325
NC_8A_3	4	322	288
C_4AF	−17	88	71

Comparisons of the coefficients obtained at 1 yr and at 6½ yr for C_2S and $KC_{23}S_{12}$ or for C_3A and NC_8A_3 suggest that at complete hydration the heat contributions of the presumed alkali substituted compounds are similar to the heat contributions of the unsubstituted compounds. However, at the age of 3 days the heat contributions of the substituted and unsubstituted compounds appear significantly different, suggesting a significant effect of alkalies, directly or indirectly at early ages.

Further elucidation of the nature of the reactions by least squares studies based on such relatively direct postulations may not be possible; Lerch [91] has shown that heat evolution depends in part and in a rather complicated way upon the mutual effects of C_3A content, fineness, alkali content, and gypsum content of the cement.

There is evidence indicating that the heat contribution coefficients of the individual compounds derived by the method of least squares have an additional significance. The amount of combined water (the nonevaporable water content) in a hydrated cement paste, can be used as a further index to the degree of hydration of cement. The nonevaporable water content, w_n/c, was determined for all the cements at all test ages and for all water-cement rations, simultaneously with the heat of hydration measurements previously discussed. Least squares analysis of this information in a manner similar to that used with the heat of hydration results is most instructive. The number of moles of water associated with each mole of the clinker compounds can be derived by such analysis and compared with the heat contributions derived for the same test conditions, as is shown in figure 17. These relationships reveal that the derived coefficients for heat contributions and for moles of combined water for both C_3S and C_2S approximate as a limit a point closely corresponding to the ultimate heat of hydration and water content of the products C_3S+3H_2O and C_2S+2H_2O respectively. For less than complete hydration, it can be observed that both the derived heat coefficients and the combined water coefficients indicate

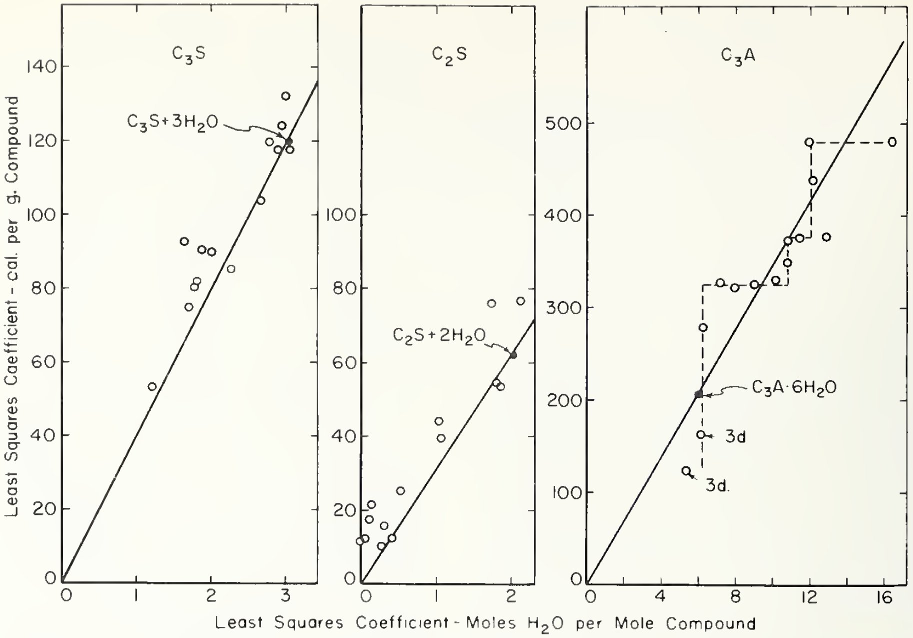

FIGURE 17. *Comparison of least squares coefficients for heat evolution and combined water of* C_3S, C_2S, *and* C_3A.

approximately the same degree of hydration of the compound, in further support of the significance of heat contributions derived by least squares.

The relationship obtained for C_3A indicates that both the derived heat contribution and combined water for this compound exceed the ultimate heat of hydration and water content of $C_3A{\cdot}6H_2O$ except at the earliest test age, 3 days. The relationship obtained suggests an irregular relationship (dashed line) corresponding to hydrates higher than $C_3A{\cdot}6H_2O$. More detailed study suggests that higher hydrates are formed which slowly reconvert to lower hydrates as the cement continues to hydrate with time. Such a relationship as shown in figure 18 supports the possibility of slow secondary changes in the C_3A hydrated product, where it can be seen that both the heat coefficients and combined water coefficients reflect similar changes with time.

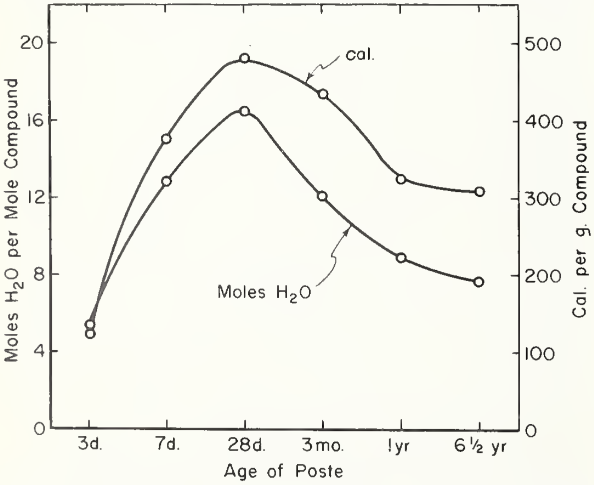

FIGURE 18. *Least squares coefficients for heat evolution and combined water of* C_3A *at various ages.*

0.80 water-cement ratio pastes.

It is believed that the degree to which the derived heat coefficients and combined water coefficients permit equal estimates of the degree of hydration and of observed secondary changes serves to support the significance of such derived coefficients. However, there are several other factors which can contribute to or alter heat evolution and which are not normally included in least square analysis. Cement constituents such as free calcium oxide and magnesium oxide will hydrate with evolutions of heat that usually are not considered in least squares analysis. In addition, the glass content of the clinker and the ignition loss of the original cement, which represents a degree of partial prehydration and carbonation of the clinker minerals have not usually been considered but do have a significant effect on the heat of solution of the original cement.

The effect of glass content on heat of solution and heat of hydration as reported by Lerch [92, 93] and shown in table 18 is most interesting. The average increase in heat of hydration observed with an increase in glass content is 7.9 cal/g at the 28-day test age. This increase corresponds within experimental error with the 6.8 cal/g increase in heat of solution of the original cement. These data suggest that the observed increase in heat of hydration is due solely to the increased energy content of the clinker with an increase in glass content and that although the glass phase during hydration eventually attains the same state as the corresponding crystalline phase, the glass phase hydrates less rapidly than the crystalline phase.

Table 18. *Effect of glass content on heat of solution and heat of hydration*

Average heat of solution [92] cal/g				Average heat of hydration [93] cal/g		
Orig. cement	3 days	7 days	28 days	3 days	7 days	28 days
638.8	564.2	552.4	544.9	74.6	86.4	93.9
641.9	567.2	555.0	546.0	74.7	86.9	95.9
645.6	570.9	554.7	543.8	74.7	90.9	101.8

The heats of solution of the original cements and hence the observed heats of hydration also depend significantly upon the partial prehydration of the original cement. Studies at this laboratory [52] have shown that the ignition loss of a cement represents loss of chemically combined water and CO_2 and loss of evaporable water, the latter presumably associated with the calcium sulfate in the cement. The amounts of CO_2 and of these different classes of water vary appreciably among cements and as shown in table 19 significantly affect the heats of solution of the cements and hence the observed heats of hydration. An approximate correction can be made to the heats of solution of cements from measurements of the CO_2 content and the content and distribution of the water within the cement assuming that the combined water and CO_2 have reacted with calcium oxide and that the original cement should have an evaporable water content corresponding to the dihydrate of the $CaSO_4$ in the cement. Approximate corrections calculated on this basis for 26 cements are significant in amount and variability as shown in table 19.

Table 19. *Range and analysis of losses on ignition and the corresponding corrections to heats of solution of 27 commercial cements*

Range	Ignition loss	Combined water	CO_2	Evaporable water	Correction to heat of solution of original cement, cal/g
	%	%	%	%	
Maximum	1.60	1.11	0.33	0.49	+9.5
Average	0.82	0.45	.17	.19	+3.5
Minimum	.35	.13	.08	.00	+0.4

Results of a least squares analysis based on a selected group of these cements in which the correction for heats of solution of the original cements ranged from +0.7 to +4.9 are compared in table 20, with results of a similar analysis based on the uncorrected heats of solution.

Table 20. *Results of least squares analyses based on uncorrected and corrected heats of solution of original cements*

Basis of analysis	Least squares coefficients heats of hydration, cal/g compound 0.80 water-cement ratio, 6½ yr			
	C_3S	C_2S	C_3A	C_4AF
Uncorrected heats of hydration	132	77	321	73
Corrected heats of hydration	137	81	325	62

It is observed that the coefficients for C_3S, C_2S, and C_3A were higher for the corrected heat analysis, indicating that the chemically combined water and CO_2 do not react primarily with either the C_3S or C_3A component of the cement. Other studies indicate some relation between the amounts of free CaO and alkali in the various cements and the amounts of combined water and CO_2 which they contain.

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Discussion

J. H. Taplin

Copeland and Kantro discuss the effect of W_0/C on the kinetics of the hydration of portland cement paste. They quote some data of mine for a cement A2 which, in the early part of the reaction, reacted more rapidly at the lower water-cement ratios. They propose an explanation in terms of the greater temperature rise to be expected during the first 24 hr in pastes of higher cement content. This explanation was not given by me because the effect was not found in similar experiments with other cements. The effect of W_0/C on the hydration rate at 25 °C is shown for three of these cements in figure 1. It seems safe to conclude that, with some cements, W_0/C does have an appreciable effect on the rate during the first 3 or 4 days.

As a further test of the temperature-rise explanation for the behavior of cement A2, some of the experiments were repeated, and the temperature of the paste relative to the curing cabinet was obtained by means of a thermocouple in the paste and a recording potentiometer. For paste with a W_0/C ratio of 0.35, cured at 25 °C in a six-gang steel mold which was wrapped in polyethylene sheet, the greatest temperature difference between the paste and the curing cabinet was attained at 15 hr, and amounted to only 0.7 °C, whilst the mean difference during the period 5 to 22 hr was less than 0.25 °C. Assuming an apparent activation energy of 10 kcal, an increase of 0.25 °C will increase the rate by only 1.3 percent. For a 0.25 W_0/C paste which was cured at 25 °C in a single polyvinyl chloride mold in a stoppered glass tube, the maximum temperature rise was 0.85 °C at 15 hr, and the mean rise between 5 and 22 hr was 0.5 °C, which corresponds to a rate increase of 2.5 percent. These temperature rises are too small to account for much of the rate increases of up to 20 percent actually observed for cement A2 at low W_0/C.

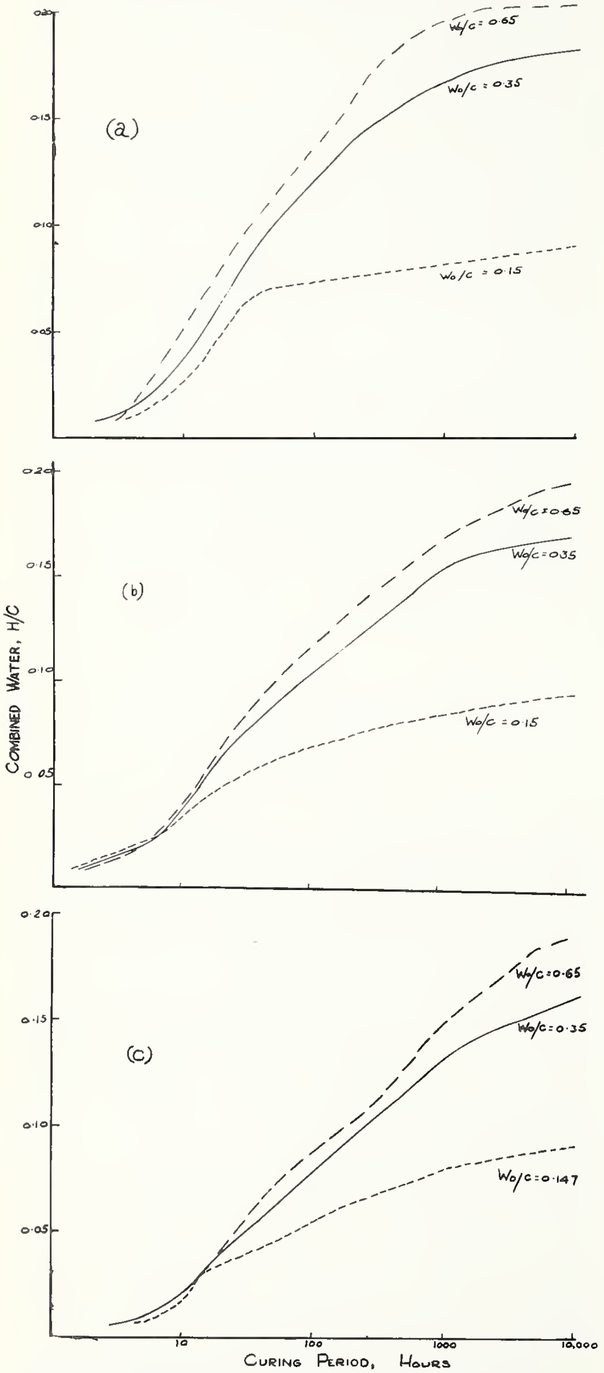

FIGURE 1. *Effect of* W_o/C *on rate of increase of combined water in portland cement paste. The* W_o/C *is marked on each curve. (a) Cement B1, (b) Cement C1, (c) Cement D1.*

Copeland and Kantro also describe a large increase in hydration rate for paste which is cured continuously saturated. As we had not observed this effect we carried out the experiment described below.

Two six-gang ebonite molds for 4 x ½ x ½-in specimens were filled from the same batch of 0.35 W_0/C paste. The cement, A3, was a different batch of the same brand as A2, i.e., an ordinary portland cement with a high alkali content. One mold was half immersed in a dish of water in such a way that the paste made contact with the water through the lower joints of the mold. The upper surface of the mold was sealed by a polyethylene sheet in contact with the paste. After 2½ hr it was observed that a pool of solution had collected above the paste, between it and the polyethylene. This osmotic flow proves that the paste and water were in contact through the mold joints. The other mold was simply wrapped in a polyethylene sheet. Both molds were stored side by side in a large constant-temperature room at 21 °C and stripped after 19 hr. The specimens from the continuously saturated mold were placed in stoppered glass tubes containing a few ml of water. Those from the self-desiccated mold were placed in dry tubes.

TABLE 1. *The effect of curing condition on the hydration of an 0.35* W_o/C *paste at 25 °C*

10^4 H/C

Curing period	Saturated	Self-desiccated	Mean difference
hr 19. 5	412 423	438 432	−17. 5
26	538 575	570 562	−9. 5
43	802 796	865 831	−49. 0
68	1100 1148	1072 1042	+67. 0
144	1171 1160	1107 1136	+44. 0
237	1260 1313	1249 1240	+42. 0
646	1403 1382	1317 1332	+68. 0
1730	1505 1485	1367 1412	+105. 5
Mean	1029. 6	998. 3	+31. 3

After various curing periods, samples were taken in duplicate from both sets of specimens, and measurements were made of the combined water [1], H/C, with the results shown in table 1. The mean difference in H/C of 0.0031 between saturated and self-desiccated specimens is significant at the 95 percent probability level and corresponds to the hydration of about 1.5 percent of the cement. (Copeland and Kantro, in their figure 4, show a difference which corresponds to the hydration of about 15 percent of the cement.) The mean negative difference in table 1, for curing times less than 48 hr, is not significantly different from zero. It must be concluded that, for this cement at least, the difference in hydration between continuously saturated and self-desiccated paste is very small for the first 48 hr and corresponds to the hydration of only 5 percent of the cement after about 10 weeks.

Copeland and Kantro briefly discuss possible reaction mechanisms for portland cement. The structure of cement clinker is such that the more reactive major components tend to be surrounded by thin shells of the less reactive minor components. This makes it very difficult to analyze experiments designed to show the effect of particle size, depth of reaction, or mineral composition on the hydration rate. It seems probable that the inner and outer products [1] are different in composition and/or structure, but as yet, there is little evidence about this.

Verbeck discusses the effect of curing temperature on the rate of hydration of portland cement. The apparent activation energy obtained from his Arrhenius plots is less than the 10 kcal obtained in this laboratory [2]. However, the apparent activation energy obtained from Verbeck's figure 14 should be doubled, because if one assumes a square-root law, one must use the square of the slope, heat of hydration against the square root of time, as an estimate of hydration rate.

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Discussion

H.-G. Smolczyk

The following discussion is for the purpose of contributing a new idea to the most interesting paper by the gentlemen of the Portland Cement Association. Throughout cement chemistry, X-ray investigation is a valuable means of determining clinker components as well as of observing the hydration of cements. For very many cases the procedures using an internal standard, as described in detail by Copeland and Bragg [1], and more recently by Brunauer, Copeland, Kantro Weise, and Schulz [2], and by Midgley, Rosaman, and Fletcher [3], are the best and most exact methods of quantitative X-ray analysis.

There are cases, however, for which the method of direct X-ray analysis without a standard (or with an external standard serving only as a control of intensities) is to be preferred. One example is the X-ray investigation of the rate of hydration of minerals in a cement as dependent on the time of hydration. Hereby the absolute amounts of these minerals in percentage of the hydrated cement are of minor interest, for the results can be compared only if these values are expressed as percentage of the original dry cement. The major interest is not in the absolute amount of newly produced hydrates expressed as percentage of the hydrated matrix, but in the percentage of the formerly unhydrated cement that is combined with water.

The method using an internal standard will measure only absolute amounts obtained as percentage of the hydrated matrix, so the loss on ignition has to be determined first before the wanted relations between the dry components can be calculated.

On the other hand use of the method of direct analysis permits neglecting the influence of the water on the X-ray intensities, because of the very low mass absorption coefficient of H_2O. By direct analysis the results will also be obtained as percentage of the original dry cement. The error arising from neglecting the influence of the water is so small, compared with the other errors of X-ray analysis, that it is of no importance at all, as demonstrated by the following two examples:

1. *Hydration rate of alite in portland cement.*

Suppose the 50 percent of alite in the cement to be 80 percent hydrated and the cement paste to have an H_2O content of 25 percent. Then the dry paste without water content will contain 10 percent of alite, and the hydration rate of the alite will be

$$HR=\frac{50-10}{50}=0.80$$

The matrix with water content, however, contains 7.5 percent of alite and 25 percent of water.

Now let us calculate the X-ray line intensity for the alite that can be expected. The following rough values are introduced:

μ_C = the mass absorption coefficient of the original dry cement $=100$
μ_H = the mass absorption coefficient of $H_2O = 10$
μ_A = the mass absorption coefficient of the alite $=100$
I°_A = the X-ray line intensity for 100 percent of alite $=160$.

In the unhydrated cement containing x_1 fraction of alite, the intensity is:

$$I_{A1}=I^\circ_A x_1 \frac{\mu_A}{\mu_C}=160\cdot 0.50\cdot\frac{100}{100}=80$$

After the cement has taken in 25 percent of water, the mass absorption coefficient of the matrix is $\mu_M=75+2.5=77.5$. Therefore the intensity for the 7.5 percent of alite in the matrix will be:

$$I_{A2}=I^{\circ}_{A}x_2\frac{\mu_A}{\mu_M}=160\cdot 0.075\cdot\frac{100}{77.5}=15.5$$

If now the calculation is performed without paying regard to the mass absorption coefficients, and if only the measured absolute intensities of the alite in the two X-ray diagrams of the cement before and after hydration are introduced in the equation, the rate of hydration will be

$$HR=\frac{80-15.5}{80}=0.806$$

So the neglect of the mass absorption coefficients has caused an absolute error of only +0.6 percent. The other errors of X-ray investigation methods exceed by far the one introduced by this procedure, for 10 percent of alite cannot in any case be determined exactly to ±0.3 percent.

2. *Determination of the percentage of original cement bound in ettringite.*

In order to perform such a determination the measuring of intensities alone will not be sufficient, but it will be necessary to know the I°_{E} and the μ_E of ettringite as well as the μ_C of the dry original cement.

Suppose 10 percent of the original cement changed into ettringite, and the cement to have taken in again 25 percent of water. Let the mass absorption coefficient of the dry cement μ_C be again 100, then that of the set cement, μ_M, will be again 77.5. For the ettringite the following values have to be introduced:

μ_E=the mass absorption coefficient of ettringite=50

I°_{E}=the X-ray line intensity for 100 percent of ettringite=500.

The matrix contains 7.5 percent of $C_3A\ (Cs)_3$ where $s=SO_3$, equivalent to 13.9 percent of $C_3A\ (Cs)_3\ H_{32}$, and the intensity for the ettringite in the matrix will be

$$I_E=I^{\circ}_{E}x\frac{\mu_E}{\mu_M}=500\cdot 0.139\cdot\frac{50}{77.5}=44.9$$

If this measured intensity is introduced in the equation

$$x=\frac{I_x}{I_0}\cdot\frac{\mu_G}{\mu_x}$$

and the mass absorption coefficient of the dry cement is applied in place of μ_G, the content of ettringite in percentage of the dry cement may be calculated as follows

$$x_E=\frac{I_E}{I^{\circ}_{E}}\cdot\frac{\mu_C}{\mu_E}=\frac{44.9}{500}\cdot\frac{100}{50}=0.18$$

Now the hydration water of the ettringite (46 percent) has to be subtracted from the 18 percent of ettringite, and the value 9.7 percent of $C_3A\ (Cs)_3$ is obtained.

In this determination, too, an error of only −0.3 percent has been introduced, which is of no importance compared with the well-known inaccuracy of the X-ray analysis of hydrates.

By applying this method the hydrated percentages of the original cement can be determined directly with only a very small error and without the necessity of knowing the water content of the matrix. Hereby a very careful preparation of the samples is of great importance. As the method of avoiding preferred orientation, described by Copeland and Bragg [1], cannot be applied here, only those hydrates can be determined the preferred orientation rates of which are fully known and reproducible.

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Paper IV–S1. Role of Gypsum in the Hardening of Hydraulic Cements*

P. P. Budnikov

Synopsis

On the basis of his investigations, the author has shown that the high-sulfated form of calcium hydrosulfoaluminate that forms in cement as a result of interaction of calcium sulfate with aluminates is under proper physicochemical conditions a structurally useful compound in the hardened cement.

The addition of an elevated amount of gypsum (or anhydrite) to high-C_3A portland cement increases the resistance to the action of water solutions of Na, Mg, and Ca sulfates; this is explained by the formation of hydrosulfoaluminate. The greater the amount of C_3A bound with calcium sulfate at early hardening periods (under 28 days), the higher is the sulfate resistivity of the hardened cement. The optimum content of gypsum in portland cement is that binding the C_3A to calcium hydrosulfoaluminate in the early period of hardening of the cement.

In sulfate-slag (clinkerless or low-clinker) cements based on acid and basic granulated blast furnace slags, in presence of a liquid phase (water) and of a small amount of alkali ($Ca(OH)_2$ or $Mg(OH)_2$) and of calcium sulfate there forms calcium hydrosulfoaluminate. The latter, jointly with other new formations—calcium hydrosilicate, $3CaO \cdot 2SiO_2 \cdot aq$, and calcium hydroaluminate, $2CaO \cdot Al_2O_3 \cdot 7H_2O$, and in the case of acid slag, $2CaO \cdot Al_2O_3 \cdot 7H_2O$ and $2CaO \cdot SiO_2 \cdot aq$—determines the hardening and durability of the cement stone.

In aluminous cement the addition of about 30 percent of gypsum in presence of a liquid phase interacts chemically with calcium aluminates forming hydrosulfoaluminate which influences positively the properties of this cement. When hardening occurs under moist conditions, an expanding cement is obtained which possesses a high water impermeability, without any decrease of strength at elevated temperature conditions due to exothermy or external heating. If about 25 percent of insoluble anhydrite is added to aluminous cements, a non-shrinking cement is obtained, hardening normally under conditions close to adiabatic. Concrete with that cement has an increased resistivity in aggressive media containing NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$ and $CaSO_4$.

Résumé

Comme suite de ses recherches l'auteur a démontré que la forme de hydrosulfoaluminate de calcium à haute teneur de sulfate qui ce forme dans le ciment à cause de l'interaction du sulfate de calcium avec les aluminates, sous des conditions physico-phimiques correspondantes, présente une liaison structurellement utile dans la pierre de ciment solidifié.

L'addition d'une quantité élevée de gypse (ou d'anhydrite) au ciment portland à haute teneur d'aluminate augmente la résistibilité de la pierre de ciment à l'action de solutions d'eau de sulfates de Na, Mg et Ca, ce qui s'explique par la formation de hydrosulfoaluminate. Le plus de C_3A entre en liaison avec le sulfate de calcium dans les termes de début de la solidification du ciment (avant 28 jours), la plus haute est la résistivité aux sulfates de la pierre de ciment. La quantité optimale de gypse dans le ciment portland doit être celle qui lie le C_3A à former l'hydrosulfoaluminate de calcium pendant la période de début de durcissement du ciment.

Dans les ciments sulfate-laitier (sans clinker ou avec peu de clinker), obtenus sur la base de laitiers granulés acides ou basiques, en présence d'une phase liquid (eau) et d'une petite quantité d'alcalis ($Ca(OH)_2$ ou $Mg(OH)_2$) et de sulfate de calcium, est formé l'hydrosulfoaluminate de calcium, lequel, ensemble avec d'autres nouvelles formations—silicate hydrocalcique $3CaO \cdot 2SiO_2 \cdot aq$ et aluminate hydrocalcique $2CaO \cdot Al_2O_3 \cdot 7H_2O$ et dans le cas de laitier acide $2CaO \cdot Al_2O_3 \cdot 7H_2O$ et $2CaO \cdot SiO_2 \cdot$ aq.,—stipule la solidification et la longévité de la pierre de ciment.

Dans le ciment alumineux le gypse additionné à celui-ci dans une quantité d'à peu prés de 30% en présence d'une phase liquide entre en interaction chimique avec les aluminates de calcium en formant l'hydrosulfoaluminate qui influence positivement les propriétés de ce ciment:on obtient un ciment dilatable se solidifiant sous des conditions humides avec une haute imperméabilité sous des conditions de températures élévées pour le compte d'exothèrmie ou d'échauffement externe. En additionnant au ciment alumineux près de 25% d'anhydrite insoluble, on obtient un ciment incontractable se solidifiant normalement sous des conditions s'approchant aux adiabatiques. Le béton avec ce ciment possède une stabilité élevée dans les milieux agressifs contenant des sels de NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$ et $CaSO_4$.

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Zusammenfassung

Auf Grund seiner Untersuchungen hat der Verfasser gezeigt, daß die hoch-sulfatische Form von Calciumhydrosulfoaluminat, die sich im Zement infolge der gegenseitigen Wirkung von Calciumsulfat mit Aluminaten bildet, unter entsprechenden physikalisch-chemischen Bedingungen eine strukturell nützliche Verbindung im erhärteten Zementstein ist.

Die Zugabe einer erhöhten Menge von Gips (oder Anhydrit) zu hochaluminatigem Portland-Zement erhöht die Beständigkeit von Zementstein der Einwirkung von wässerigen Lösungen von Na, Mg und Ca gegenüber, was sich durch die Bildung von Hydrosulfoaluminat erklärt. Je größer die Menge des in frühen Bindezeiten des Zements (unter 28 Tagen) mit Calciumsulfat gebundenen C_3A ist, desto höher ist die Sulfatbeständigkeit des Zementsteines. Die optimale Menge von Gips im Portland-Zement soll die sein, die C_3A in Calciumhydrosulfoaluminat während der Beginnungszeit des Zementhärtens bindet.

In Sulfatschlackenzementen (klinkerlosen oder wenig Klinker enthaltenden), die ausgehend von sauren oder basischen granulierten Hochofenschlacken beim Vorhandensein von einer flüßigen Phase (Wasser), in Anwesenheit einer kleinen Menge von Alkali ($Ca(OH)_2$ oder $Mg(OH)_2$ und Calciumsulfat, erhalten werden, wird Calciumhydrosulfoaluminat gebildet, das zusammen mit anderen Neubildungen—Hydrocalciumsilikat $3CaO{\cdot}2SiO_2{\cdot}aq$ und Hydrocalciumaluminat $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$, und im Fall einer sauren Schlacke $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$ und $2CaO{\cdot}SiO_2{\cdot}aq.$,—das Härten und die Beständigkeit des Zementsteins verursacht.

Im Aluminatzement tritt der ihm in einer Menge von etwa 30% zugegebene Gips in Anwesenheit einer Flüßigen Phase in eine chemische Zusammenwirkung mit Calciumaluminaten ein unter Bildung von Hydrosulfoaluminat, das die Eigenschaften dieses Zements günstig beeinflußt—es wird ein expandierender Zement beim Härten unter feuchten Bedingungen erhalten, der eine hohe Wasserdichtigkeit, ohne Einbüßen seiner Dauerhaftigkeit unter Verhältnissen hoher, durch Exothermie oder äußere Erwärmung hervorgerufener, Temperaturen besitzt. Bei einer Zugabe von etwa 25% unlöslichen Anhydrits zum Aluminatzement wird ein volumbeständiger Zement erhalten, der unter den adiabatischen nahen Bedingungen normal erhärtet. Beton mit diesem Zement besitzt eine erhöhte Beständigkeit in agressiven, NaCl-, $MgCl_2$-, Na_2SO_4-, $MgSO_4$-, und $CaSO_4$- Salze enthaltenden Mitten.

Introduction

The role of gypsum and other forms of calcium sulfate (hemihydrate, insoluble anhydrite) varies in different binding materials. Gypsum is used in the cement industry as an addition controlling the setting time. In some cases it slows the rate of setting (portland cement); in others it accelerates the hardening of the cement (for instance of slag portland cement) and increases its strength.

About 2.5 percent, computed as SO_3, is usually reckoned to be an admissible amount of gypsum in portland cement.

Many investigations have been devoted to the influence of gypsum on the properties of different cements. But the optimum percentage of gypsum in cement is expressed in different papers by different values.

Some investigations show that the optimum amount of gypsum in portland cement favorably influencing the strength of hardened cement paste is that quantity bound with C_3A in the initial period of hardening. A further increase of gypsum content can lead to a decrease of strength of the cement paste and even to its disintegration during further hardening.

The C_3A of portland cement enters speedily into a reaction with gypsum under suitable physicochemical conditions, especially if calcium hydroxide is contained in the liquid phase, forming a complex calcium hydrosulfoaluminate compound, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}30\text{–}31H_2O$. The formation of this salt, crystallizing in the shape of thin needles or prisms, is accompanied by a considerable increase in volume.

If hydrosulfoaluminate has formed at early stages of hardening, i.e., during the formation of the structure of cement paste, it is a structurally useful compound increasing the strength of the paste. The formation of crystalline sulfoaluminate in hardened cement paste, however, is accompanied by a disintegration of the paste because of the growth of the crystals and the considerable inner strains arising as a result.

Thus in some cases the formation of hydrosulfoaluminate in concrete structures based on portland cement can lead to their destruction, and in others it is a useful factor contributing to an increase of strength of the concrete.

The amount of gypsum to be added to portland cement depends principally on the amount of C_3A present and on the velocity with which it combines with gypsum [1].[1]

It is known that gypsum combines not only with C_3A to form calcium hydrosulfoaluminate, but also with C_4AF; but the rate of reaction with C_4AF is very much slower than that of the reaction with C_3A.

In order to study the rate of reaction of gypsum with tricalcium aluminate, we synthesized the latter by burning a mixture of fine powders of reagent-quality CaO and Al_2O_3. Out of a moistened mixture of these components (three equivalents of CaO and one of Al_2O_3) were pressed at 300 kg/cm² bricks subsequently fired to sintering at 1380 °C. This temperature was maintained for 3 hr. The fired bricks were crushed to pass completely the 4900 mesh/cm² sieve. Bricks were again pressed from the moistened powder and refired at the same temperature. After the fourth

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[1] Figures in brackets indicate the literature references at the end of this paper.

firing, free lime was absent in the product. A chemical analysis showed a CaO content of 62.25 percent. Petrographic investigation showed that the fired product was formed of irregularly shaped fine isotropic crystals with refractive index $N=1.710$.

A photomicrograph of isometric $C_3A \cdot 6H_2O$ crystals obtained as a result of hydration of C_3A in water for two days is shown in figure 1.

Amounts of 10, 20, and 30 percent of gypsum were added to the C_3A. To determine the amount of unreacted gypsum, we used a method based on the different solubilities of gypsum and calcium sulfoaluminate in a saturated $Ca(OH)_2$ solution.

The results of determination of the rate of reaction of gypsum with tricalcium aluminate are shown in table 1.

The results showed that with 10 percent of gypsum in the mixture only 0.80 percent of unbound SO_3 remained after 6 hours and that SO_3 was absent in the solution after 24 hr. With 20 percent of gypsum, SO_3 disappeared from the solution in 7 days, and with 30 percent, in 28 days.

The time of binding of C_3A lengthened when gypsum dihydrate was introduced, and with 10 percent of gypsum the period of binding diminished.

TABLE 1. *Rate of reaction of gypsum with tricalcium aluminate*

Amount of gypsum in mix		Amount of unreacted SO_3 in:					
Gypsum	Calculated as SO_3	6 hrs	24 hrs	3 days	7 days	16 days	28 days
Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
10	5.88	0.80	0	--------	--------	--------	--------
20	11.76	3.44	1.80	0.32	0	--------	--------
30	17.64	6.60	4.93	2.63	1.18	0.64	0

An investigation of the interaction of C_3A with gypsum (saturated solution) showed the formation of characteristic calcium sulfoaluminate needles with refractive indices $N_g=1.462 \pm 0.002$ and $N_p=1.458$.

In figure 2 we see calcium sulfoaluminate crystals formed in 6 hr as a result of interaction of C_3A with gypsum in the liquid phase. In figure 3 are shown calcium sulfoaluminate crystals formed in the liquid phase in 6 hr as a result of interaction of gypsum with cement clinker containing 11.04 percent of C_3A.

In investigations on the influence of different amounts of gypsum on portland cement with different C_3A contents, three clinkers were taken whose mineralogical composition is shown in table 2.

TABLE 2. *Mineralogical composition of clinkers (in %)*

No. of clinker	C_3S	C_2S	C_3A	C_4AF	MgO	$CaSO_4$	Free CaO
I	56.21	19.00	5.00	16.00	1.70	0.49	0.60
II	41.15	32.20	8.45	15.25	1.31	.68	.96
III	49.58	23.91	11.04	10.20	3.30	.71	1.03

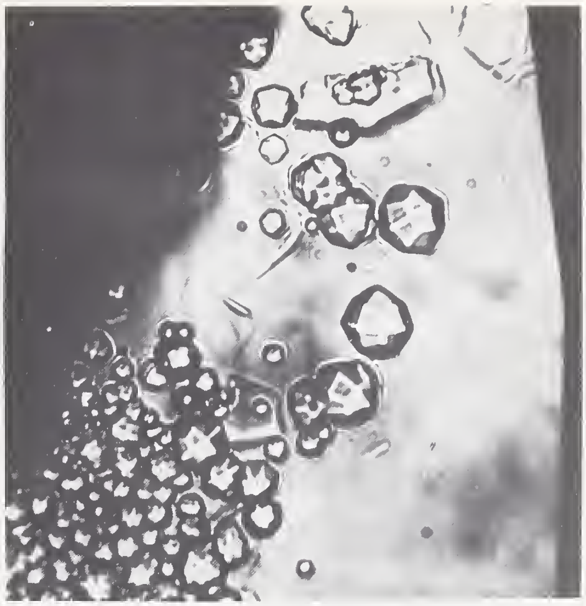

FIGURE 1. *Photomicrograph of isometric $C_3A \cdot 6H_2O$ crystals obtained as a result of hydration of C_3A in water for two days.*

Photograph made with the aid of a green light filter. Magn. 800 times.

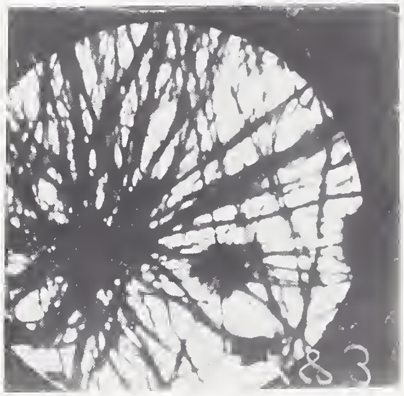

FIGURE 2. *Calcium sulfoaluminate crystals formed by the interaction of C_3A with gypsum.*

Photograph made under electronic microscope. Magn. 4000 times.

FIGURE 3. *Calcium sulfoaluminate formed by interaction of cement clinker with gypsum.*

Photograph made under electronic microscope. Magn. 4000 times.

The clinkers were ground to a specific surface of 3,200 cm^2/g. Hemihydrate was added in proportions of 3.5 and 10 percent, reckoned as anhydrous calcium sulfate.

The determinations of the rate of binding of gypsum as a function of the content of C_3A in portland cements showed that cement containing 5 percent of C_3A bound the 3 percent of added gypsum completely in 24 hr. The same phenomenon was noted also in cement with 11.04 percent of C_3A, to which 3 and 5 percent of gypsum had been added. A slower interaction takes place in the case of cements containing 10 percent of gypsum. Thus, in a high-C_3A portland cement containing 6.30 percent of SO_3 at 6 hr after mixing, the percentage of unbound gypsum in the cement was 2.9, at 24 hr 1.87, at 3 days 1.10, at 7 days 0.441, and at 28 days 0.10.

The retarding of the binding of gypsum can take place because of the formation of a large amount of hydrated compounds covering the particles of cement and thus hampering the access of calcium sulfate molecules to the unreacted part of the cement. Obviously this factor plays the largest part in the case of the high-C_3A portland cement.

Cements with a different C_3A content without any addition of gypsum, in contrast to synthetic C_3A, as would be expected, set quickly; if 3 percent of gypsum is added to the same cements, the setting takes longer.

With an increase of the percentage of gypsum the term of binding shortens, leading to a reduction of the interval of binding.

The influence of gypsum as a retarder of setting of portland cement can be explained by the fact that in the presence of the liquid phase the gypsum reacts quickly with the calcium aluminate hydrate, forming submicroscopic hydrosulfoaluminate crystals; the latter, settling on the surface clinker particles, envelop them and thus retard the hydration of cement, i.e., its setting. These deposits are voluminous, because of a simultaneous formation of a gel of calcium silicate hydrates, and draw off the water from the cement particles.

The strength of cement samples as a function of gypsum content was determined for the bending strength on prisms measuring 1 x 1 x 3 cm and for the compressive strength on cubes measuring 1.41 x 1.41 x 1.41 cm prepared from a 1:3 plastic mortar with sand (sand passing the 144 mesh/cm^2 sieve and remaining on the 256 mesh/cm^2 sieve was used).

It was found that in the cases of 3 and 5 percent content of gypsum in high-alumina portland cement (C_3A—11.04%) the intensity of growth of strength[2] was rather regular up to 28 days of hardening [3]. In the case of the same cement with 3 percent of gypsum after 28 days and especially after 90 days hardening a considerable slackening of the rate of increase of strength took place; at the same time, the strength of samples of the same cement with 7 and especially with 10 percent of gypsum grew considerably only after 28 days of hardening. The slackening of the increase of strength before 28 days in the case of high-C_3A portland cement with 7 and 10 percent of gypsum is to be explained by a continuous breaking up of the structure because of the formation of sulfoaluminate. After 28 days hardening, when practically all gypsum was bound, the strength of cement paste sharply increased.

The bending strength of samples from high-C_3A portland cement was determined for 3, 5, 7, and 10 percent of gypsum.

The investigations showed that in the case of cement with 10 percent of gypsum the increase in bending strength was continuous, in contrast to cement with 3 percent of gypsum whose increase in strength ceased after 2 months.

When investigating the sulfate resistance of cements with different C_3A contents as a function of the amount of gypsum added, we prepared samples from a 1:3 plastic cement mortar. After 28 days hardening in water the samples were immersed in 5-percent Na_2SO_4 and 1-percent $MgSO_4$ solutions and in a saturated gypsum solution. The salt solutions were replaced every month.

It was found that in the case of storage of samples in a Na_2SO_4 solution the highest strength was shown by high-alumina portland cement (C_3A—8.45%) containing 7 and 10 percent of gypsum, and the greatest lowering of strength was observed in the case of cement containing 3 percent of gypsum.

Complete disintegration of cement (C_3A—11.04%) with a 3-percent gypsum content took place first with samples stored in a sodium sulfate solution, then with those stored in a magnesium sulfate solution, and lastly, in 12 months, in a saturated gypsum solution (fig. 4).

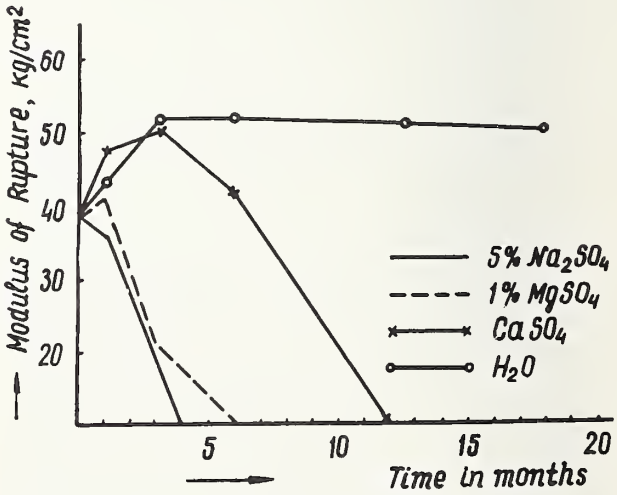

FIGURE 4. *Bending strength of cement samples stored in sulfate solutions* (C_3A *in cement, 11.04%; gypsum, 3%*).

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[2] By intensity of growth of strength is understood the percentage relation of strength at a given age to that at 3 days.

Samples of high-alumina portland cement (C_3A—11.04%) containing 10 percent of gypsum showed the highest bending strength when stored in a 5 percent sodium sulfate solution and the lowest in a saturated gypsum solution (fig. 5).

Aluminous cement presents another example in which gypsum influences essentially the properties of cement.

Many investigators have studied the processes of hydration and hardening of aluminous cement. In the process of hydration of the $CaO \cdot Al_2O_3$ and $5CaO \cdot 3Al_2O_3$ contained in aluminous cement there is formed a colloidal phase that gradually takes the shape of a fine-grained mass. The finest hexagonal crystals of $2CaO \cdot Al_2O_3 \cdot 7H_2O$ speedily grow in size, forming a firm crystalline network, and the cement hardens in 5–6 hr, the mortar with sand attaining a strength of about 200 kg/cm^2 and higher; in 10–15 hr, 400–500 kg/cm^2; and on the third day of hardening about 600 kg/cm^2 and more. Thereafter the strength of the cement increases slowly and insignificantly. But this hardening process, as is known, takes place under normal temperature conditions, i.e., at 5–25 °C.

As has been shown by many investigations and in practice, an increase in the temperature from 30 to 70 °C influences unfavorably the strength of this cement, the strength of the cement stone falling more than 50 percent.

The unfavorable influence of elevated temperatures of the medium on the strength of aluminous cement is explained by the formation of Thorvaldson aluminate in the shape of fine cubic crystals of $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

The formation of these cubic crystals in the mass of the $Al_2O_3 \cdot nH_2O$ gel and the absence of a crystalline network are the fundamental causes of the low strength of aluminous cement hardened at elevated temperatures.

The possibility is not excluded that the strength of aluminous cement depends not only on the shape of the crystalline components, but also on the amount of alumina hydrate that forms in the earliest stages of hardening, in the shape of a gel-like mass, and, filling up all voids, creates a dense structure.

When the temperature increases, the alumina gel forms in a considerably smaller amount than at 18–20 °C which presumably is insufficient for the creation of high density and strength.

As has been shown by our investigations, it is possible to avoid this negative phenomenon by introducing gypsum or anhydrite into the batch of aluminous cement. The calcium aluminates in aluminous cement, $CaO \cdot Al_2O_3$ and $5CaO \cdot 3Al_2O_3$, dissolving in water, begin to interact with calcium sulfate with the formation of the complex compound calcium hydrosulfoaluminate, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$. The temperature increase accompanying the hydration of aluminous cement contributes to this process. The binding of calcium sulfate as hydrosulfoaluminate takes place at the first stage of hardening, when the cement paste does not yet have a stiff skeleton, and the volume changes of the system connected with the lower density of this new product (calcium hydrosulfoaluminate), do not influence negatively the mechanical strength of the hardened cement paste obtained as a result of these chemical and physical processes.

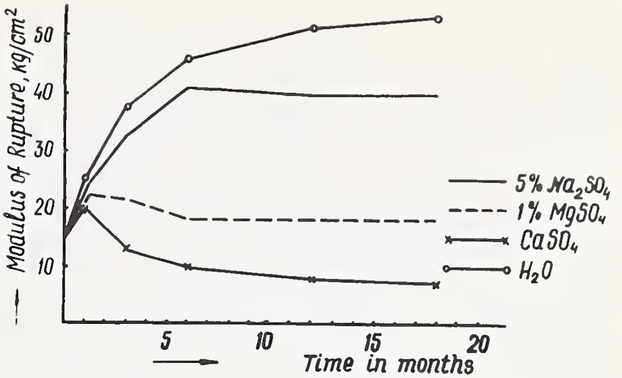

FIGURE 5. *Bending strength of cement samples stored in sulfate solutions* (C_3A *in cement, 11.04%; gypsum, 10%).*

We took an aluminous cement of the following chemical composition (in %):

SiO_2	10. 36	Fe_2O_3+FeO	1. 85
Al_2O_3	47. 25	MgO	0. 39
CaO	38. 91	SO_3	. 38
		S	. 81

It was shown by the investigations that the most active addition to aluminous cement is anhydrite obtained by firing gypsum at about 600–700 °C.

If aluminous cement showed a crushing strength amounting in 3 days to 525 kg/cm^2 and in 7 days to 550 kg/cm^2, the same cement with an addition of 25 percent of artificial insoluble anhydrite showed at the same ages 580 and 660 kg/cm^2. The packing of anhydrite-aluminous cement into molds at 2 hours after mixing did not influence negatively the mechanical strength of the cement. The addition of artificial insoluble anhydrite to aluminous cement accelerates the setting of the cement, and of natural anhydrite retards it.

Characteristic properties of aluminous cement in the case of an addition of calcium sulfate to it are: high early strength, expansion when stored in moist conditions, high water impermeability, and an increased mechanical strength when hardening under high-temperature conditions (when the whole mass of the mixture or concrete is being equally warmed up from 35 to 80 °C because of exothermal self-heating or of external heating). Hydrosulfoaluminate formed during the hydration of anhydrite-aluminous cement is not only an excellent structural element of hardened cement paste, lending it a high mechanical strength, but also changes the character of the heat evolution curve in the process of cement hydration.

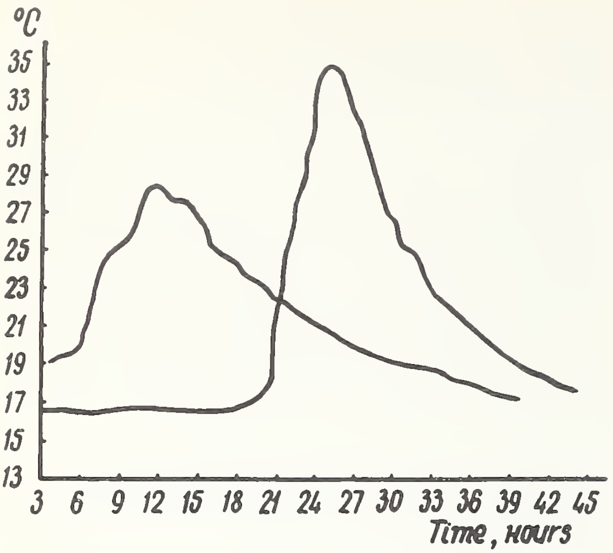

FIGURE 6. *Time-temperature curves of cements in concrete.*
1—aluminous cement; 2—anhydrite-aluminous cement.

The total amount of heat evolved during the hardening of anhydrite-aluminous cement is somewhat lower than in the case of aluminous cement of equal strength. When the strength is about 600 kg/cm², the heat evolution of aluminous cement equals about 100 cal/g and of anhydrite-aluminous cement about 70 cal/g. In the velocity and character of heat evolution anhydrite-aluminous cement differs from aluminous cement. Self-heating of anhydrite-aluminous cement begins much earlier, but the interval between the beginning of self-heating and the temperature maximum is much longer, though the latter comes somewhat earlier than in the case of aluminous cement. Thus the evolution of heat and the increase of temperature in the case of anhydrite aluminous cement occurs more regularly than in the case of aluminous cement; with the latter this process is somewhat retarded at first but is greater later on. Figure 6 illustrates the character of the exothermic processes of hydration of both cements [6].

The character of the heat evolution in the case of anhydrite-aluminous cement has a positive importance for its practical use: firstly, the self-warming taking place soon after mixing and laying of concrete is advantageous to the hardening process; secondly, the inner temperature strains in bulk concrete will be somewhat lower; and, thirdly, an early self-warming better preserves the concrete mass from freezing under conditions of winter concrete-laying.

A specific peculiarity of anhydrite-aluminous cement is the considerable increase of its mechanical strength when self-heating of the hardening mortar and concrete takes place or when warmth is applied from outer sources; on the contrary, the strength of aluminous cement is considerably lowered under these conditions.

Thus, if at 3 days normally cured aluminous cement had a compressive strength of 560 kg/cm², when hardening under adiabatic conditions at 60 °C its strength was lowered to 132 kg/cm². Under the same conditions the strength of anhydrite-aluminous cement (with 25 percent of anhydrite) increased from 490 to 520 kg/cm² and in 28 days to 650 kg/cm². These cements conduct themselves similarly in concrete.

It is known that among binding materials, aluminous cement is the most resistant in aggressive media, if a temperature of the medium not exceeding 20–25 °C is maintained during the building of structures.

In this respect anhydrite-aluminous cement is of interest; concrete made with this cement has a good resistance in aggressive media containing soluble $NaCl$, $MgCl_2$, Na_2SO_4, $MgSO_4$, and $CaSO_4$. In solutions of these salts the tensile strength of one-year samples did not decrease.

The adhesiveness of aluminous and anhydrite-aluminous cements to iron is equal under normal temperature hardening conditions; on the other hand, under nearly adiabatic conditions of hardening the adhesiveness of anhydrite-aluminous cement to iron is nearly twice that of aluminous cement.

The anhydrite-aluminous cement is non-shrinking and under certain circumstances expanding under moist conditions. The phenomenon of expansion of cement during hardening takes place because of the formation of calcium hydrosulfoaluminate.[3]

The expansion of aluminous cement manifests itself especially well if 30 percent of gypsum is added to it [7].

In the case of water curing of samples of aluminous cement containing 30 percent of gypsum (1:0 mortar), about a half of the combined linear expansion takes place during the first day. Samples of 1:3 mortar with the same regime of hardening showed an expansion of 0.08 percent in one day and 0.09 percent in 3 days, further expansion ceasing afterwards.

The expanding gypsum-aluminous cement is characterized by a high water impermeability. Cylindrical samples 230 mm in diameter and 50 mm in length were prepared from a 1:2.5 by weight cement mortar, as well as concrete samples 100 mm in length of the following composition for 1 m³ of concrete: cement—280 kg, water—170 l, building sand—690 kg, crushed granite of 30 to 5 mm size—1300 kg.

At three days, samples of expanding cement proved to be sufficiently impermeable to water under 8 atm. pressure.

It was found that gypsum-aluminous cement in rich mortars of 1:2 and 1:2.5 (by weight) compositions and in concrete with 377 kg/m³ of cement and a water-cement ratio of 0.45 is frost resistant; in mortars and concretes of the consistency and

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[3] On the influence of temperature conditions on the stability of calcium sulfoaluminate and sulfoferrite see P. P. Budnikov and V. S. Gorshkov. Reports of Academy of Sciences of U.S.S.R., 1959, vol. 126, No. 2, p. 337.

composition shown it withstands over 200 cycles of alternate freezing (at −17 to −22 °C) and thawing for 16 hr in water at 17±3 °C.

Trial determinations of the adhesion to reinforcing steel of concrete made with expanding cement were undertaken by the method of pressing down steel bars 14.4 mm in diameter and 125 mm in length. The concretes tested had a w/c ratio$=$0.60. The concrete cubes measures $100\times100\times100$ mm. In the case of air curing the average value of adhesion proved to be 64 kg/cm^2, and in the case of water curing, 40 kg/cm^2.

The temperature rise during the hardening of expanding cement does not influence its strength. Tests showed that at 60–65° with alternate drying and saturating with water the expanding cement was stable.

Crushed granulated blast furnace slags when mixed with water, as is known, possess very feeble binding properties or do not possess them at all. In order to call forth a reaction between slag and water, an addition of an alkaline stimulator is needed. The presence of an inconsiderable amount of alkali is sufficient to establish on the surface of slag particles an extensive formation of hydrated products bringing about a binding and hardening of granulated slag similar to cement. An addition of sulfate to the slag in the presence of an alkaline stimulator, as was demonstrated by our investigations, intensifies the process of hydration and hardening [2, 8, 9, 10, 11].

When studying the phenomena taking place in the liquid phase of hardening slag cement paste, we found that $CaSO_4$, whose content in cement as gypsum amounted to about 20 percent, disappeared from the liquid phase in 25–45 hr when the blast furnace slag contained about 20 percent of Al_2O_3 and in 70–115 hr when the content of Al_2O_3 amounted to about 10 percent. When $CaSO_4$ is present in the liquid phase, alumina does not appear in the solution or appears in quite inconsiderable amounts. Alumina appears in the liquid phase only after the disappearance of $CaSO_4$. Simultaneously there takes place also an increase of the calcium oxide content of the solution.

When finely divided basic granulated blast furnace slag interacts with calcium sulfate (different modifications) in the liquid phase in the presence of a small amount of alkali, there form calcium hydrosulfoaluminate $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$, calcium hydroaluminate $2CaO\cdot Al_2O_3\cdot 7H_2O$, and calcium hydrosilicate of the composition $3CaO\cdot 2SiO_2\cdot$aq. and, in the case of acid slag, calcium hydrosulfoaluminate and calcium hydrosilicate $2CaO\cdot SiO_2\cdot$aq. When the calcium oxide content of the liquid phase is not high and there are present large amounts of alumina in the slag, the formation of $2CaO\cdot Al_2O_3\cdot 7H_2O$ is also possible.

The formation of calcium hydrosulfoaluminate in sulfate-slag cement paste during mixing exhibits also in this cement a positive action creating the initial strength of the cement, and by its formation there develops the process of formation of other new compounds—calcium hydroaluminates and hydrosilicates—that stimulate a further growth of the strength of cement paste.

The character of the hardening processes of sulfate-slag cement depends on the concentration of free lime in the solution, the presence of magnesium hydroxide, and the amount of calcium sulfate added.

An alkaline medium is necessary for the normal hardening of sulfate-slag cements. In this respect the best addition is magnesium hydroxide, which corrodes the slag particles and thus communicates to them an increased activity. Practically, dolomite fired at 800–1100 °C is used for this purpose [12, 13]. In the case of basic slag the amount of lime introduced must be the least and therefore the dolomite is fired at about 800–900 °C, but in the case of acid slags it must be fired at 1,000–1,100 °C in order to attain also the decarbonation of calcium carbonate.[4]

The free lime from the dolomite in the latter case is necessary to supply calcium hydroxide for the reaction with the active silica of granulated blast furnace slags taking place during the mixing of the cement with water, leading to the formation of calcium hydrosilicate [14, 15, 16].

For the fulfilment of this condition it is necessary that not more than 3 percent of lime or about 7 percent of portland cement be present in the mixture of crushed granulated blast furnace slag and calcium sulfate, for calcium hydroxide is split off by the slag in a very inconsiderable amount and is quickly absorbed to form calcium hydrosulfoaluminate. This mechanism is confirmed by the experimentally established dependence of the crushing strength of sulfate-slag cement paste on the percentage of calcium oxide contained in the liquid phase (fig. 7).

Curve 1 corresponds to the crushing strength in kg/cm^2 of standard samples after 7 days hardening in water, curve 2 to that after 27 days under the same conditions of hardening.

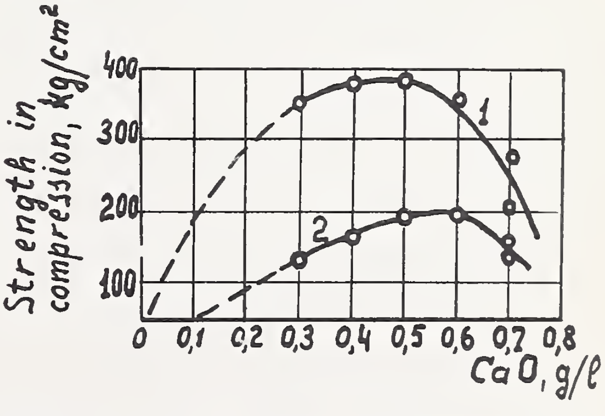

FIGURE 7. *Dependence of the crushing strength of sulfate-slag cement paste on the percentage of calcium oxide present in the liquid phase.*

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[4] $CaCO_3$ of dolomite fired at about 800–900 °C is not only a microfiller of cement, but in the hydration process it can react with C_3A with the formation of $C_3A\cdot CaCO_3\cdot 11H_2O$, which promotes the increase of strength of sulfate-slag cement (P. P. Budnikov, V. M. Kilbasov, A. S. Panteleev, Reports of the Acad. Sci. U.S.S.R., 1959, v. 129, No. 5, 1104; Silikattechnik 1960, No. 6, p. 271–272).

Because the velocity of binding of calcium oxide during the formation of calcium sulfoaluminate and hydrosilicate exceeds the velocity of dissolution of calcium hydroxide, the concentration of CaO in solutions decreases quickly, and the aluminates, when dissolving, form the hydrosulfoaluminate without swelling. As has been shown by our investigations, a higher solubility of calcium aluminates is attained at a calcium oxide concentration of 0.4–0.5 g/l [17].

The rate of increase of strength of cement paste depends on the chemical composition of the slag and the potential energy supply—the faster the molten blast furnace slag is cooled and the more calcium oxide and alumina it contains, the greater is the strength of sulfate-slag cement.

The chemistry of the hardening process of slag cements is influenced by the composition of the cement, its specific surface, the amount of water added for mixing, and the temperature of the medium.

In order to study the properties of sulfate-slag cement, two slags were taken whose chemical composition is shown in table 3.

Table 3. *Chemical composition of granulated blast furnace slags (in %)*

Oxides	Slag samples		Oxides	Slag samples	
	I	II		I	II
SiO_2	35.21	36.96	MnO	2.56	2.02
Al_2O_3	9.35	20.20	Fe_2O_3	1.43	1.26
CaO	46.41	34.10	SO_3	2.05	0.32
MgO	2.43	3.45	S	------------	0.21

To form cements, slag I was ground with 5 percent of dolomite burnt at 800 °C and 5 percent of anhydrite (gypsum burnt at 700 °C): and slag II was ground with 7 percent of dolomite burnt at 1,100 °C and 5 percent of anhydrite.

The fineness of grinding of the cements: residue on sieve 900 mesh/cm²—0.2-0.3 percent and on sieve 4,900 mesh/cm²—6-7 percent. The setting time of cement I: beginning 45 min, end, 1 hr 40 min; of II: beginning 2 hr 10 min, end, 3 hr 42 min.

In table 4 are shown the test data of the sulfate-slag cements in rammed samples (7.07×7.07×7.07 cm) from a 1:3 mortar when stored in water.

Table 4. *Crushing and tensile strength of sulfate-slag cements (mortar 1:3), kg/cm²*

Age	Cement I		Cement II	
	Crushing	Tensile	Crushing	Tensile
4 days	185	16.0	98	7.8
7 days	281	26.8	121	11.3
28 days	333	30.3	341	22.4
3 months	363	35.2	435	37.3
6 months	396	37.4	464	39.5
1 year	406	38.8	532	45.3
5 years	458	39.4	------------	------------
12 years	509	41.4	------------	------------

When acid blast furnace slags with an increased alumina content [5] was used, with 10 percent of anhydrite and 10 percent of burnt (at 900 °C) dolomite jointly ground, sulfate-slag cement was obtained that had the following strength characteristics in kg/cm² (numerator—tensile strength, denominator—crushing strength):

in 4 days	19.9/184
in 7 days	23.3/277
in 28 days	32.8/425
in 3 months	37.1/431.

Investigation data show that granulated blast furnace slags can be successfully used to obtain sulfate-slag cement of the 300–400 strength class [18].

For plastic mortars the strength characteristics of sulfate-slag cement are higher than for other cements.

In the case of wet grinding of blast furnace slags jointly with calcium sulfate or with 5 or 10 percent of lime in a ball mill, as the investigations have shown, a very plastic workable mass is obtained. The trial of the cement obtained from a plastic-consistency 1:3 mortar showed the possibility of obtaining cement paste with a strength limit of 200 kg/cm² and higher [19].

Based on investigations and factory practice, there has been established the following approximate dependence of the quality of sulfate-slag cement on the properties of the initial slag (table 5) [20].

Table 5. *Influence of the properties of the initial slag on the quality of sulfate-slag cement*

Kind of slag	Modulus		MnO	Possible strength class
	Basic	silicate		
			Percent	
Basic	>1	≦3.0	≦1.0	300–400
Basic	>1	3.0–4.0	≦1.5	200–300
Acid	0.90–1.0	≦2.0	≦1.0	400–500
Acid	.75–0.90	≦2.0	≦3.0	250–300
Acid	.70– .75	≦2.0	≦3.0	150–200

Sulfate-slag cement from granulated blast furnace slags with an elevated index with an MnO content of the order of 4 percent and higher has a lowered strength.

One of the causes of the decrease of strength of slag cements in the case of an increased MnO content in granulated blast furnace slags is obviously the formation in acid slags of manganous anorthite, $MnO \cdot Al_2O_3 \cdot 2SiO_2$, manganous cordierite $2MnO \cdot 2Al_2O_3 \cdot 5SiO_2$. and also the formation of a solid solution $2CaO \cdot SiO_2–2MnO \cdot SiO_2$ which is characteristic of basic slags.

On the other hand, the negative part played by MnO in blast furnace slags from manganous cast iron, from the point of view of their hydraulicity, is limited to an increase of waterproofness of vitreous slag matter.

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[5] Chemical composition of acid slags (in %): SiO_2, 28.60; Al_2O_3, 24.93; CaO, 41.25; MgO, 2.19; MnO, 0.60; FeO, 1.54; SO_3, 1.03.

Manganese has a further negative influence because the compound MnS present in granulated blast furnace slags, increasing in volume when interacting with water, creates inner stresses in the hardening cement and in this way lowers its strength.

Sulfate-slag cement is characterized by a high resistance to the destructive action of sweet, sea, and mineralized waters, considerably exceeding in this respect portland cement, pozzolanic portland cement, and slag-portland cement, and stands near to aluminous cement. This valuable peculiarity of sulfate-slag cement (clinkerless cement) is provided by the chemical composition of the cement and by the peculiar nature of the processes and products of its hardening.

The evolution of heat on account of the exothermal processes taking place during the setting and at the beginning of the hardening of sulfate-slag cement is considerably lower than in the case of aluminous, portland, and slag-portland cements. After 7 days of hardening of a normal mortar of a stiff consistency, the heat evolved is 15–26 cal/g, allowing this cement to be used successfully in massive concrete.

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Paper IV–S2. The Mineralogical Examination of Set Portland Cement*

H. G. Midgley

Synopsis

The methods used for the mineralogical examination of set portland cement at the Building Research Station are microscopy, differential thermal analysis, X-ray diffraction, infrared absorption spectrometry, and electron microscopy and diffraction. By a combination of the methods it is possible to get a semiquantitative estimate of the various constituents of the cement paste of neat cements, mortars, and concretes. Differential thermal analysis appears to be the most sensitive and most likely to give quantitative results for the calcium silicate hydrate. The results so obtained are indicative that the main calcium silicate hydrate formed is a gel-like phase related to tobermorite, probably with a $CaO:SiO_2$ ratio greater than 1.5. The calcium aluminates formed are C_4AH_x with varying water content, ettringite solid solutions, and low-sulfate sulfoaluminate. There seems some evidence that all these crystalline aluminates can be formed at any age and that kinetic conditions such as CaO and SO_3 concentrations at the C_3A crystal face may govern the phase produced.

Résumé

Les méthodes dont dispose la *Building Research Station* pour l'examen minéralogique de la prise du ciment Portland sont la microscopie, l'analyse différentielle thermique, la diffraction des rayons X, la spectrométrie d'absorption infra-rouge, et la diffraction et la microscopie électronique. En combinant ces méthodes il est possible de faire une évaluation semi-quantitative des constituants variés de la pâte de ciment des ciments purs, des mortiers et bétons. Il semble que ATD est la méthode la plus sensible et la plus susceptible de donner des résultats quantitatifs pour l'hydrate de silicate de calcium. Les résultats obtenus jusqu'à présent indiquent que le principal hydrate de silicate de calcium formé est une phase comparable à un gel semblable au tobermorite, avec un rapport de $CaO:SiO_2$ probablement plus grand que 1.5. Les aluminates de calcium formés sont C_4AH_x avec une teneur en eau variable, ettringite, et le sulfo-aluminate avec une teneur plus basse en sulfate. Certains faits semblent prouver que tous ces aluminates cristallins peuvent être formés à tout âge et que les conditions cinétiques telles que les concentrations en CaO et SO_3 à la facette du cristal peuvent régir la phase produite.

Zusammenfassung

Die Methoden für die mineralogische Analyse des erstarrten Portlandzements, die in der *Building Research Station* angewandt werden können, sind die Mikroskopie, die differentielle Thermalanalyse, die Röntgenbeugungsbestimmungen, die Ultrarotabsorptionsspektrometrie, die Elektronenmikroskopie und die Elektronenbeugung. Durch eine Kombination der Methoden ist man in der Lage, eine halbquantitative Abschätzung der Bestandteile der Zementpaste des Purzements, des Mörtels und des Betons vorzunehmen. Die differentielle Thermalanalyse scheint die größte Empfindlichkeit zu haben, sie gibt wahrscheinlich die besten quantitativen Ergebnisse für Hydrate des Kalziumsilikats. Die Ergebnisse, wie sie bis jetzt erhalten worden sind, besagen, daß das Haupthydrat des Kalziumsilikat, welches sich formt, eine gelähnliche Phase ist, die mit Tobermorit verwandt ist, und in der das Verhältnis $CaO:SiO_2$ vermutlich größer als 1.5 ist. Die gebildeten Kalziumaluminate sind C_4AH_x mit verschiedenen Wassergehalten, Ettringit und der gering sulfatige Sulfoaluminat. Vermutlich können sich alle diese kristallinen Aluminate in jedem Alter bilden; die kinetischen Bedingungen, wie die CaO- und SO_3-Konzentrationen an der Kristalloberfläche des C_3A beeinflussen vermutlicherweise die gebildete Phase.

Introduction

The mineralogical method of examining set portland cement has a long and important history. The use of the thin section and the petrographic microscope was described by Parker and Hirst [1][1], who also extended the work of dye absorption to help differentiate the cementitious phase, called by them gel. About the same time Brown and Carlson [2] carried out a very comprehensive petrographic study of set portland cement pastes. These two papers probably represent all the data that may be obtained by such methods.

Alternative methods were now needed to advance the knowledge of the mineralogy of set portland cement. Ordinary powder X-ray diffraction analysis had not proved very successful. Firstly, the cameras in normal use did not record low angles, and secondly, the diffraction patterns of any possible cement hydrate minerals were swamped by the patterns of the still remaining unhydrated cement minerals.

The next big step forward in technique for mineralogical examination of set cements came

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Building Research Station, Department of Scientific and Industrial Research, Watford, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

from Kalousek, who with Davis and Schmertz [3] in 1949 used the method of differential thermal analysis (DTA) for the first time. By this method these workers were able to identify in setting portland cement pastes the minerals ettringite, $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$, and $Ca(OH)_2$. Although in the same paper they investigated the thermograms given by synthetic calcium silicate hydrates, they were unable to use the DTA method to identify the calcium silicate hydrate in set portland cement.

Although a considerable amount of data was known [4–6] on the phase chemistry of the systems $CaO–SiO–H_2O$, $CaO–Al_2O_3–H_2O$, and $CaO–Al_2O_3–SO_3–H_2O$, it was not until 1947 that the team under Bernal began its work on the crystallography of the minerals of the system $CaO–SiO_2–H_2O$. This work, summarized by Bernal, Jeffery, and Taylor [7] and Taylor and Heller [8], led to an attempt to identify the calcium silicate hydrate in set portland cement. Nurse and Taylor [9] reported X-ray diffraction data on a number of set cements, indicating that the calcium silicate hydrate present was of the tobermorite type. The method of separation used was very involved and tedious, involving elutriation and continuous centrifuging in very large quantities of anhydrous alcohol. Taylor [10] later made a separation using only limited quantities of material and centrifuging in bromoform-benzene mixtures. By this method Taylor identified the calcium silicate hydrate as CSH I or II.

Another important method of investigation available is electron microscopy and diffraction, and although a large amount of work has been done on calcium silicate hydrates it is only recently that attention has been paid to set portland cement pastes or mortars. Gille, et al. [11] have investigated set portland cement pastes by replica methods and have identified the plates of calcium hydroxide. Grudemo [12], one of the most important workers in this field, has recently published pictures of calcium aluminate hydrate and calcium silicate hydrate from set portland cement pastes.

The other methods available for mineralogical examination—infrared absorption analysis, nuclear-magnetic-resonance spectrometry and microprobe technique—so far have not been used extensively to determine the mineralogy of set portland cements. Hunt [13] has given infrared absorption spectra of some of the cement minerals, and the author of this paper has used the method extensively and reports the results here for the first time.

Using the techniques described before, together with a much more refined X-ray diffraction method involving X-ray diffractometers instead of film cameras, Turriziani [14] and Copeland, Kantro, and Verbeck [15] have recently described the mineralogy of set portland cements.

This paper sets out the methods and results obtained in similar studies at the Building Research Station.

Methods of Investigation

Microscopy

Reflection microscopy is not yet of great value in investigating the mineralogy of set portland cements, although the method is of some value in determining the microhardness of the minerals. The technique for preparing polished surfaces of set portland cements is under investigation, and a method of preparing good surfaces has been evolved. The method is simple—the section is cut on a high speed, resin-bonded diamond wheel, and the surface is then lapped on a similar diamond high speed plate.

For thin-section work, the required section should be as thin as possible; by the usual techniques sections of about 30μ are possible, but by a technique evolved by Smith [16] at the Building Research Station sections of about 10μ thickness have been prepared. Farran [18] has used microscopy in his investigations into the binding of cement paste and aggregate, but he was not able to deduce anything of the mineralogy of set portland cement from the microscope.

X-ray Diffraction

X-ray diffraction methods have been used extensively in the study of set portland cement pastes, mortars, and concretes. Most of the work has been done using cylindrical Debye-Scherrer cameras of varying radii, but all capable of recording at least 20A with copper K-alpha radiation. More recently some work has been done using a recording diffractometer. This latter method gives greater resolution and gives a better idea of quantities of identifiable minerals, but is not as good as photographic techniques in differentiating weak reflections from background.

An adjunct to X-ray diffraction identification is the possibility of concentrating the cementitious minerals. The method found most effective with concretes and mortars is to crush the sample with an iron pestle and mortar and sieve the fragments first through a 14-mesh sieve; further crushing and passing through a 100-mesh sieve removes a considerable quantity of the aggregate. This method of course precludes the quantitative determination of the cementitious minerals.

A further concentration of the cementitious phases has also been attempted using the technique described by Taylor [10]. This involves centrifuging of a benzene-ground sample in appropriate bromoform-benzene mixtures to produce a light fraction in which the cementitious hydrates are concentrated.

Differential Thermal Analysis

The differential thermal analysis (DTA) of set portland cements has been carried out in an apparatus especially designed for the purpose. The furnaces are of nichrome winding capable of reaching 1,000 °C; they are programed to give better than 10/min ±1 °C accuracy, the temperature of the sample and the amplified difference temperature between the sample and the inert body are recorded on a 0–50 mv, potentiometric recorder. The crucible and thermocouple setup received special attention (figure 1). The crucibles used were ceramic (fired alpha alumina), which were found to give better resolution than metal crucibles. By using two thermocouples, one in the sample and one in the inert body, a high degree of symmetry was obtained. The thermocouples found to be best for this work were chromel-alumel. Care was also taken to match the heat properties of the sample and the inert body. For most of the work about 0.7 g of sample was used. By these methods it has been possible to resolve the low-temperature endotherm around 120 °C into three peaks (figure 2). This resolution is repeatable, and full reliance can be given to the resolution.

Infrared Absorption Spectrophotometry

For these investigations a commercial spectrometer, recording between 2.5- and 15-μ wavelength, was used.

Three methods of sample preparation were used. In the first, about 10 mg of sample was pressed with about 1 g of anhydrous KBr into a disc of 13-mm diameter by means of a vacuum press[17] This method was successful for anhydrous minerals, but there appeared to be interfering chemical reactions when hydrates were tried.

The second method was to mill the sample with an inert oil and make a thin film of the suspension between sodium chloride plates. This method gave good resolution but strong absorptions at 3.6, 7.0, and 7.4 μ due to the oil interference with the pattern.

The third method was to mill the sample with isopropyl alcohol. A sample was pipetted onto a NaCl disk and the alcohol allowed to evaporate. This method gave very good resolution at wavelengths greater than 5 μ, but owing to the specular reflection due to the difference in retractive index between the sample and air, there was a considerable absorption at less than 5 μ. This reflection, however, did not interfere with that part of the spectrum (around 10 μ) of most value in differentiating between the different minerals.

Figure 1. *DTA ceramic crucibles and holders showing two symmetrically disposed thermocouples.*

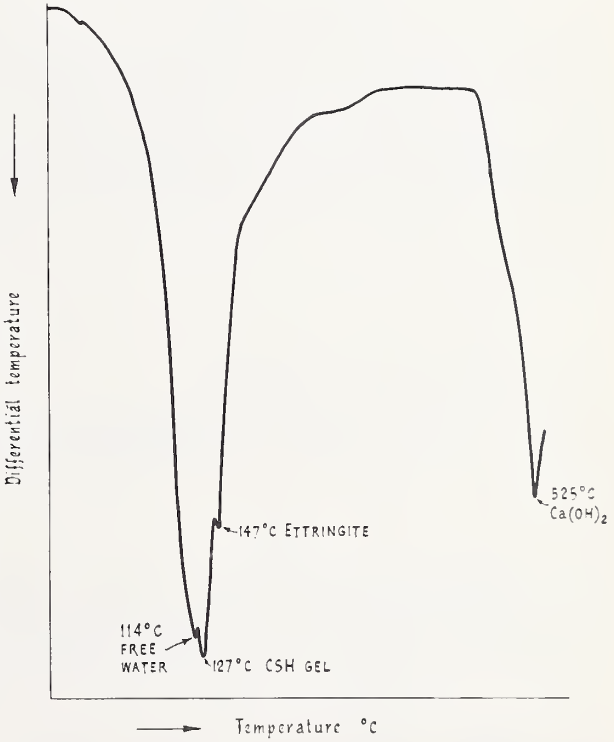

Figure 2. *Differential thermogram of set portland cement.*

Experimental Results

Microscopy

With the advent of very thin sections prepared by the Smith method, a new interest has been aroused in thin-section microscopy. Sheaths of isotropic gel have been seen around $3CaO{\cdot}SiO_2$ and $2CaO{\cdot}SiO_2$ grains, as is shown in figure 3. These are taken to be reaction rims of what is probably the calcium silicate hydrate gel phase.

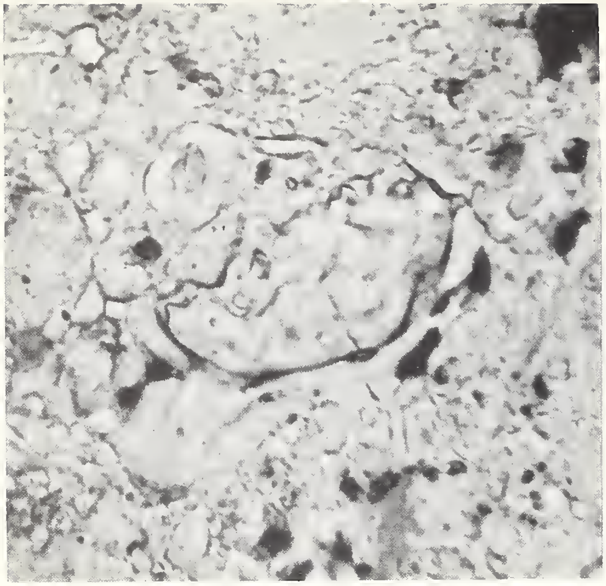

Figure 3. *Photomicrograph of thin section of set portland cement paste (normal water-cement ratio) showing rim of calcium silicate hydrate gel around silicate grains.*

X-Ray Diffraction

By film techniques it is possible to detect the presence or absence of the unhydrated minerals; the data used are those of Midgley [19]. Of the hydrate minerals, ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot aq.$–$3CaO \cdot Al_2O_3 \cdot 3Ca(OH)_2 \cdot aq.$) can be detected by its reflection at 9.8A, and the solid-solution composition can be detected by a change in the value of this reflection [20], although DTA would be more accurate. The low-sulfate sulfoaluminate $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ is detected by its reflection at 8.92A, and the carbonate-aluminate $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 12H_2O$ can be detected by the change in value of the reflection to 7.59A. The $4CaO \cdot Al_2O_3 \cdot aq.$ series [21] can be detected by their reflection in the region of 8.05A. Calcium hydroxide and calcium carbonate are easily recognized from their patterms.

Calcium silicate hydrates have not been identified by this method so far. The only strong reflection for CSH I or II at 3.06A is very close to the strong reflections of alite and calcite, so that, if there is more than a trace of either of these minerals, any possible CSH reflection is masked.

In counterdiffractometry the aluminate and aluminate salt hydrates are detectable using the same reflections as by film camera technique, but it is also possible to make quantitative estimates of the amounts.

Figure 4 is the trace given by a neat cement paste 7 days old. The ettringite peak at 9.1 °2θ (d=9.7A) and the C_4AH_{13} peak at 10.84 °2θ (d=8.13A) are clearly seen. Similarly, figure 5 is for a neat cement paste 3 years old. Here the ettringite peak is seen again at 9.1 °2θ and the aluminate peak is spread between 10.4° and 11.0 °2θ, suggesting that more than one hydration state is present.

In both these samples no aggregate was used, and great care was taken to keep CO_2 away so that the amount of calcium carbonate present is very small. So in the case of the cement paste 3 yr old, which is fully hydrated, calcium silicate

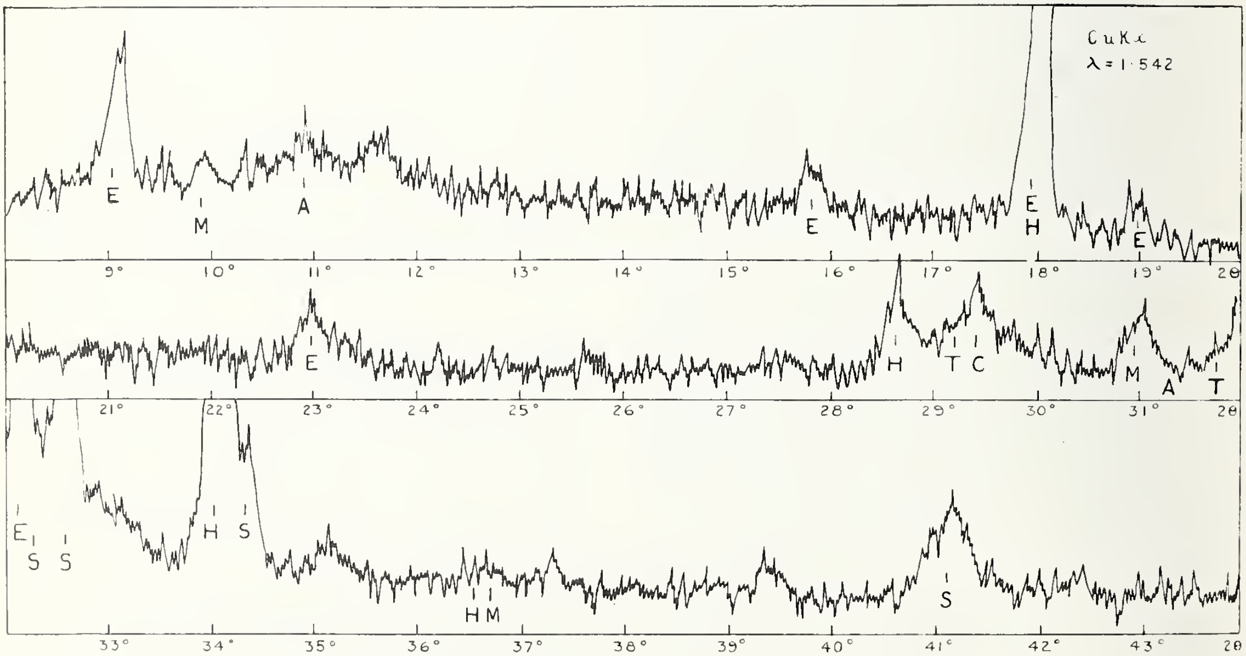

Figure 4. *X-ray diffractometer trace of set portland cement, neat; w/c 0.45.*
Made 2/6/60; examined 8/6/60 (see figure 5 for key).

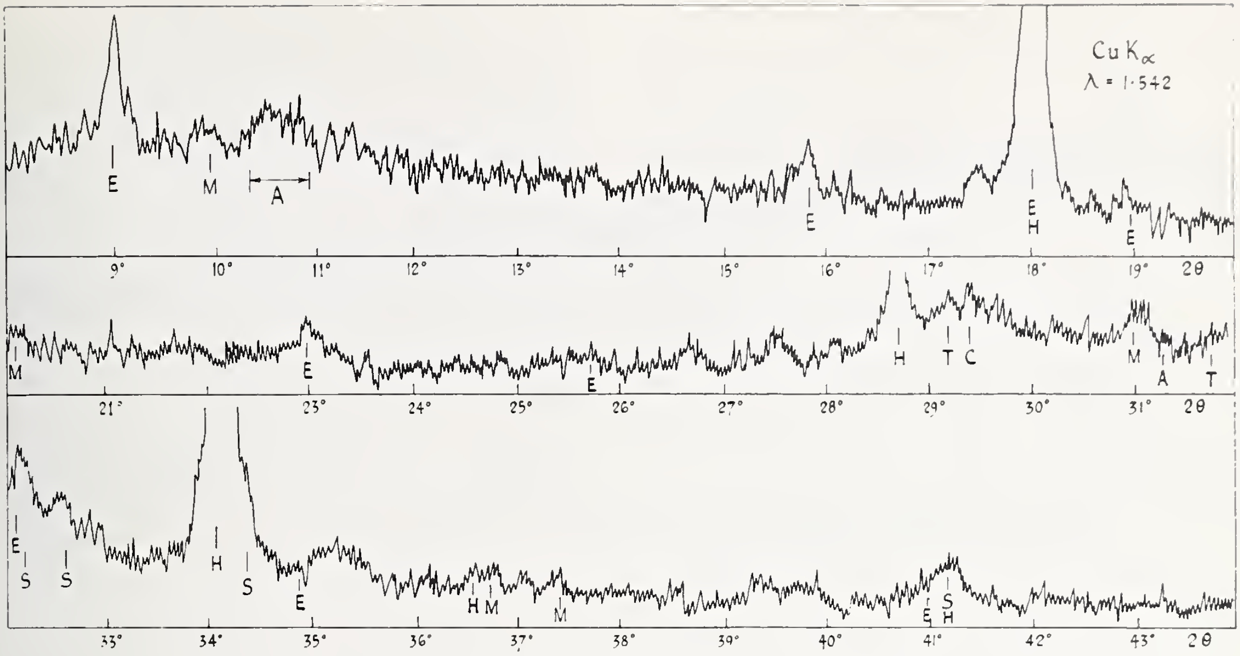

FIGURE 5. *X-ray diffractometer trace of set portland cement, neat; w/c 0.45.*

Made 10/4/57; examined 4/6/60. Key: E=Ettringite, M=$C_3A\cdot CaSO_4\cdot 13H_2O$, H=$Ca(OH)_2$, T=CSH, C=$CaCO_3$, A=C_4AH_x, S=βC_2S, L=Alite, Q=Quartz.

hydrate is detected by the 3.06A reflection at 29.2 °2θ (fig. 5). Even in this sample where only a very small quantity of anhydrous silicate β-$2CaO\cdot SiO_2$, is detected the peak size for the CSH phase is disappointingly small.

The diffraction trace of the sample 7 days old shows that the CSH phase is undetectable owing to the presence of beta dicalcium silicate.

As the samples referred to above were stored in CO_2-free atmospheres, there is no calcite interference. In normal mortars and concretes CO_2 will not be absent, and figure 6 shows what happens when a 1:3 mortar is stored without precautions. After 3 and 6 days water storage the possible detection of CSH at 29.2 °2θ (d=3.06A) is masked by the alite peak (L) at 29.55 °2θ (d=3.03A). Prolonged storage in conditions which would allow carbonation gives patterns such as shown at 3 and 6 months. Here any possible detection of CSH is masked by the very strong calcite peak at 29.4 °2θ (d=3.04A).

Similar results are obtained from the cement fraction extracted from a concrete, figure 7. The concrete was from a roadway and was about 4 yr old. The diffraction pattern shows that ettringite, $Ca(OH)_2$, and calcite, together with quartz from the aggregate, may be detected.

Taylor [10] has shown that a concentration of the hydrate minerals is possible, but repeated attempts by the author and some of his colleagues have failed to repeat Taylor's results.

Recently, Fletcher [22] has modified the method and made an extraction. The method is similar to Taylor's but after grinding the cement in benzene the suspension is put into a centrifuge

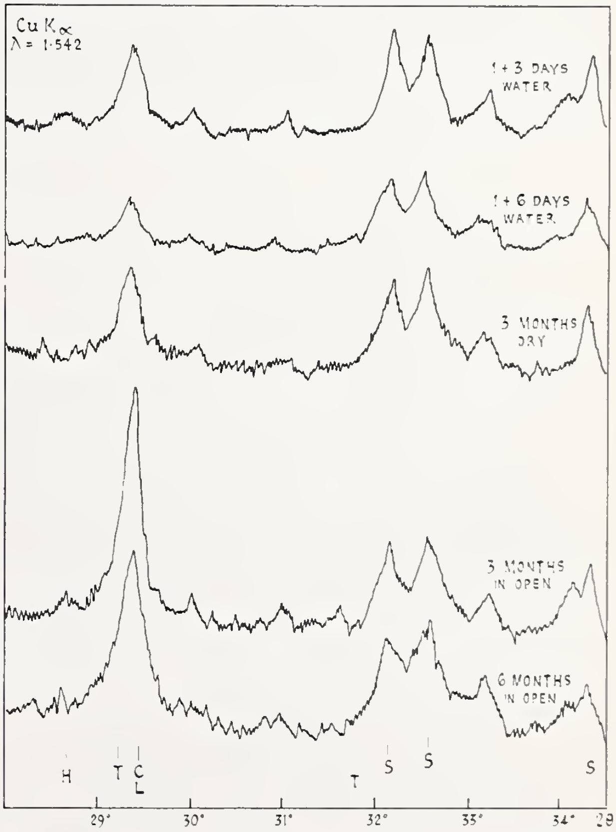

FIGURE 6. *X-ray diffractometer trace of cement fraction from portland cement mortars.*

1:3 standard sand; w/c 0.52 (see figure 5 for key).

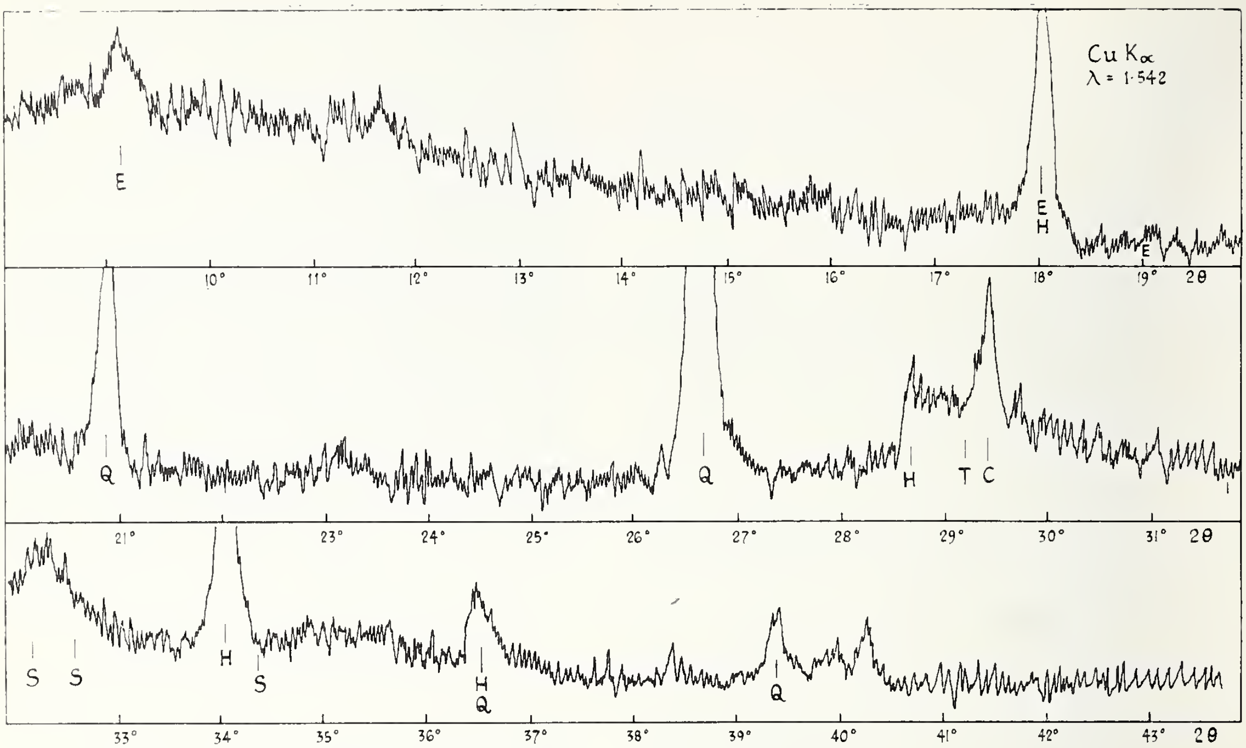

FIGURE 7. *X-ray diffractometer trace of cement fraction from concrete.*
(See figure 5 for key.)

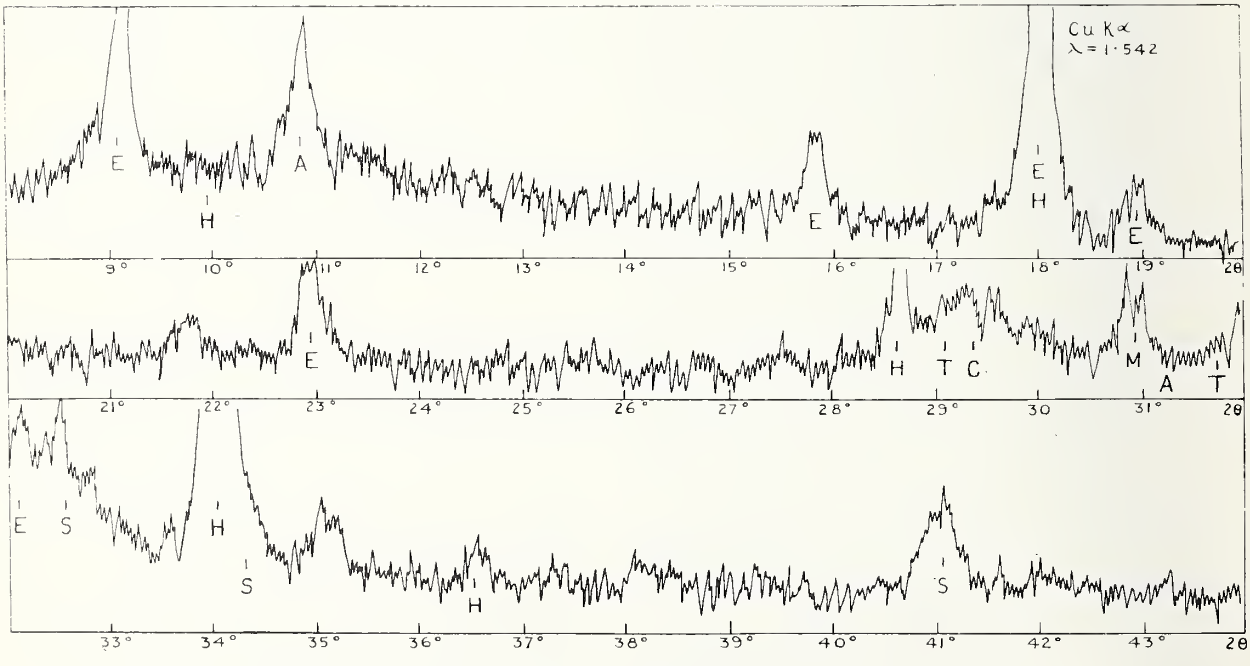

FIGURE 8. *X-ray diffractometer trace of set portland cement, neat; w/c 0.45.*
Made 2/6/60; examined 8/6/60. Light fraction from bromoform-benzene S.G. 1-78 (see figure 5 for key).

tube and drops of bromoform added until a separation is effected. The light fraction contains the concentration of hydrates. In the experiments reported here the specific gravity of the liquid used was 1.78, much lower than that used by Taylor. These experiments seem to suggest that each separation has to be taken on its own and a suitable liquid density determined by trial and error.

A diffraction pattern obtained from such a separation is given as figure 8. This sample is the light fraction of the same cement as shown in figure 3, a neat portland cement paste 7 days old. The C_4AH_{13} is considerably concentrated, and to a lesser extent the ettringite and the calcium hydroxide, but there does not appear to be any concentration of the CSH phase. The beta dicalcium silicate is reduced.

By X-ray methods it is therefore possible to detect the calcium aluminate and aluminate salt hydrates, $Ca(OH)_2$, and $CaCO_3$, and in favorable circumstances the CSH phase may be just identified.

Differential Thermal Analysis

The problems associated with the DTA of set portland cements are the interpretation of the low-temperature endotherms, for, as can be seen from figure 2, the endotherm is made up of three peaks. The temperatures of the peaks on DTA's are known to vary with quantity of mineral present, and it has been suggested by various authors, Keith and Tuttle [23] for example, that the characteristic temperature of a DTA peak should be the inflection point on the low-temperature side of the peak. This point is found to be consistent irrespective of amount. In the case of multiple peaks such as those given by a set portland cement, the inflections of the second and third peaks are not measurable, and the only easily measured parameter is the peak temperature.

If the peak temperature is plotted against the logarithm of the peak area, for reasonable dilutions, a straight line is obtained. This plotting has been done in figure 9 for the important constituents likely to occur in a set portland cement. The ettringite (pure end member $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}aq.$), C_4AH_{13}, and $C_3A{\cdot}CaSO_4{\cdot}aq.$ were prepared in the normal way. The free water was ordinary distilled water added to alpha alumina in the DTA crucible. (In all cases reported in this paper, alpha alumina was used as diluent.) The phase labeled tobermorite gel caused some difficulty, for although the middle of the three peaks in figure 2 was thought to be due to a calcium silicate hydrate [24, 25], some difficulty was experienced in preparing a synthetic sample.

Calcium silicate hydrate I prepared by double decomposition and by shaking silica sol with $Ca(OH)_2$ produced gels which contained very large quantities of free water, giving peaks on the DTA which agreed with the "free water" line on the graph. All attempts to dehydrate the sample by drying at various humidities caused the sample to crystallize and produce tobermorite which was well crystallized, that is, gave good basal spacings at about 11A on an X-ray diffraction diagram.

The only sample of calcium silicate hydrate which gave an endothermic peak anywhere near the middle of the three endotherms found in set portland cement (fig. 2) was CSH II. The sample was prepared by hydrating pure C_3S for 2 yr in a paste at room temperature. The sample was analyzed for $Ca(OH)_2$ and $CaCO_3$ by DTA and thermogravimetry, and the remainder was assumed to be calcium silicate hydrate of the formula $1.77CaO{\cdot}SiO_2{\cdot}3.00H_2O$. ($CaO/SiO_2=1.77$). The X-ray pattern is of a poorly crystallized tobermorite type, reflections occurring only at 3.06, 2.98, and 1.83A. This mineral is equivalent to the CSH II of Taylor [26] and the tobermorite gel of Midgley and Chopra [24, 25].

Using the results obtained from the pure synthetic minerals and the graph in figure 9, it is possible to interpret the DTA thermograms of set portland cements.

Figure 10 shows the interpretation of the DTA thermogram given by a portland cement paste 14 days old. The scale of the curves given for the pure substances has been adjusted so that the peaks are of about the size of those given by the minerals in set portland cement. From this diagram it may be seen that free water, tobermorite gel (CSH II), ettringite, and $Ca(OH)_2$ may be detected. (In these experiments no attempt has been made to determine the ettringite composition by the method of Midgley and Rosaman [20].)

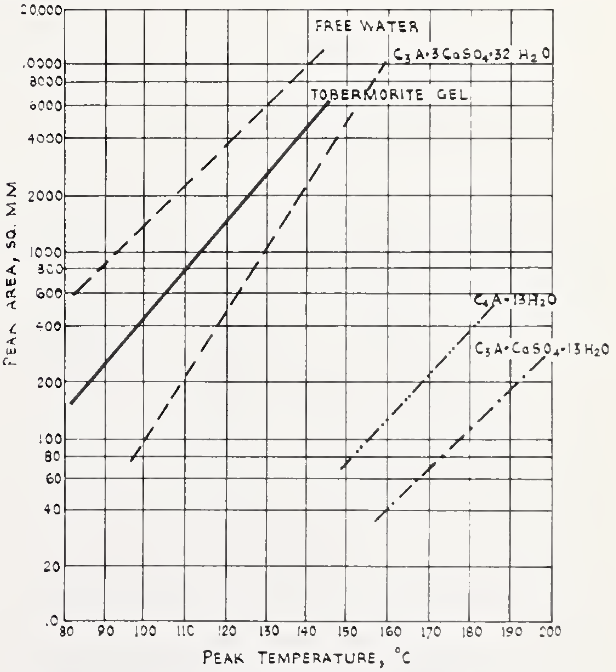

FIGURE 9. *Relation between peak temperature and peak area.*

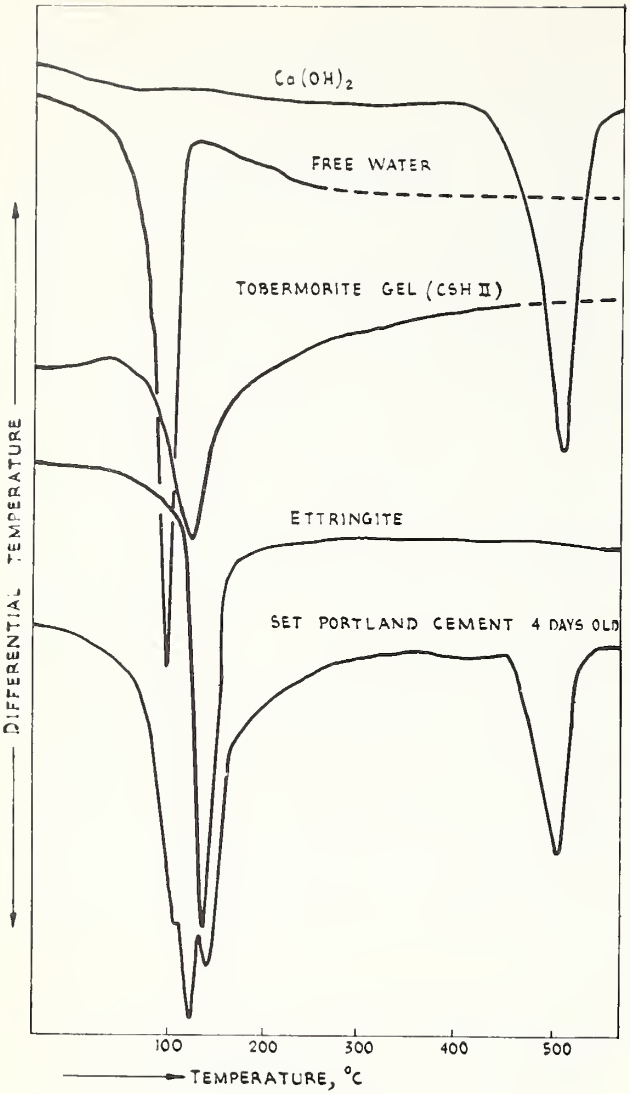

FIGURE 10. *Differential thermograms of set portland cement and constituents.*

A similar interpretation is shown in figure 11 for a portland cement paste 1 yr old, where tobermorite gel, ettringite, and low-sulfate sulfoaluminate are detected.

Now that it is possible to identify the peaks on a DTA, some quantitative estimate of the minerals present can be made by setting up calibration curves for the DTA apparatus, relating peak area to mass of mineral. This calibration has been done for all the important constituents mentioned so far. There is one serious difficulty not wholly overcome; that there is no simple way of determining the constituent parts of a triple peak. The method used in this paper is to construct graphically with reference to standard peaks the two outside peaks (free water and ettringite) giving the remainder as tobermorite gel. This method, although not very precise, is the best available at the moment, and has been employed on a series of setting portland cements stored at 18 °C in water, with the results shown in table 1.

TABLE 1. *Weight percent of cement hydrate minerals in a hydrating 1:3 mortar, w/c 0.52*

Age	Wt percent of		
	tobermorite	ettringite	Ca(OH)$_2$
1 day	1	10	9
3 days	2	35	10
7 days	14	27	10
28 days	18	28	8

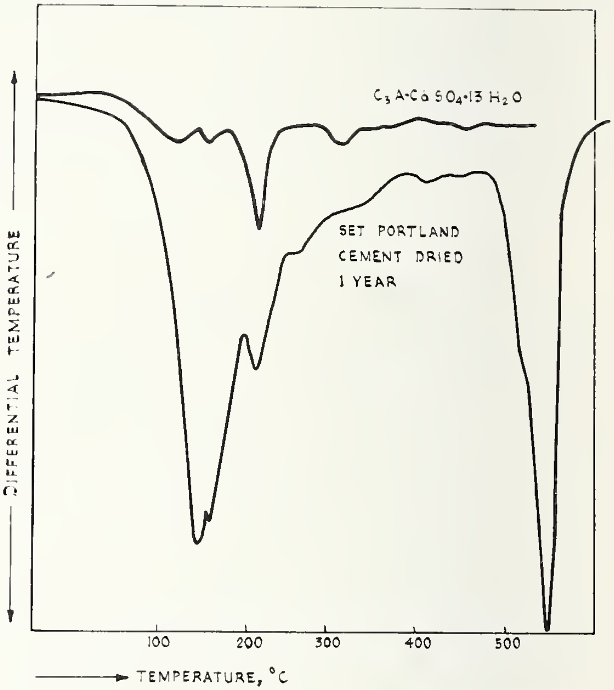

FIGURE 11. *Differential thermogram showing presence of* $C_3A \cdot CaSO_4 \cdot 13H_2O$ *in set portland cement.*

Infrared Absorption Spectroscopy

Absorption curves for all the compounds likely to be met in set portland cement have been prepared. These curves have been obtained for the four main components of portland cement clinker, C_4AF, C_3A, C_2S, and C_3S, shown in figure 12; for gypsum, and hemihydrate, figure 13; and for quartz, MgO, CaO, Ca(OH)$_2$, and calcite, in figure 14. The absorption spectrograms for some of the possible calcium silicate hydrates—Flint's CSH (A), C_2S gamma hydrate, C_2S beta hydrate, and C_2S alpha hydrate—are given in figure 15, C_3SH_2 and tobermorite plus afwillite in figure 16, and crystalline tobermorite and tobermorite gel in figure 17. The spectra for the two important aluminate hydrates are given in figure 18.

The data published here for the first time agree well with the data of Hunt [13] given in his as yet unpublished thesis.

The absorption spectrum of a set portland cement paste is given in figure 19. It is possible to identify the contributions of the various minerals as follows:—unhydrated C_3S by its peak at 10.5 μ; tobermorite gel by its peak at 10.0 μ; (ettringite by its peak at 9 μ, and also possibly calcite from the peak at 11.3 μ. The tobermorite peak is distinguished from the other calcium silicate hydrates by the simplicity of the peak at 10 μ and also by the presence of the double peak at 6.6 and 7.1 μ. Both Hunt [13] and Kalousek and Roy [27] have observed that the ratio of the peak absorption at 7 μ to that at 10 μ is related to the $CaO:SiO_2$ ratio of the tobermorite. Where the 7-μ peak is almost equal to the 10-μ peak, the $CaO:SiO_2$ ratio is highest.

The evidence from the absorption curve of set portland cement 4 days old is that the tobermorite has a high $CaO:SiO_2$ ratio.

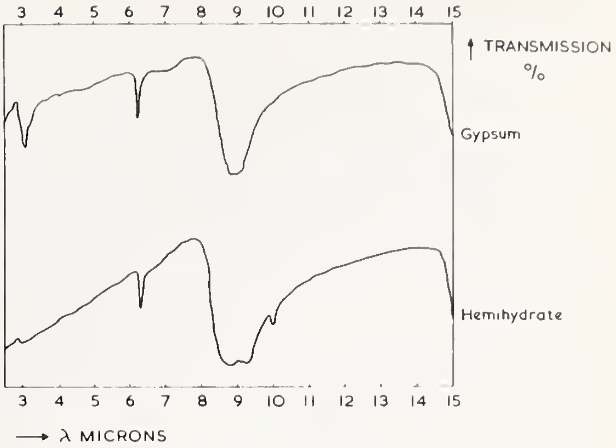

FIGURE 13. *Infrared absorption curves.*

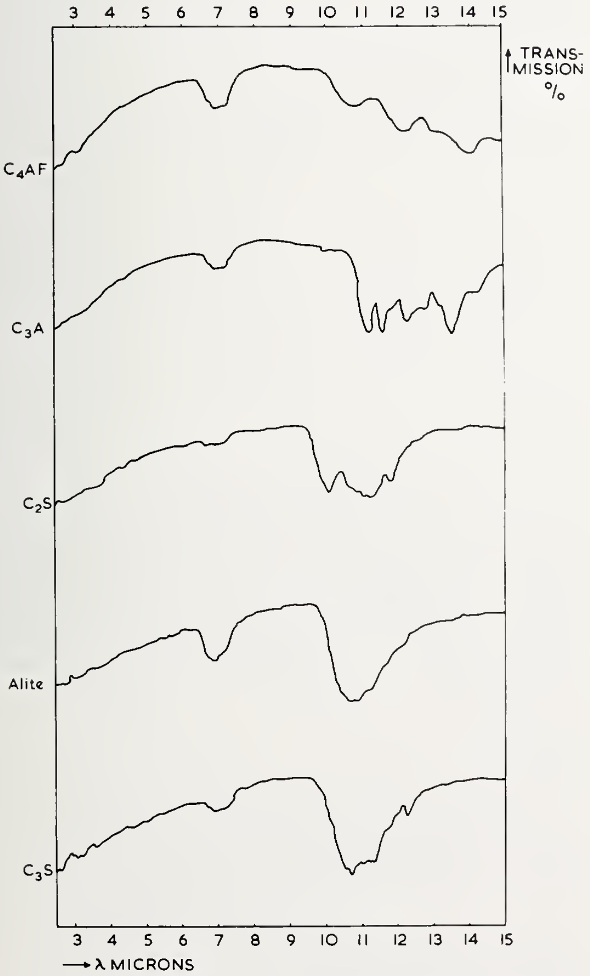

FIGURE 12. *Infrared absorption curves.*

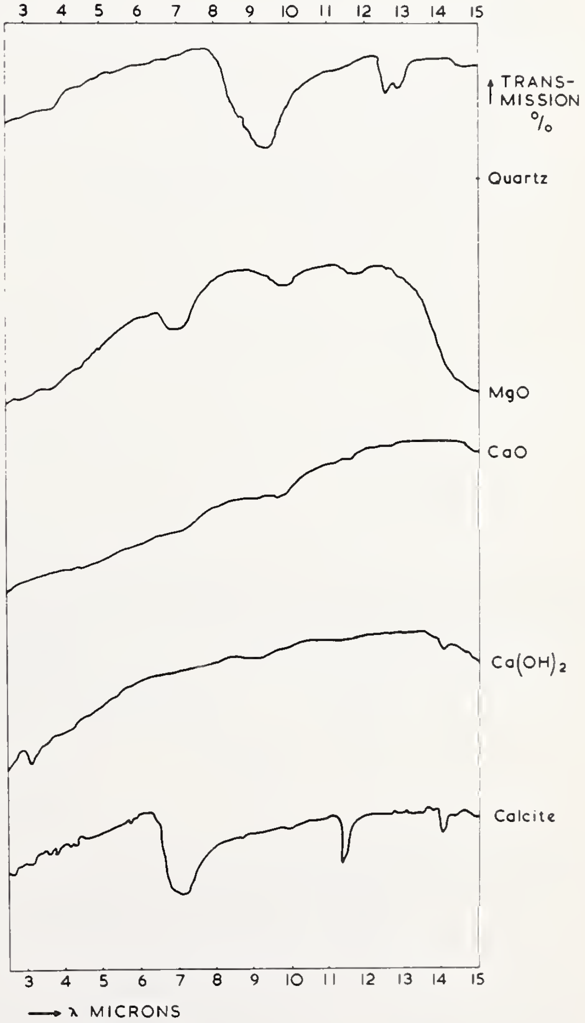

FIGURE 14. *Infrared absorption curves.*

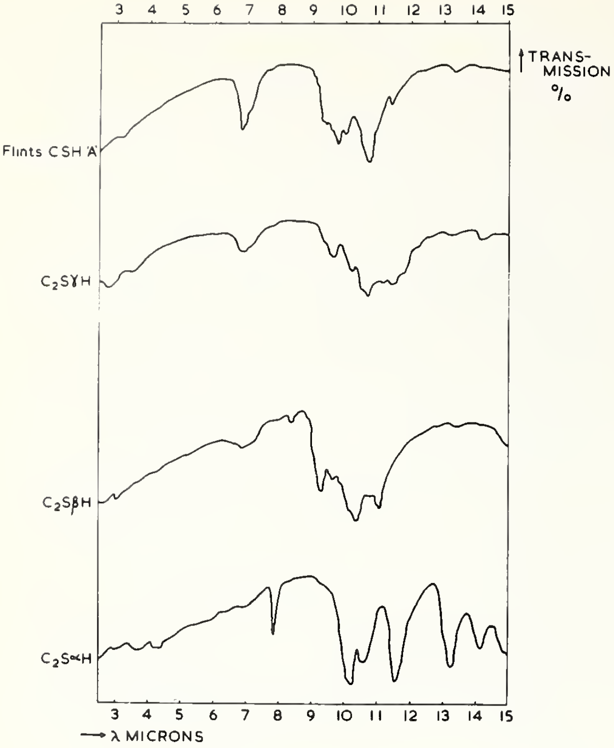

Figure 15. *Infrared absorption curves.*

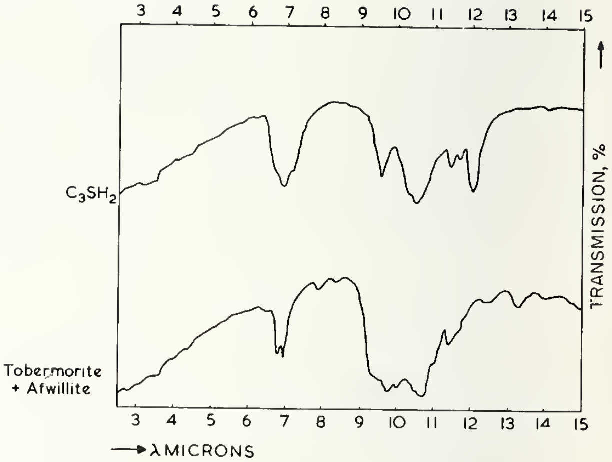

Figure 16. *Infrared absorption curves.*

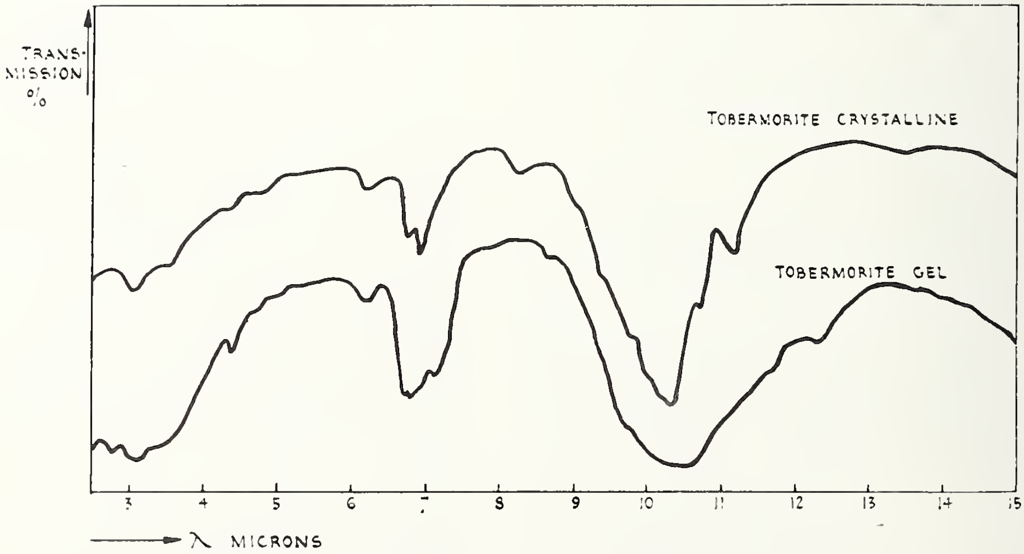

Figure 19. *Infrared absorption curve of set portland cement.*

FIGURE 17. *Infrared absorption curves.*

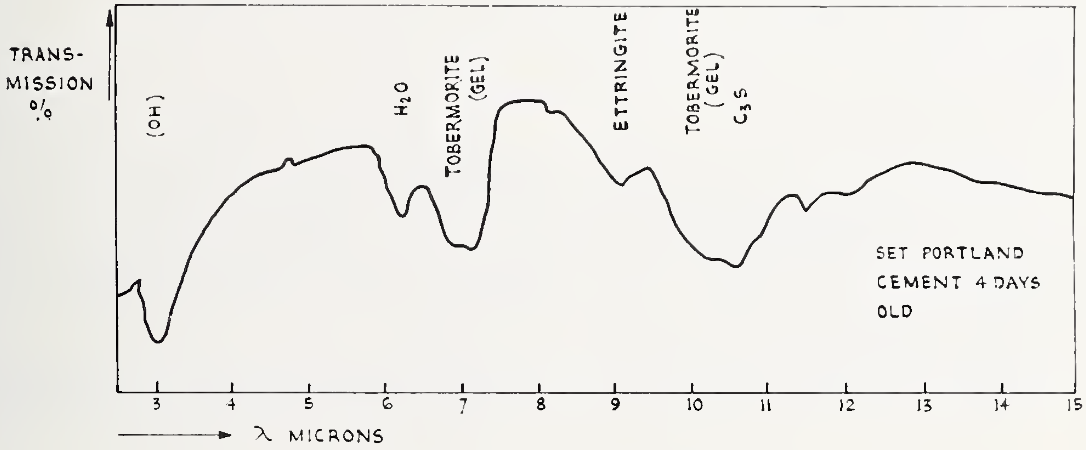

FIGURE 18. *Infrared absorption curves.*

Mineralogy of Set Portland Cements

All the various methods of examining the set portland cement pastes seem to indicate that the main calcium silicate hydrate formed is a gel-like phase related to tobermorite, probably with a $CaO:SiO_2$ ratio greater than 1.5; the calcium aluminates formed are C_4AH_x with varying water, ettringite, and low-sulfate sulfoaluminate. There seems some evidence that all these crystalline aluminates can be formed at any age, and that kinetic conditions, such as CaO and SO_3 concentrations at the C_3A crystal surface, may govern the phase formed.

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Discussion

H. Dutz

I will make a brief discussion of the very interesting paper of Midgley.

In the infrared spectrum of calcium hydroxide in figure 14, most of the sample must have consisted of $CaCO_3$. The absorption bands at 7, 11.4, and 14 μ are typical of $CaCO_3$. It is very difficult to get a calcium hydroxide free of carbonate. Therefore, the relation of the absorption bands in figure 19 based on that examination is partly incorrect.

(Editor's note: The comments by Dr.-Ing. Dutz are applicable only to the original version of the paper presented at the Symposium. The author subsequently submitted a corrected copy of figure 14, in which a new absorption spectrum for $Ca(OH)_2$ was substituted.)

Paper IV–S3. Nuclear Magnetic Resonance Study on Hardened Cement Paste*

K. Watanabe and T. Sasaki

Synopsis

To study the hydration of cement and calcium silicate, the nuclear-magnetic-resonance (NMR) absorption method was used. In measurement, samples were cooled from room to liquid nitrogen temperature.

In NMR absorption curves of cement paste cured for 1 day, two peaks were observed during cooling. The inner peak showed the same behavior as that obtained when free water was cooled, and the outer one was similar to that of hydrate water. Further, in this case the peak could be divided into three parts. It seems that these parts correspond to free, adsorbed, and combined water, respectively.

The peak for free water decreased gradually with increase in curing period. In the paste cured for 2 months, two peaks were not observed. This result seems to indicate that the free water has almost disappeared.

The amount of combined water in the paste was determined by integration of the curve. The results obtained were compared with those obtained by the method of Powers. It was found that there are slight differences between these results.

The results obtained by measuring the water-vapor pressure of cement paste showed a similar tendency to those obtained by NMR experiments.

Résumé

Pour étudier l'hydratation du ciment et du silicate de calcium, la méthode d'absorption de la résonnance magnétique nucléaire (RMN) a été utilisée. Dans la mesure, des échantillons furent refroidis de la température de laboratoire à celle de l'azote liquide.

Dans les courbes d'absorption RMN de la pâte de ciment conservée pendant un jour, deux maxima furent observées durant le refroidissement. Le maximum intérieure indiquait le même comportement que celui obtenu dans le cas du refroidissement de l'eau libre, et le maximum extérieure était semblable à celle des hydrates. De plus, dans ce cas-ci on peut diviser le maximum en trois parties. Il semble que ces parties correspondent respectivement à l'eau libre, adsorbée, et combinée.

Le maximum pour l'eau libre diminuait peu à peu avec l'augmentation de la période de conservation. Dans la pâte conservée pendant 2 mois, on ne pouvait pas observer les deux maxima. Il semble que l'on puisse attribuer ceci au fait que l'eau libre est alors presque disparu.

De plus, la quantité d'eau combinée dans la pâte fut déterminée par l'intégration de la courbe. Les résultats obtenus furent comparés à ceux obtenus par la méthode de Powers. On trouva qu'il y a de légères différences entre ces résultats. Les résultats obtenus en mesurant la tension de vapeur de la pâte de ciment indiquaient une tendance semblable à ceux obtenus par l'expérience RMN.

Zusammenfassung

In der Erforschung der Hydratation des Zements und des Kalziumsilikats wurde die kernmagnetische Resonanzabsorptionsmethode benutzt. Während der Messungen wurden die Proben von Zimmertemperatur bis zur Temperatur des flüssigen Stickstoffs gekühlt.

In den Resonanzabsorptionskurven der Zementpasten, die für einen Tag erhärtet worden waren, wurden zwei Extremalwerte während der Abkühlung gefunden. Das innere Maximum war dasselbe wie das, welches erhalten wird, wenn freies Wasser abgekühlt wird; das äußere Maximum war dem des Hydrats sehr ähnlich. In diesem Falle zeigt das Maximum auch eine Feinstruktur; es besteht aus drei Teilen, die scheinbar bzw. dem freien, dem adsorbierten und dem gebundenen Wasser zugeordnet werden können.

Das Maximum für freies Wasser bekam langsam kleiner, wenn die Erhärtungszeit verlängert wurde, und in Pasten, die für 2 Monate erhärtet waren, wurden die beiden Maxima nicht mehr beobachtet, was so erklärt werden muß, daß das freie Wasser dann vollständig verschwunden ist.

Der Betrag des gebundenen Wassers in der Paste wurde auch durch Integration der Kurve bestimmt. Die Ergebnisse, die man auf diese Weise gewann, wurden mit denen verglichen, die Powers veröffentlicht hatte. Ein geringer Unterschied in den beiden Ergebnissen wurde gefunden.

Die Ergebnisse der Dampfdruckmessungen der Zementpasten stimmten im großen Ganzen mit denen der kernmagnetischen Resonanzabsorption überein.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Central Research Institute, Ube Industries, Ltd., Ube-Shi, Yamaguchi-Ken, Japan.

Introduction

Nuclear magnetic resonance (NMR) absorption has recently been considered a useful method for studying the properties of water. Kawachi, Murakami, and Hirahara [1][1] reported that the amount of combined water in set cement can be determined by analyzing the NMR curve, and French and Warder [2] investigated the rate of hydration of cement by measuring the amplitude of the NMR curve. In these experiments, samples were cooled from room to liquid nitrogen temperature. The results obtained were compared with those obtained by the method of Powers [3].

Apparatus and Method

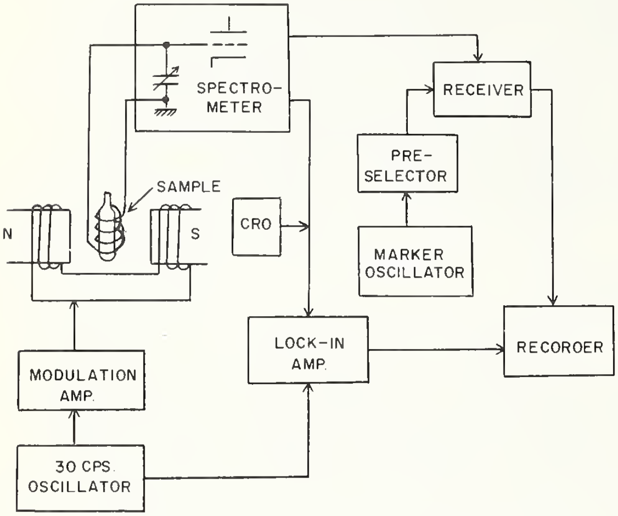

Figure 1. *Schematic diagram of NMR apparatus.*

The apparatus used consists mainly of a permanent magnet and a Pound-Watkins type spectrometer [4]. The magnetic field is about 6,500 gauss, its homogenity is 0.2 gauss/cm, and the frequency at the middle point of measurement is about 28 Mc. The schematic diagram and photograph of the apparatus are shown, figures 1 and 2, respectively.

The experiment was performed by the sweeping method of oscillation frequency. To cool the sample, liquid nitrogen was used. First, the change in the line-width of the absorption curve of water during cooling was examined. Subsequently, similar experiments were also made on cement paste and calcium silicate hydrate. Some of the results obtained have been reported previously [5].

Water

Distilled water containing a small amount of liquid extracted from cement paste was used. The line-width of the absorption curve of the water down to about −80 °C is similar to that at room temperature, but during further cooling, the line-width broadens suddenly, becoming about 11 gauss at the liquid nitrogen temperature.

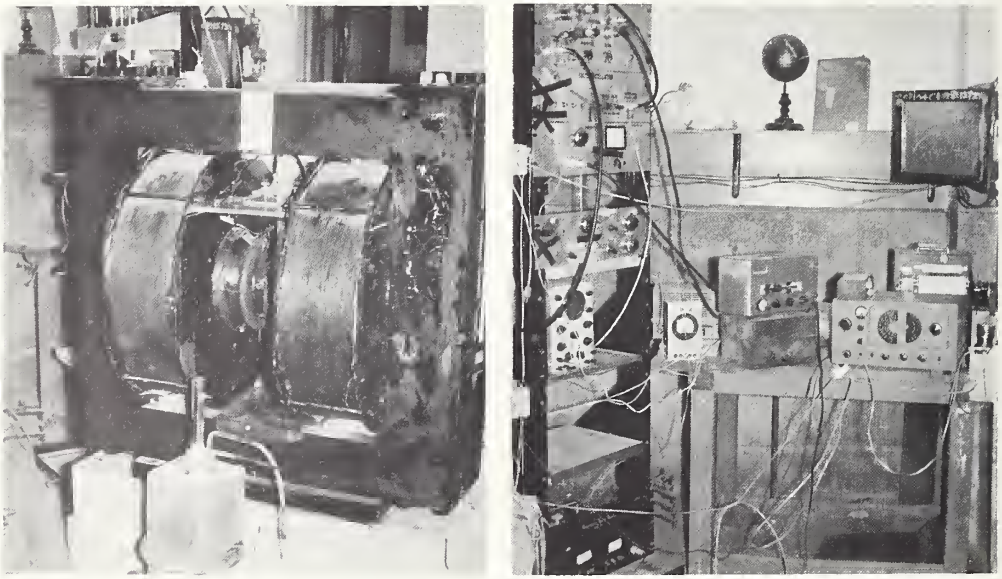

Figure 2. *NMR apparatus.*

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[1] Figures in brackets indicate the literature references at the end of this paper.

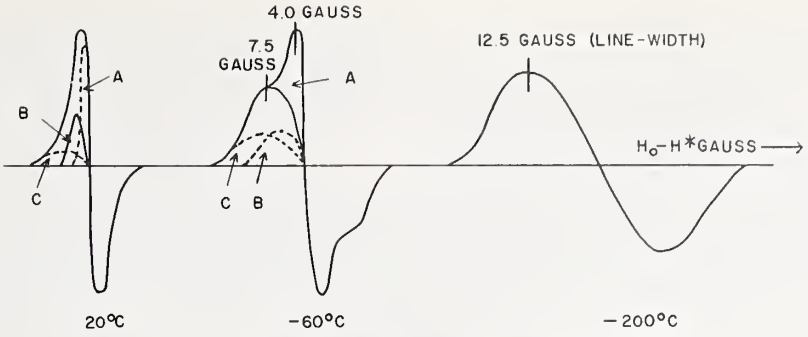

FIGURE 3. *NMR absorption curves of cement paste cured for 1 day.*

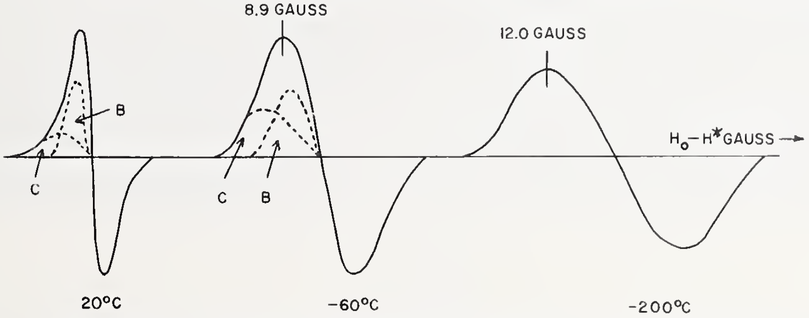

FIGURE 4. *NMR absorption curves of cement paste cured for 3 months.*

Cement

Experiments were made on cement pastes (W/C=0.40) at various curing ages. Some of the results obtained are shown in figures 3 and 4.

As shown in figure 3, the absorption curves of cement paste cured for 1 day showed a sharp curve at room temperature, and two peaks were observed during cooling. These peaks broaden during further cooling. The inner peak showed behavior corresponding to that of free water, and the outer one was similar to that of hydrate water.

In this case, the peak can be divided into three parts (A, B, and C) by the shape and line-width of the NMR curve which indicates the degree of binding of the water. The change in the line-width of each part during cooling is shown in figure 5. Parts A, B, and C of the NMR curve represent free, weakly bound, and strongly bound water, respectively, i.e., these parts correspond to free, adsorbed, and combined water, respectively.

The peak corresponding to free water decreased gradually with the increase in curing period, and in cement paste cured for 1 month only a small peak of free water was observed. In the paste cured for 2 months two peaks were observed at about −20 °C, but not at −60 °C, and this result seems to indicate that the free water has almost disappeared, i.e., the water in paste cured for more than 2 months consists mainly of adsorbed and combined water.

The amount of combined water (part C) in the pastes was determined by the integration of the area of the C part of the curve. It was found that the amount of combined water in cement paste cured for 3 days, 7 days, 1 month, and 6 months was 12.4, 15.2, 18.8, and 23.2 percent, respectively.

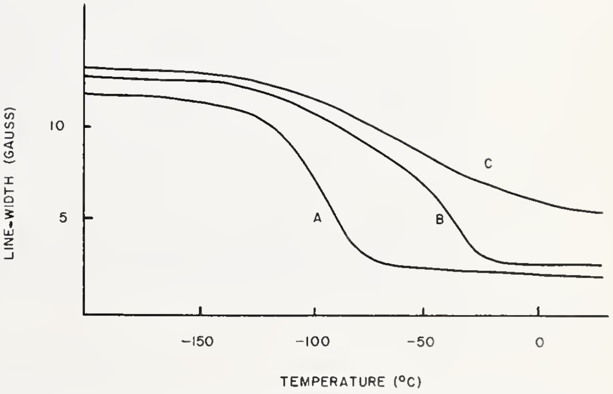

FIGURE 5. *Change in line width of parts A, B, and C of NMR curve.*

On the other hand, the amounts of combined, adsorbed, and free water obtained by the method of Powers [3] are: 3 days 9.2, 7 days 11.4, 1 month 15.9, 3 months 17.1; 3 days 6.0, 7 days 7.9, 1 month 10.2, 3 months 11.1; 3 days 22.7, 7 days 19.3, 1 month 13.2, 3 months 11.3 percent, respectively. In this case, the drying of the sample was done in an oven at 105 °C, and the value of 3 V_m was adopted as that of adsorbed water [6].

C_3S and $Ca(OH)_2$

To C_3S and $Ca(OH)_2$, 40 percent by weight of water was added, and after curing for 1 day, NMR measurements were made on these pastes. The curves obtained were similar to those of cement paste cured for 1 day, but the line width of these pastes was slightly lower than that of cement paste. This seems to be due to the fact that the proton-proton distance in cement paste is narrowed by the effect of the coexistence of other components. Furthermore, no sudden increase in the line-width of C_3S hydrate during cooling was observed. It seems that water is combined in many ways in C_3S hydrate.

Measurement of Vapor Pressure

Measurements of the water-vapor pressure of cement paste ($W/C=0.40$) were made. It was found that the results obtained showed a similar tendency to those obtained by NMR.

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Paper IV–S4. Rate of Hydration of Cement Compounds and Portland Cement Estimated by X-Ray Diffraction Analysis*

G. Yamaguchi, K. Takemoto, H. Uchikawa, and S. Takagi

Synopsis

The influence of gypsum on the rates of hydration of cement compounds and cement was investigated by X-ray diffraction quantitative analysis. Calibration curves were prepared from mixtures of standard $Mg(OH)_2$, cement compounds or cement, and its completely hydrated material. The probable total error for the rate of hydration was considered to be smaller than 2 percent.

From the rates of hydration of C_3S, β-C_2S, C_3A, C_4AF, and the individuals in their mixtures, determined on the pastes for the test of setting time, it was shown that the vigorous hydration of C_3A after mixing with water was depressed remarkably in the presence of gypsum and $Ca(OH)_2$ or $Ca(OH)_2$ dissolved from C_3S. The rates of hydration after 1 day decreased in the order C_3S, C_3A, C_4AF, and β-C_2S in the case of pastes mixed with 40 percent of water. The hydration of C_3S was accelerated at early ages by the addition of gypsum, but was not accelerated at later ages by its addition in large quantity.

Vigorous hydration of the tricalcium aluminate phase in cement after mixing with water was largely depressed by the addition of gypsum. The degree of hydration of the minerals in cement after 1 day decreased in the order alite, tricalcium aluminate, ferrite solid solution, and belite in the case of pastes mixed with 50 percent of water. The hydration of alite in cement after 1 day was accelerated by the addition of an optimum quantity of gypsum.

Résumé

Par analyse quantitative de la diffraction des rayons X on étudia l'influence du gypse sur les vitesses d'hydratation du ciment et des composés du ciment. Des courbes d'étalonnage étaient préparées à partir de mélanges de $Mg(OH)_2$ normal, de composés du ciment, ou de ciment, et de ses matériaux complètement hydratés. On considéra que l'erreur totale probable en ce qui concerne la vitesse d'hydratation était inférieure à 2%.

D'après les vitesses d'hydratation de C_3S, β-C_2S, C_3A, C_4AF et des composés dans ses mélanges, déterminées sur les pâtes pour l'expérience sur la durée de la prise, on put voir que la vigoureuse hydratation de C_3A après que le mélange avec l'eau a eu lieu, diminuait de façon remarquable en présence de gypse et de $Ca(OH)_2$ ou de $Ca(OH)_2$ dissous provenant de C_3S. Les vitesses d'hydratation après une journée indiquaient l'ordre de C_3S, C_3A, C_4AF, et β-C_2S dans le cas de pâtes mélangées à 40% d'eau. L'hydratation de C_3S était accélérée par l'addition de gypse, mais n'était pas accélérée plus tard par son addition en grande quantité.

L'addition de gypse diminuait grandement la vigoureuse hydratation de la phase d'aluminate tricalcique dans le ciment après le mélange avec l'eau. Le degré d'hydratation des minéraux du ciment après une journée indiquaient l'ordre suivant: alite, aluminate tricalcique, solution solide de ferrite, et belite dans le cas de pâtes mélangées à 50% d'eau. L'hydratation de l'alite dans le ciment après une journée était accélérée par addition d'une quantité optimum de gypse.

Zusammenfassung

Der Einfluß des Gipses auf die Hydratationsgeschwindigkeiten der Zementverbindungen und des Zements wurde durch quantitative Röntgenbeugungsanalyse bestimmt. Eichkurven wurden für Mischungen aus $Mg(OH)_2$, Zementverbindungen oder Zement, und auch aus vollständig hydratisierten Materialien. Der wahrscheinliche Gesamtfehler für die Hydratationsgeschwindigkeit ist vermutlich kleiner als 2%.

Aus den Hydratationsgeschwindigkeiten des C_3S, des β-C_2S, des C_3A, des C_4AF und der einzelnen Mischungsbestandteile, wie sie in den Pasten für die Abbindezeitprüfungen bestimmt wurden, wurde gefunden, daß die lebhafte Hydratisierung des C_3A nach dem Mischen mit Wasser in der Gegenwart von Gips und $Ca(OH)_2$, oder $Ca(OH)_2$ welches aus C_3S herausgelöst wurde, merklich zurückging. Die Hydratationsgeschwindigkeiten nach einem Tage können der Größe nach als die Reihe C_3S, C_3A, C_4AF, β-C_2S ausgedrückt werden, wenn die Pasten mit 40% Wasser angemacht wurden. Die Hydratation des C_3S wurde durch die Gipsbeimischung beschleunigt, aber in älteren Mischungen konnte das nicht beobachtet werden wenn viel Gips vorhanden war.

Die lebhafte Hydratation der Trikalziumaluminatphase in Zement nach der Wasserzumischung wurde durch eine Gipszugabe sehr heruntergesetzt. In den Mineralien des Zements kann nach einem Tage der Hydratationsgrad durch die Reihe: Alit, Trikalziumaluminat, feste Ferritlösung, Belit ausgedrückt werden, wenn die Pasten mit 50% Wasser angemacht worden sind. Die Alithydratation im Zement wurde nach einem Tag beschleunigt, wenn gerade der richtige Betrag Gips verwendet wurde.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Central Research Laboratory, Onoda Cement Company, Ltd., Tokyo, Japan.

Introduction

X-ray diffraction analysis as the method for measuring the rate of hydration is more effective than other methods, in that the individual unhydrated components in the hydrated sample can be estimated directly, regardless of the reaction of hydration. At the present time, however, the published data are very few, as mentioned by the authors of the principal paper.

The present authors have effectively applied X-ray diffraction analysis to clarify the influence of gypsum on the rates of hydration of cement compounds [1] [1] and the minerals in cement [2] during setting and hardening.

Method of X-ray Diffraction Analysis

The hydrated sample and the standard $Mg(OH)_2$ were carefully mixed and ground in an agate mortar in a decarbonated desiccator until their mean diameter reached 5μ so as to avoid the effects of preferred orientation of crystals and microabsorption of X-rays. The conditions of X-ray diffraction were selected after Klug and Alexander's "Time Width" [3], and the mixing ratios with standard $Mg(OH)_2$ were chosen to obtain nearly equal intensities for the sample and the standard. Calibration curves were prepared from the mixtures of standard $Mg(OH)_2$, cement compounds or cement, and its completely hydrated material which was prepared by Brunauer's method [4].

The lines for X-ray diffraction analysis were the 2.19 (319 etc.) and 1.77A(620)$(\bar{6}20)$ lines for C_3S [5]; the 1.89(231), 2.19(013), 2.79$(1\bar{3}0)(1\bar{1}2)$(200)(112), and 2.88A(102) lines for β-C_2S [6]; the 1.907(800), 2.20(444), and 2.70A(440) lines for C_3A [7]; and the 2.646(141)(200) and 1.930A (202) lines for C_4AF [8]. In the case of the 1.930A line for C_4AF the diagramatic determination was used, because its calibration curve was not linear. The lines used for cement were 1.77A for the alite phase, 2.88A for the belite phase, 2.70A for the tricalcium aluminate phase, and 2.65A for the ferrite solid-solution phase.

The intensities of the lines were counted by the Geiger-Müller tube in the range of $2\theta=1-2°$, and reduced by the value of background near the lines. The source of X-ray was CuKα.

The difference between the values obtained for the rate of hydration using the different lines for the same compound was below the experimental error which was obtained in the reproduction of the specimen for X-ray diffraction. The probable total error for the rate of hydration was considered to be smaller than 2 percent.

Rate of Hydration of Cement Compounds

The compounds C_3S, C_3A, and C_4AF were synthesized pure, and β–C_2S was synthesized with 1 percent of Cr_2O_3 as mineralizer.

Rate of Early Hydration

In order to investigate the relation between the rate of hydration and the setting phenomenon of a cement compound, the setting time was tested with a small specimen, and the rate of hydration of its paste was determined by X-ray diffraction analysis. Some of the results are shown in figures 1, 2, and 3.

The rate of early hydration of C_3S after mixing with water was small, regardless of the addition of gypsum, and the pastes showed normal setting.

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[1] Figures in brackets indicate the literature references at the end of this paper.

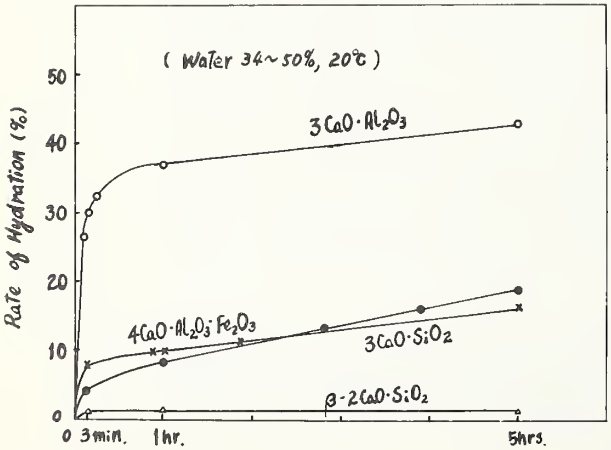

FIGURE 1. *Rate of early hydration of cement compounds.*

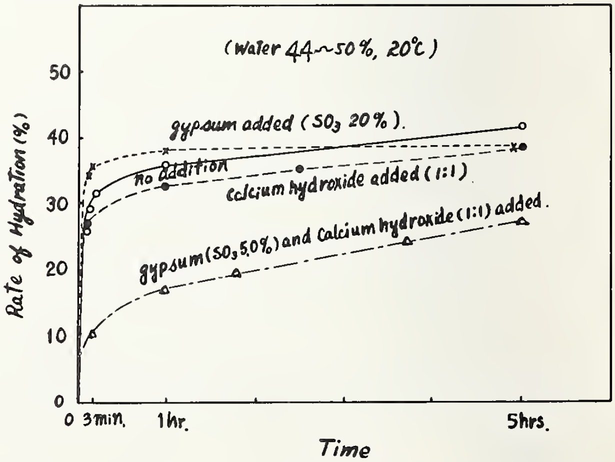

FIGURE 2. *Effects of gypsum and calcium hydroxide on rate of early hydration of C_3A.*

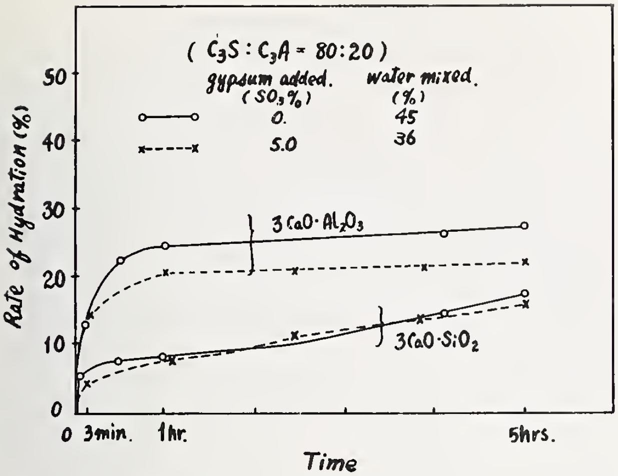

FIGURE 3. *Effects of gypsum on rate of early hydration of* C_3S-C_3A *mixture.*

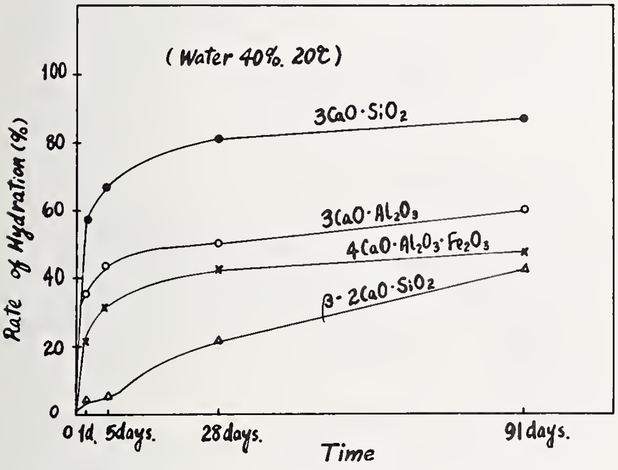

FIGURE 4. *Rate of later hydration of cement compounds.*

The rate of hydration was increased several percent by the addition of gypsum.

The rate of early hydration of C_3A was large at 3 min after mixing with water, regardless of the addition of gypsum (20 percent as SO_3), and the pastes showed flash setting. The difference between the rates of hydration of C_3A with and without gypsum was not great. This result showed that the vigorous hydration of C_3A after mixing with water was not depressed by the addition of gypsum, and that quick setting was caused by the formation not only of calcium hydroaluminate, but also of high-sulfate bacillus.

The rate of early hydration of C_4AF was not as large as that of C_3A, regardless of the addition of gypsum, and the pastes showed normal setting.

The rate of early hydration of C_3A was decreased by the addition of a large quantity of $Ca(OH)_2$, and this retardation was much more marked when both $Ca(OH)_2$ and gypsum were added.

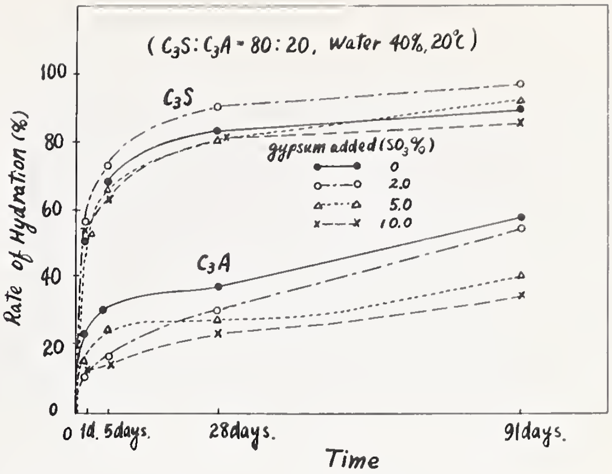

FIGURE 5. *Effect of gypsum on rate of later hydration of* C_3S-C_3A *mixture.*

In the case of the mixture of C_3S and C_3A, the rate of early hydration of C_3S was almost the same as that of C_3S alone, regardless of the addition of gypsum, but that of C_3A was smaller than that of C_3A alone, and was further reduced by the addition of gypsum. The paste without gypsum showed quick setting, and with gypsum showed normal setting.

In the case of the mixture of β-C_2S and C_3A, the rate of early hydration of β-C_2S was very small as was that of β-C_2S alone, and that of C_3A was large, as was that of C_3A alone, regardless of the addition of gypsum. The pastes with and without gypsum both showed flash setting.

In the mixture of C_4AF and C_3S or β-C_2S, the rates of hydration of these compounds were as small as those of the individual components, regardless of the addition of gypsum. The pastes with and without gypsum showed mostly normal setting.

The results above mentioned agreed with those of Forsén [9] who has reported that the rate of hydration of C_3A in a large quantity of water is decreased in saturated $Ca(OH)_2$ solution and further remarkably decreased in saturated $Ca(OH)_2$-$CaSO_4$ solution.

Rate of Later Hydration

The rates of hydration of cement compounds after 1 day were determined by X-ray diffraction analysis on pastes mixed with 40 percent of water. Some of the results are shown in figures 4 and 5.

The rates of hydration after 1 day decreased in the order C_3S, C_3A, C_4AF, and β-C_2S. Those of C_3A and C_4AF were smaller than that of C_3S, and it seemed that the completion of hydration of C_3A and C_4AF needed much more water.

Hydration of C_3S after 1 day was accelerated by the addition of gypsum, especially at the early ages. In the case of the mixture of C_3S (80 parts) and C_3A (20 parts), the addition of gypsum equal to 2 percent of SO_3 accelerated the hydration of C_3S up to 91 days, but the addition of a larger quantity of gypsum did so only at the earlier ages.

Three laboratory and two plant clinkers of various chemical compositions were examined with and without gypsum. In this review, the representative results on a laboratory clinker (G–3) low in CaO and high in Al_2O_3, and a plant clinker (K–2) of the normal composition of Type I are shown in figures 6 and 7. Their mineral compositions are shown in table 1. The values of the mineral compositions determined by X-ray diffraction analysis in table 1 were not always perfectly reliable. Therefore, at the present time, the degrees of hydration of the individual minerals in the clinker, not the rate of hydration of the whole clinker, were to be considered.

Table 1. *Mineral compositions of clinkers*

No.	Kind	Potential composition				Determined by X-ray diffraction analysis			
		C_3S	C_2S	C_3A	C_4AF	alite	belite	tricalcium aluminate	ferrite solid solution
K–2	Plant clinker	% 49.5	% 30.2	% 8.8	% 9.4	% 48.3	% 31.9	% 12.2	% 8.9
G–3	Laboratory clinker	4.8	65.2	14.4	15.7	11.1	59.2	23.2	10.6

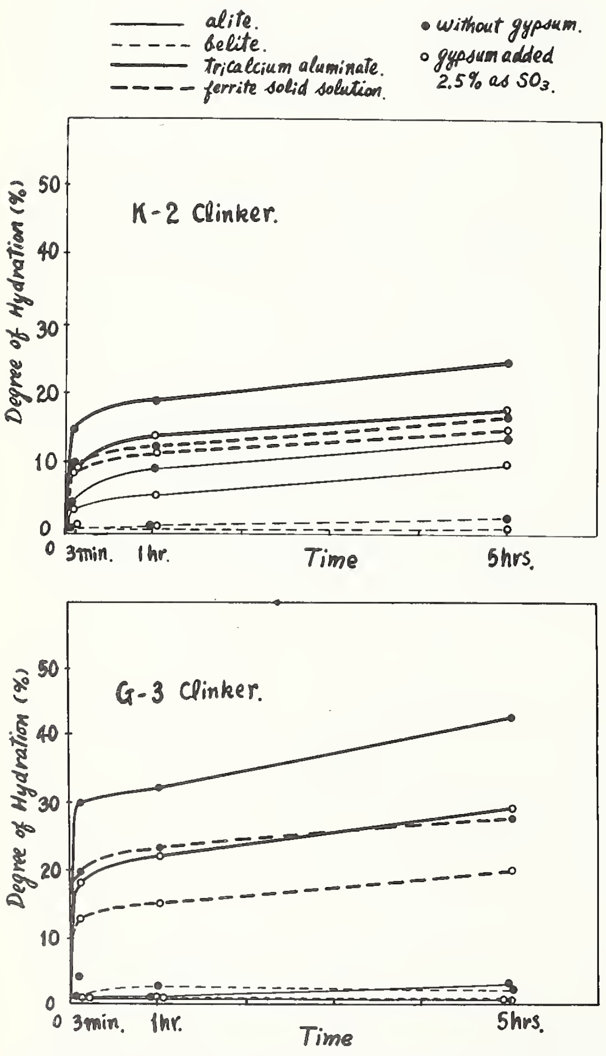

Figure 6. *Degree of hydration of minerals in cement during setting.*

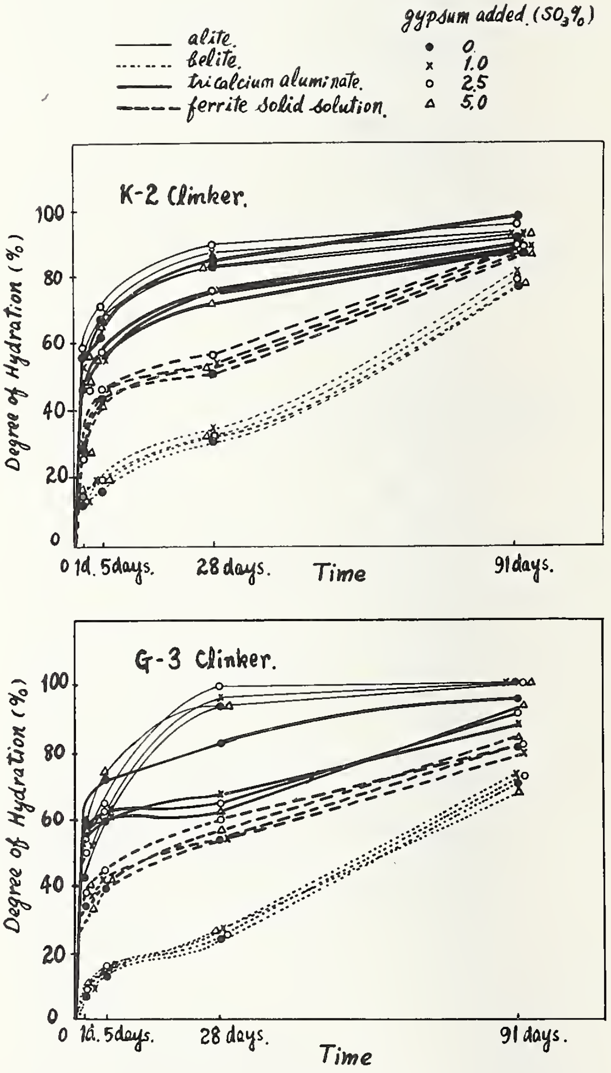

Figure 7. *Degree of hydration of minerals in cement during hardening.*

Degree of Hydration During Setting

The pastes for the test of setting time of cement with or without gypsum were examined by X-ray diffraction analysis.

The degree of hydration of the tricalcium aluminate phase was the greatest of the four minerals in clinker, reaching 10 to 30 percent at 3 min. after mixing with water. The largest value was shown in the flash setting of clinker G–3 (low in CaO and high in Al_2O_3) without gypsum. The degree of hydration of the tricalcium aluminate phase was decreased markedly by the addition of gypsum.

The degree of hydration of the ferrite solid-solution phase was 8 to 20 percent at 3 min. after mixing with water, and was decreased a little by the addition of gypsum. The degree of hydration of the alite phase was a few percent at 3 min. after mixing with water, and about 10 percent at 5 hr. The degree of hydration of the belite phase was negligible.

It was concluded from the above results that gypsum depressed the hydration of the tricalcium aluminate phase in cement, and that this action of gypsum needed the coexistence of $Ca(OH)_2$ dissolved from the alite phase.

Degree of Hydration During Hardening

The hardened pastes of cement mixed with 50 percent of water, with or without gypsum, were examined by X-ray diffraction analysis. The strength of the cements was tested on 1:3 cement-sand mortars; w/c=50 percent.

The degree of hydration of the alite phase was the greatest of the four minerals in clinker; it reached 40 to 70 percent in 1 day, 80 to 100 percent in 28 days. That of the tricalcium aluminate phase was next, 40 to 60 percent at 1 day, 60 to 80 percent at 28 days, and 85 to 95 percent at 91 days. It was shown that the tricalcium aluminate phase hydrated very quickly after mixing with water, but hydrated gradually at the later ages. On the other hand, the alite phase hydrated gradually after mixing with water, but had hydrated almost completely at 28 days. The degree of hydration of the ferrite solid-solution phase was 20 to 40 percent at 1 day, 50 to 70 percent at 28 days, and 80 to 85 percent at 91 days.

The degree of hydration of the tricalcium aluminate phase was much lower in cement with gypsum than in cement without gypsum.

Except for clinker G–3, low in CaO and high in Al_2O_3, i.e., low in the alite phase, cement mixed with gypsum equal to 2.5 percent of SO_3 showed the maximum degree of hydration of the alite phase and the maximum strength in four cements mixed with gypsum equal to 0, 1.0, 2.5, and 5.0 percent of SO_3. This result seemed to show that the optimum content of gypsum was preferable to develop the maximum strength by accelerating the hydration of the alite phase, although the strength development of the cement was considered to depend not only on the degree of hydration of the alite phase but also on many other factors.

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Paper IV–S5. Proton Magnetic Resonance in Hydrated Portland Cements*

R. L. Blaine

Synopsis

Exploratory studies are reported of the proton magnetic resonance line widths and peak signal amplitudes for a number of variously hydrated cements and cement compounds. The results confirm the utility of the NMR techniques in the study of such materials. They suggest that the water in the hydration products may not be present as water of crystallization, but as adsorbed water. The peak signal amplitude of cements decreased with increasing time of hydration and with removal of evaporable water. Different cements exhibited different line widths in the fresh pastes. Hydrated cements frozen in liquid nitrogen indicated greatly increased proton mobility with rising temperature.

Résumé

On présente des études exploratoires des largeurs de la ligne de résonnance magnétique du proton et des amplitudes de signal maximales pour plusieurs ciments hydratés et pour plusieurs composés de ciment hydratés tous en manières diverses. Les résultats confirment l'utilité des techniques de la résonnance magnétique nucléaire (RMN) pour l'étude de tels matériaux. Les résultats indiquent la possibilité que l'eau dans les produits d'hydratation puisse exister non pas sous forme d'eau de cristallisation, mais sous forme d'eau adsorbée. L'amplitude de signal maximale des ciments diminuait avec l'accroissement du temps d'hydratation et avec l'enlèvement d'eau évaporable. Les différents ciments présentaient dans les pâtes fraiches différents largeurs de la ligne. Les ciments hydratés congelés dans l'azote liquide indiquaient avec la croissance de la température une forte augmentation de la mobilité du proton.

Zusammenfassung

Forschungsstudien über die Linienbreiten der Energieabsorption und die Signalschwingungsweiten bei Protonresonanzfrequenz für eine Anzahl hydratisierte Zemente und Zementverbindungen sind berichtet. Die Ergebnisse bestätigen die Nützlichkeit der Technik der Protonresonanzfrequenz beim Studien solcher Materialien. Sie mögen andeuten, dass das Wasser in diesen hydratisierten Produkten nicht als Kristallwasser, aber als adsorbiertes Wasser vorhanden ist. Die Signalschwingungsweite der Zemente verminderte mit der Zunahme der Hydratationszeit und mit der Abnahme des verdampfbaren Wassers. Verschiedene Zemente haben in frischen Pasten verschiedene Linienbreiten aufgewiesen. Hydratisierte Zemente, die im flüssigen Stickstoff gefroren wurden, zeigten zunehmende Protonbeweglichkeit mit steigender Temperatur.

Introduction

The principal compounds formed in the hydration of portland and other hydraulic cements are recognized to be, in addition to calcium hydroxide, the hydrates of the calcium silicates and aluminates. These hydrates are generally assumed to be compounds formed with water of crystallization in more or less stoichiometric ratios. In addition, water in excess of that required for hydration remains within the structure as free or adsorbed water. The colloidal nature of the hydration products as well as the effect of minor constituents have made it difficult to assess the true nature of the compounds formed, and the determination of the role of water in the hydration products has been especially difficult.

Studies of adsorption of water vapor, nitrogen, and other gases have indicated to some extent the nature of the gel in the hydrated cement, and electron microscopy has indicated that plate or layerlike and lathlike hydration products are formed. Electron diffraction has indicated that these materials are crystalline although of very small size.

Powers and Brownyard [1, 2][1] have distinguished between evaporable and nonevaporable water. Drying experiments on hydrated cements have indicated that although some of the water is readily removed, some is apparently more closely bound and can only be removed after weeks of evacuation at room temperature [3]. The apparent surface area of hydrated cement as measured by water vapor increases as water is removed, whereas the surface area, as measured by nitrogen adsorbed at liquid nitrogen temperature, has a much lower value than that obtained by water vapor adsorption determination [3]. This behavior has also been found with certain other materials as diverse as montmorillonite [4] and textile fibers [5].

Many techniques have been used in the study of the nature of water in inorganic materials,

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the National Bureau of Standards, Washington, D.C.,

[1] Figures in brackets indicate the literature references at the end of this paper.

among the most recent being the use of broad-band nuclear-magnetic-resonance apparatus tuned to the proton frequency (PMR). The technique was originally developed independently by Bloch, Hansen, and Packard [6], and Purcell, Torrey, and Pound [7]. A comprehensive explanation of the principles involved has been presented by Andrews [8], Pake [9], and others.

The techniques of nuclear magnetic resonance (NMR) were applied to studies on cement by Kawachi, Murakami, and Herahara in 1955 [10]. The ratio of bound (crystal) water to free water in the cements was noted by measuring the proton resonance absorption as a function of time. The authors reported that some crystal water occurred even in the original cement powder. Comparisons were made relating quantity of bound water with mechanical properties.

In 1959, French and Warder [11] applied the NMR method to a study of the rates of hydration of cements and calcium silicates. Test of line width as a function of time after start of hydration showed an altered line width expected from hydration in only 3 of 9 cements. Other tests were made with cements and calcium silicate hydrates at liquid oxygen temperatures. It was claimed that, at this temperature, no signal was given by the frozen "free" water and that the amplitude of the signal received was a measure of the quantity of bound water. It was concluded that the hydration of calcium silicates occurred in steps with intervening latent periods. Progress in hydration was dependent on temperature, the range of 17 to 45 °C being studied.

In 1959 Pickett and Lemcoe [12] reported the results of an NMR study on clay-water systems. The value of this investigation to cement studies lay in its demonstration of the utility of radio frequency spectroscopy as an analytical tool in research on silicate-water systems. Complete quantitative data essential to the proper evaluation of such parameters as bond type and bond energy were not obtained. It was concluded, however, that measurements of the viscosity of the liquid phase under various conditions, inferences which could be drawn from the shape of the NMR derivative curve, and plots of line width versus water content should provide worthwhile contributions to an understanding of the systems under study.

Scope

The above investigations suggest the feasibility of NMR techniques for the study of cements and cement hydration products. The experience of specialists in the field of radiofrequency spectroscopy has shown, however, that results of dependable precision can be expected only from intensive investigations embodying the most exacting refinements in technique and equipment. It seems advisable, therefore, that exploratory studies be made to cover parts of the field with a qualitative rather than quantitative objective. The present investigation was initiated to contribute to that objective.

Measurements of the energy absorption at or near the proton resonance were made at room temperature of hydrated cement compounds, of cements hydrated both at normal temperature and at 38 °C, as well as of cement pastes autoclaved at 295 psi. The measurements were made after various periods of hydration of the moist samples and after drying by evacuation and after carbonation. A limited study was made of the thawing of water in a frozen sample of hydrated cement. Typical derivative absorption curves are presented as well as observed absorption line widths and peak signal amplitudes.

Apparatus

In this work a Model 104 Schlumberger Nuclear Magnetic Resonance Analyzer was used. This apparatus, which has been described by Rubin [13], is of the wide-band type and utilizes a 1720-gauss permanent magnet with a 2 in gap between the 10 in diameter pole faces. A sweep coil on the magnet varies the field by amounts up to 20 gauss. The sample, of approximate volume 1¼ in diam and 2 in height, is held in a glass test tube and inserted in a radiofrequency coil which in turn lies between the pole pieces of the magnet. The radiofrequency circuit has a fixed frequency of 7.3 Mc/s which is the precession frequency of hydrogen nuclei in the particular permanent magnetic field used. As the hydrogen nuclei shift from one of the two possible energy states to the other, under the influence of the radiofrequency energy, some of the latter is absorbed. This energy absorption is measured. If the hydrogen nuclei, or protons, are in a solid, and hence not mobile, the magnetic field experienced by a particular proton will be that of the external field modified by the fields of neighboring protons, whereas if they are in a liquid, the motion of the molecules is so rapid that the local magnetic field is smoothed out to a small average value. Different protons, depending upon the degree of binding of their neighbors, are in resonance at different values of the external magnetic field. Therefore, as the magnetic field strength is continuously varied above and below the value H_0 of the permanent magnet by the sweep coil, an absorption spectrum is obtained. The width of the line produced by protons in a liquid is essentially only that due to inhomogeneity in the permanent magnet. The width of proton resonance lines in nonliquid materials depends, among other things, on the mobility of proton-containing groups or molecules, such as H_2O. Actually, the instrument plots, within certain limitations to be mentioned later, the derivative of the absorption as a function of the external field strength in gauss.

Figure 1 shows the absorption line for a liquid containing protons and also the derivative curve as plotted by the instrument. If the width of the absorption line is defined as the width at maximum slope, the horizontal displacement between the positive and negative peaks of the derivative curve is a measure of the line width. In this paper the term "line width" refers to the distance "ΔH" as measured from the absorption curve.

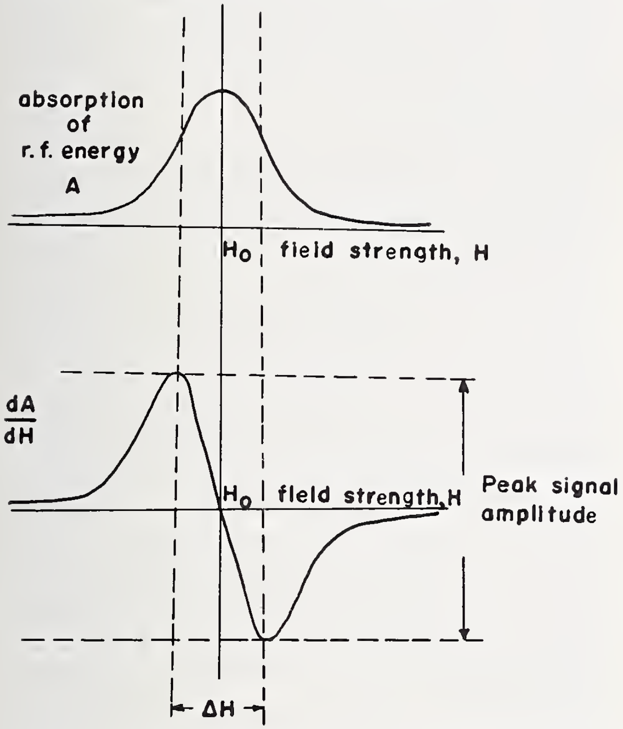

FIGURE 1. *Curves showing NMR absorption and the derivative of the absorption as a function of external magnetic field strength for a simple material.*

The area under the absorption curve is proportional to the energy absorbed and hence to the number of protons [9]. The peak value of the derivative curve is related to this area and hence is used to furnish a rough estimate of the number of protons involved. In this paper the term "peak signal amplitude" refers to the distance "a" as measured on the absorption curve for free or relatively free water.

Figure 2 shows a possible absorption spectrum and corresponding derivative curve for a sample containing both protons in a solid and protons in a liquid. The use of the derivative curve, which is employed for the improvement of the signal-to-noise ratio, has the additional advantage of showing, through the location of the signal peaks, the approximate widths of the superimposed absorption lines.

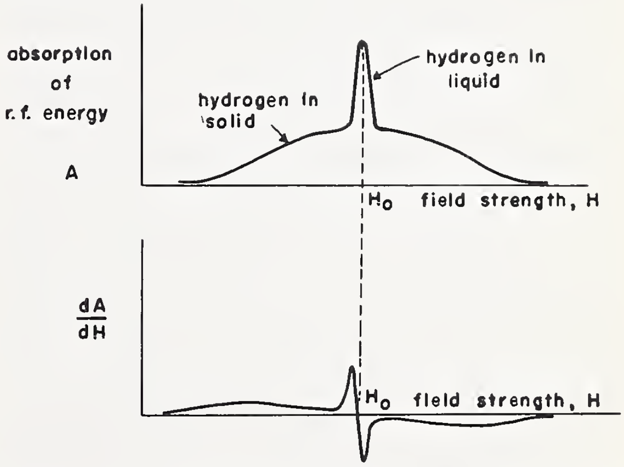

FIGURE 2. *Curves showing NMR absorption and the derivative of the absorption as a function of external magnetic field strength for a material containing hydrogen in both the solid and the liquid state.*

Materials

β-C_2S, C_3S, and C_3A were prepared by procedures similar to those discussed by Bogue [14]. β-C_2S was stabilized by addition of 0.4 percent boric acid to the starting mixture. Powder X-ray patterns were in agreement with ASTM patterns. The samples were pulverized to pass a No. 200 sieve and then allowed to hydrate for 28 days at 38 °C.

The sample of gibbsite was a commercial preparation. The boehmite sample was prepared by autoclave treatment of gibbsite at 200 °C. The hydrated alumina was prepared by heating gibbsite in air at 240 °C, whereby the water content was reduced to about 0.8 mole per mole of Al_2O_3.

The commercial cements used in this investigation were some of those previously studied [15]. These were samples of Types I, II, III, V, and a portland blast furnace slag cement. The average chemical analyses and physical tests are presented in table 1.

TABLE 1. *Chemical analyses and physical properties of cements*

Cement number	2	5	6	7	10
Type	I	II	IS	III	V
SiO_2 ... percent	21.73	21.24	23.22	20.76	23.48
Al_2O_3 ... percent	4.95	5.47	8.13	5.60	3.67
Fe_2O_3 ... percent	2.88	4.76	2.58	2.50	4.44
CaO ... percent	61.90	61.98	55.35	64.24	64.39
MgO ... percent	3.81	2.42	3.89	1.97	0.76
SO_3 ... percent	2.79	1.92	2.43	2.84	1.80
Loss on ignition ... percent	0.79	1.38	2.63	1.26	0.76
Insol. residue ... percent	0.23	0.18	0.53	0.21	0.14
Na_2O ... percent	0.30	0.24	0.10	0.15	0.50
K_2O ... percent	1.00	0.59	0.25	0.76	0.21
Mn_2O_3 ... percent	-------	0.09	0.64	-------	-------
Sulfide sulfur ... percent	-------	0.01	0.59	-------	-------
Initial set (Gillmore) ... hr	3.45	2.66 [a]	2.97 [a]	2.85	4.76
Final set (Gillmore) ... hr	5.48	-------	-------	4.81	7.49
Autoclave expansion ... percent	0.13	0.03	0.04	0.02	0.03
Air entrainment ... percent	8.5	9.8	11.8	7.0	8.8
Air-permeability fineness cm^2/g	3442	3573	4564	4588	2949
Compressive strength 3d ... psi	2848	1889	2208	2675 [b]	2285
Compressive strength 7d ... psi	3675	2674	3645	4794 [c]	3389

[a] Vicat method. [b] 1 day. [c] 3 day.

The hydrated C_2S, C_3S, and C_3A were pulverized to pass a No. 20 sieve prior to making the measurements. The neat hydraulic-cement pastes with 0.25 or 0.50 water/cement ratios (w/c) were made into 1 × 1 × 11-in bars, stored at 23 °C, 95 percent RH, for 24 hr, and then ground to pass a No. 20 sieve. Powdered samples were used to facilitate the removal of water by evacuation in later measurements. Portions of those powders were sealed into vials and stored at 23 °C until making the measurement at 1, 3, 7, and 28 days. Other portions were stored over water in sealed containers at 38 °C for 6 weeks. Some 1 × 1 × 11-in bars were autoclaved at 295 psi steam pressure for 3 hr. Some of the autoclaved specimens were ground to pass a No. 20 sieve, whereas measurements on some of the specimens of suitable length were made without grinding.

In another series of measurements, ½ by 2-in cylinders were made of the neat cement pastes of normal consistency, cured for 28 days at 95 percent relative humidity and then stored for 3 months in closed glass containers having relative humidities of 93, 75, 53, and 33 percent maintained by concentrated salt solutions. Samples of the cylinders were also evacuated for several weeks at room temperature using a dry-ice trap in the vacuum system.

Measurement Procedures

Approximately 50-g samples of the powdered hydrates were weighed to the nearest milligram, placed in 1.35-in o.d. glass vials and compacted to a depth of about 2 in. The vials were placed in the rf coil between the magnets and a plot made of the energy absorption, traversing in 4 min a field strength 10 gauss above and below that normally required for proton resonance of uncombined water. Measurements were made of the line width and of the peak signal amplitude.

To insure a closely approximate derivative curve, the modulation amplitude employed was less than one-fifth the line width in gauss in all reported values for ΔH. However, to improve the signal-to-noise ratio a higher modulation amplitude was employed in determining the peak signal amplitude even though this entailed some sacrifice in the validity of the peak signal amplitude as a linear measure of the total absorption. Normally 3 to 5 determinations were made of the total absorption curve, the line width values, and the peak signal amplitude values on each of the samples.

In the determination of the overall absorption curve, a 20-gauss field strength was traversed, whereas, in determination of the line width of peaks near the resonance frequency, only 1 or 2 gauss were traversed in 4 min and, in determining the peak signal amplitude, 10 gauss were traversed in 30 sec.

The sensitivity selector was set at various values when peak signal amplitudes were determined, but for comparison purposes each value of peak signal amplitude reported in the paper has been corrected to the same arbitrary sensitivity.

The time constant was maintained at 1/30 of the sweep time or less, a necessary requirement for quantitative measurements with the instrument used.

The derivative absorption curves presented have been smoothed by eye to average out the "noise" effect on the signal. The relative magnitude of the noise varied widely, depending upon the sensitivity required to produce a usable signal. Under the most unfavorable conditions reported it is estimated that the signal-to-noise ratio at the peak of the derivative curve for bound water was of the order of 4 to 1, but in most cases it was larger.

Oscillator crystals with frequencies of 7,300 and 7,325 kc/s were used to determine the sweep field traversed per centimeter of recorder chart. The calibration was further verified by using a precision gaussmeter.

Measurements were made at room temperature of the moist samples both immediately after mixing and after evacuation of the samples for periods of about 2, 4, 8, 20, 40, 80, and 120 hr at room temperature. The powdered samples were spread in thin layers in beakers during evacuation. After each evacuation the samples were replaced in the vials, stoppered, and then weighed to determine moisture loss. A few hours were allowed after each evacuation to permit the samples to approach equilibrium.

The nonevaporable water (W_n) of the hydrated materials was determined by the method described by Copeland and Hayes [16] and the CO_2 content by methods described by Hunt and coworkers [17].

For one series of determinations, the moist hydrated cement powders were spread in thin layers in beakers which were placed in a large, open container. The samples were exposed to concentrated CO_2 gas for 3 weeks during the drying process. They were stirred occasionally in order to expose the powders as uniformly as possible. PMR measurements were made on the carbonated samples both before and after evacuation to remove portions of the water.

Exploratory measurements were made of the changes in energy absorption which occurred when a sample of the pulverized hydrated cement, frozen in liquid nitrogen, was permitted to warm up in a Dewar in the apparatus. At the lower temperatures, the 20-gauss field-strength interval was traversed in 2 min. After the pattern of the curve changed, as the sample became warmer, a 5-gauss field was traversed in 2 min. Alternate measurements were made of the energy absorption and the temperature of the sample which was determined by means of a copper-constantan thermocouple.

It should be pointed out, however, that the procedure employed gives no assurance that the temperature measured is precisely that of the portion of the sample actually responsible for the narrow recorded line.

Results of Measurements

1. Cement Compounds

In figure 3 are presented the derivatives of the absorption curves of C_2S, C_3S, and C_3A after hydrating for 28 days at 38 °C followed by partial drying by evacuation for 24 hr. In figure 3 as in figures 4, 5, 6, 7, and 13, H_0 represents the magnetic field strength at which resonance would occur with protons in free water.

The peak amplitude of the signals is dependent on the number of protons in the sample and the amplification used in each experiment. The curves in figure 3 were obtained using the maximum signal amplification; two of the peaks near H_0 were off scale. Using a lower signal amplification, such that the central peaks were within the range of the chart recorder, resulted in correspondingly smaller signal amplitudes in the other portions of the curves. The predominant peaks in the curves of the C_2S and C_3S hydrates indicate small line-width values. The observed line widths of the central peaks were 0.33 and 0.36 gauss respectively after evacuation for 48 hr, using the required instrument parameters. Similar unpublished absorption curves have been obtained by the author for laminar clay minerals, such as illites and montmorillonite with ΔH values ranging from 0.3 to 0.7 gauss. Samples of tobermorite and xonotlite which were evacuated and oven dried at 110 °C exhibited curves similar to that obtained from the hydrated C_2S with no evidence of any absorption other than that close to the resonance condition for free water. The ΔH values obtained for tobermorite and xonotlite after drying 36 hr at 110 °C were 0.26 and 1.2 gauss respectively. These values are, however, all significantly greater than the value of 0.016 gauss obtained using distilled water. It may be noted also that the curve for the C_3S hydrate has shoulders with a ΔH value somewhat greater than 9 gauss. These shoulders were not evident, however, with the curves obtained for the C_2S hydrate, the tobermorite or the xonotlite, indicating that some additional reaction product is present in the C_3S hydrate.

The curve for evacuated C_3A hydrate indicated a ΔH value of 13.5 gauss with little evidence of free water.

The curves obtained with gibbsite, boehmite, and $Al_2O_3 \cdot (0.8H_2O)$ are presented in figure 4. Whereas ΔH values of about 12 gauss were obtained with the gibbsite and boehmite, the ΔH value for $Al_2O_3 \cdot (0.8H_2O)$ was 6.8 gauss.

2. Hydraulic Cements

The curves obtained on hydraulic cements are much more complex and difficult to interpret. Typical curves, as obtained on cement No. 2, mixed with the amount of water required for normal consistency and hydrated for 1, 3, 7, and 28 days as well as the curve of the autoclaved cement paste, all powdered, and then dried at 110 °C for 19 hr, are presented in figure 5. It may be noted that the peaks near H_0, associated with free or absorbed water, are prominent compared to the shoulders and that the peak signal amplitude increased with length of hydration. When these sample were measured prior to drying using the same amplification the peaks near H_0 were off the scale of the recorder. The same samples, oven dried at 110 °C for 3 days, presented patterns as shown in figure 6. Indicated on this chart by the dotted line is the type of curve which may be expected with a dry hydroxide or a compound with water of crystallization. Some cements exhibited greater peaks near H_0 than others, but with the drier samples it was not possible to determine the line width of the central peaks or of the broad peaks, because of the flatness of the curves.

The effect of carbonation of a hydrated cement on the energy absorption is illustrated in figure 7. The determinations on the two samples were made using the same instrument parameters. The curves illustrated are for the No. 5 cement, w/c 0.50, which had been hydrated at 38 °C for 6

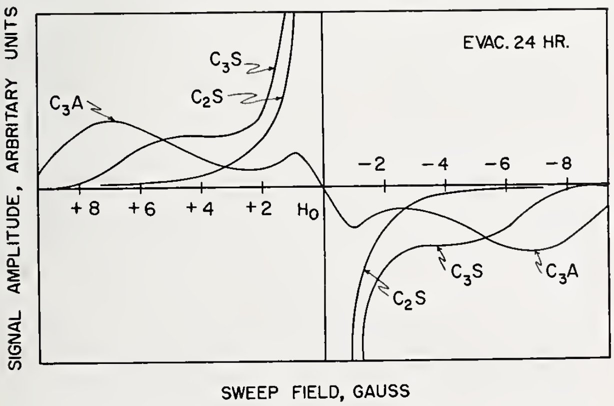

FIGURE 3. *Derivatives of energy-absorption curves obtained with hydrated dicalcium and tricalcium silicates and with tricalcium aluminate after evacuation for 24 hrs.*

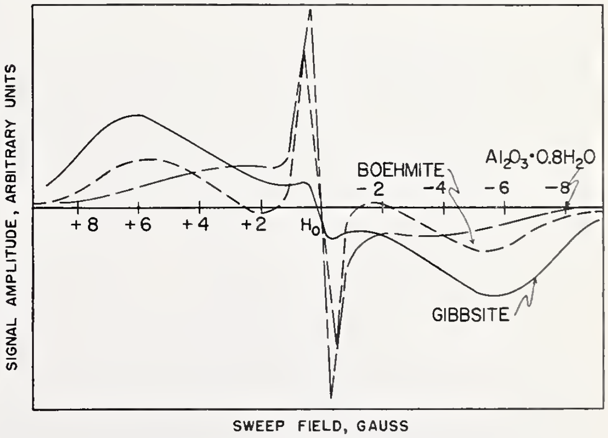

FIGURE 4. *Derivatives of energy-absorption curves obtained with gibbsite* ——, *boehmite* . . ., *and* $Al_2O_3 \cdot 0 \cdot 8H_2O$-------.

weeks. The CO_2 content of the carbonated hydrated cement was 19.7 percent. It may be noted that the energy absorption in the 6- to 16-gauss ΔH range was greatly reduced by carbonation. The decrease in signal amplitude of the shoulders of the curve may indicate the removal of $Ca(OH)_2$ from the hydrated cement. The results obtained with this cement were typical of those obtained with the other cements.

The peak signal amplitude of cement-water pastes in sealed containers decreased with time as indicated in figure 8 and presented in table 2. However, there is no apparent relation between the peak signal amplitude of the different pastes and the strength of mortars made of these cements nor with the chemical composition as presented in table 1. The results obtained on supersulfate cement appeared to correspond fairly well with those obtained on the portland and blast-furnace-slag cements, except that the line widths of the dried samples were somewhat greater than obtained with the other cements. The line width of the high-alumina cement was appreciably greater than those obtained with the portland cements and the curves of the partially dried hydrated cement exhibited very little energy absorption near the resonance condition for free water. The peak signal amplitude of moist pastes made of cements 5 and 7 with two water-cement ratios and different curing conditions (see table 2) were plotted against the nonevaporable

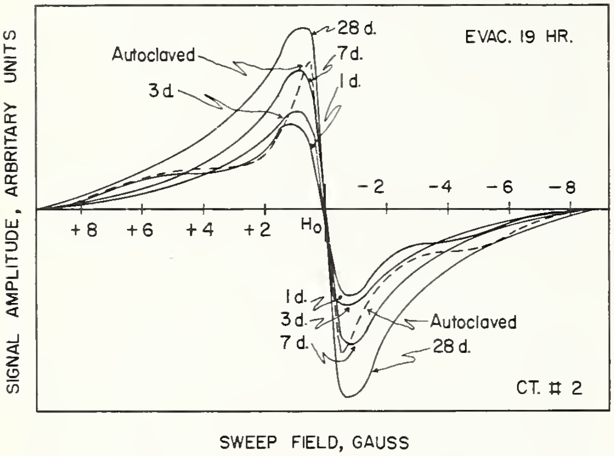

Figure 5 *Derivatives of energy-absorption curves of cement No. 2 hydrated for 1, 3, 7, and 28 days, and of this cement autoclaved after one day moist curing.*

All samples were dried for 19 hours at 110 °C before measurements were made.

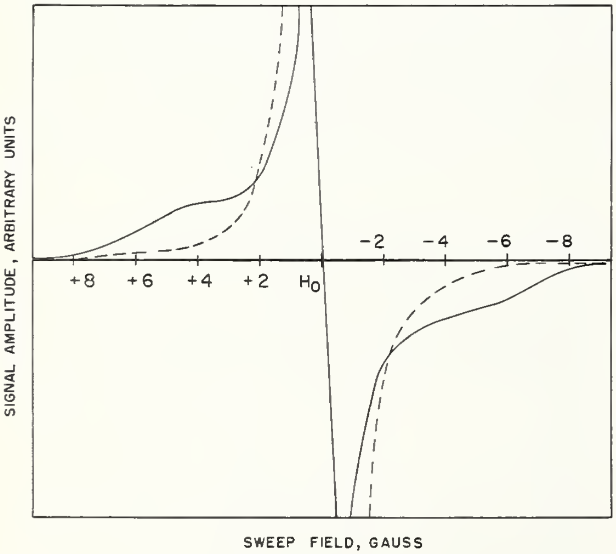

Figure 7. *Derivatives of energy-absorption curves of cement No. 5 hydrated at 38° C for 6 weeks and evacuated for 110 hrs at room temperature ——, and for this same hydrated cement after carbonation for 3 weeks ---------.*

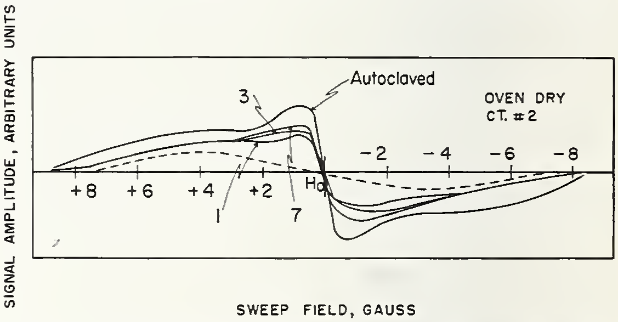

Figure 6. *Derivatives of energy-absorption curves of cement No. 2 hydrated for 1, 3, and 7 days, and of this cement autoclaved after one day moist curing.*

All samples were dried for 3 days at 110 °C before measurements were made.

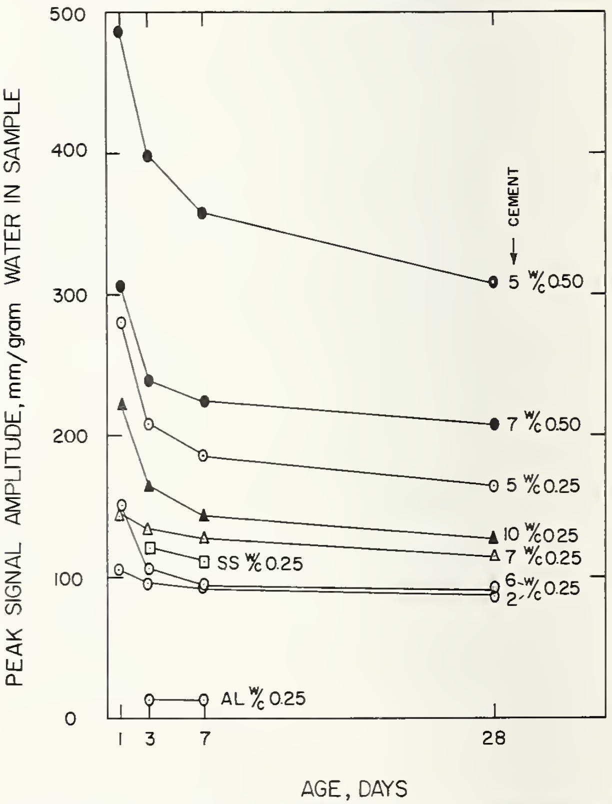

Figure 8. *Peak signal amplitudes of moist samples of cements hydrated at room temperature for various ages.*

ss=supersulfate cement; AL=high-alumina cement.

Table 2. *Nonevaporable water content, peak signal amplitude per gram of water, and line widths of moist neat cements cured for various periods and at different temperatures*

Also presented are the line widths of these cements after removal of most of the readily evaporable water

	Moist samples										Dry samples [c]
Cement number	w/c	Curing temp.	Age	CO_2	W_n	Sample weight	Cement [b]	Water [b]	Peak signal amplitude per g water	Absorption line width	Absorption line width
		°C	*days*	%	%	*g*	*g*	*g*	*mm*	*gauss*	*gauss*
2	0.25	23	1			59.1	47.3	11.8	105	1.0	1.6 8.0
	.25	23	3			58.0	46.4	11.6	96	0.9	1.6 7.3
	.25	23	7			62.6	50.1	12.5	93	1.1	1.6 6.6
	.25	23	28	0.5	9.6	63.0	50.4	12.6	87	1.0	1.6 ---
	.25	38	42	.5	13.3	50.8	39.1	11.7	114	0.85	1.5
	.50	38	42	.5	16.5	50.0	34.2	15.8	169	.49	1.1
	.25	(295psi)[a]				57.2				.53	0.7 8.3
5	0.25	23	1	0.6	6.1	51.8	41.4	10.4	280	0.25	0.56
	.25	23	3	.4	8.4	51.8	41.4	10.4	208	.27	.67
	.25	23	7	.5	9.4	52.2	41.8	10.5	186	.29	.70
	.25	23	28	.3	11.1	52.4	41.9	10.5	164	.33	.76
	.25	(295psi)[a]		.4	11.8	52.3				.24	.86 4.0
	.25	38	42	.4	12.7	50.3	39.3	11.0	180	.31	.83
	.50	38	42	.5	16.7	44.3	30.5	13.8	235	.24	.86
	.50	23	1	.5	6.8	50.2	33.5	16.7	487	.12	.47
	.50	23	3	.4	9.5	50.0	33.4	16.7	399	.14	.57
	.50	23	7	.5	12.2	49.4	33.0	16.5	358	.15	.56
	.50	23	28	.5	14.3	49.7	33.2	16.6	308	.19	.72
6	0.25	23	1	3.1	4.1	51.8	41.4	10.4	150	0.66	1.3
	.25	23	3	3.0	6.4	52.0	41.6	10.4	106	.81	1.6
	.25	23	7	3.1	7.5	52.3	41.9	10.5	92	.93	1.5
	.25	23	28	2.2	9.8	52.1	41.7	10.4	90	.86	1.5
	.25	(295psi)[a]		2.5	10.5	51.7					1.3
	.25	38	42	3.2	11.4	50.8	39.0	11.8	99	.79	1.4
	.50	38	42	4.0	14.1	49.9	34.0	15.9	141	.50	1.4
7	0.25	23	1	0.6	8.9	52.7	42.2	10.6	145	0.63	1.0
	.25	23	3	.5	10.0	52.3	41.9	10.5	135	.62	1.3
	.25	23	7	.5	10.5	51.8	41.4	10.4	128	.65	1.1
	.25	23	28	.4	11.9	52.4	41.9	10.5	114	.63	1.0
	.25	(295psi)[a]		.4	9.9	51.8					1.0
	.25	38	42	.6	16.5	50.6	38.1	12.6	157	.38	0.90
	.50	38	42	1.0	20.9	50.2	33.4	16.8	220	.30	.81
	.50	23	1	0.6	10.5	49.9	33.3	16.6	305	.24	.67
	.50	23	3	.6	15.4	50.3	33.5	16.8	239	.29	.68
	.50	23	7	.4	18.4	49.9	33.3	16.6	224	.31	.68
	.50	23	28	.5	19.2	50.7	33.8	16.9	208	.33	.79
10	0.25	23	1	0.4	5.7	51.7	41.3	10.3	221	0.42	0.87
	.25	23	3	.3	8.6	51.4	41.2	10.3	164	.55	1.14
	.25	23	7	.3	9.8	51.8	41.4	10.4	142	.53	1.00
	.25	23	28	.3	11.0	52.3	41.8	10.5	126	.63	0.87
	.25	(295psi)[a]		.3	6.9	51.8					.88
	.25	38	42	.7	12.3	50.3	39.6	10.7	159	.39	.90
	.50	38	42	.6	16.3	50.1	34.5	15.7	236	.24	.76
Super sulfate	0.25	23	3		5.3	52.1	41.7	10.4	120	1.18	1.95
	.25	23	7	0.5	6.0	53.3	41.9	10.7	112	1.24	2.06
	.25	(295psi)[a]			8.2	50.6					1.54
High alumina	0.25	23	3			52.4	41.9	10.5	13	5.8	7.3
	.25	23	7			52.4	42.0	10.5	13	6.6	7.2

[a] Autoclave steam pressure.

[b] For specimens stored at 38 °C values were computed from ignition loss, others were computed from proportions as mixed.

[c] Evacuated at room temperature 80 to 100 hr.

water of those pastes (table 2) after the various periods of hydration and are presented in figure 9. There appears to be a fairly straight-line relation between the peak signal amplitude and the nonevaporable water for each of the cements for each water-cement ratio used for the pastes stored at 23° C. Also it is noted that in the case of both cements the curves for the two water-cement ratios were approximately parallel, but that slopes for the two cements were different. Cement pastes made with a w/c ratio of 0.25 and cured at 38 °C for 6 weeks did not fall on the lines drawn through the corresponding values for the cements cured at 23 °C, but those with water-cement ratio of 0.50 did.

By comparing figures 5 and 6 it may be noted that removal of water from the hydrated pastes resulted in a decrease in the peak signal amplitude.

The decrease in peak signal amplitude with removal of water from the five cements hydrated at 38 °C for 6 weeks is shown in figure 10. The individually determined values are indicated only for cement 7 made with the 0.25 w/c and the 0.50 w/c. With the other cements, the determined values were also close to the straight lines drawn through them. The gram-weight of water in the samples was in each instance based on the ignited weight of the hydrated cement.

The actual amount of cement (ignited basis) in the sample vial for cement no. 7 was 38.06 g for the 0.25 w/c paste and 33.37 g for the 0.50 w/c paste. From the W_n values (nonevaporable water) determined for these pastes it was calculated that the quantities of water in the samples

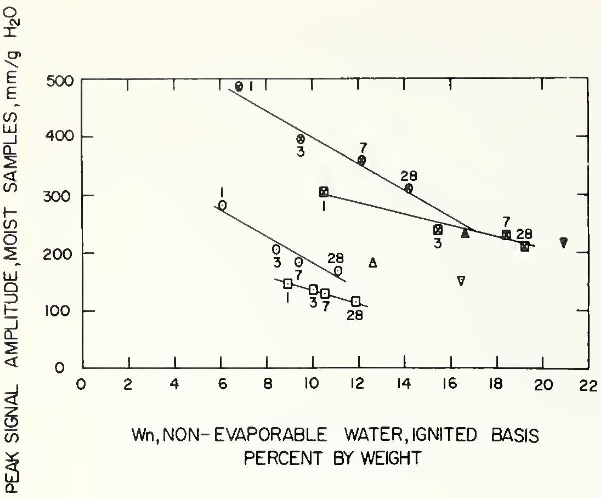

Figure 9. *Peak signal amplitude of moist samples of cement Nos. 5 and 7 of different water/cement ratios hydrated for 1, 3, 7, and 28 days at 25 °C and at 38 °C for 6 weeks versus the nonevaporable water content.*

Ct. 7	Ct. 5	w/c	Storage	Age, days
□	○	0.25	23 °C	as indicated
⊠	⊗	0.50	23 °C	as indicated
▽	△	0.25	38 °C	42
▼	▲	0.50	38 °C	42

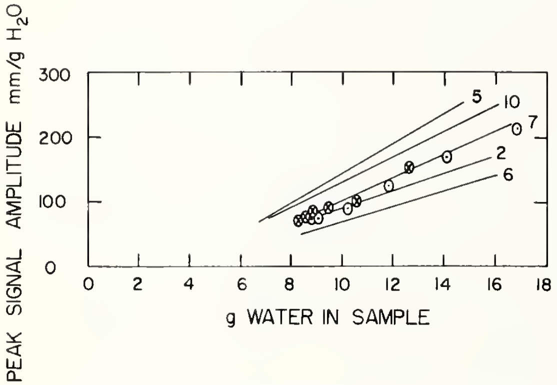

Figure 10. *Peak signal amplitudes of different cements hydrated at 38 °C for 6 weeks versus grams of water in sample containers after evacuation for various periods.*

The water content was computed from the ignition loss of the hydrated cements. Plotted points refer to cement No. 7; ⊙, w/c=0.50; ⊗, w/c=0.25.

at that degree of desiccation would be 6.3 and 7.0 g respectively, somewhat less than those for the lowest points on the graph. Similarly, for the other cements, the desiccation was not continued to the moisture content corresponding to the W_n values.

As the free or readily evaporable water is removed from hydrated cement, there is an absorption-line broadening as indicated in figure 11. If extrapolated to the respective W_n values of these cement hydrates the line widths would range from 1 to 2 gauss. It appears from this graph that the values for ΔH are different for different cements and for the same cements made with different water-cement ratios.

Different cements also exhibit different line-width values immediately after mixing with water as the following table indicates:

Cement No.	w/c	Line width
		gauss
2	0.50	0.7
2	.40	.7
2	.33	.8
5	.30	.1
6	.30	.6
7	.30	.3
10	.26	.2
10	.30	.2

It therefore appears that other factors or minor constituents in the solutions present may contribute greatly to the ΔH values obtained for the cement hydrates.

The ½ × 2-in neat cement cylinders cured for 28 days and then stored at different relative humidities for 3 months exhibited lower peak signal amplitude and ignition loss values the lower the relative humidity. This relationship is indicated in table 3 and illustrated in figure 12. There was in most instances no very significant change in either line width or peak signal-amplitude-per-gram-of-water value at relative humidites greater than 33 percent. However, the evacuated samples indicated larger ΔH values in every instance, than those stored at relative humidities of 33 percent or greater. It was noted that specimens stored at the 33 percent relative humidity exhibited very large peaks on the curve near the resonance condition for free water, indicating that a large number of mobile protons can be present in hydrated cement at normal atmospheric humidities. This factor may account for the continued hydration of cement and gain in strength under relatively dry conditions.

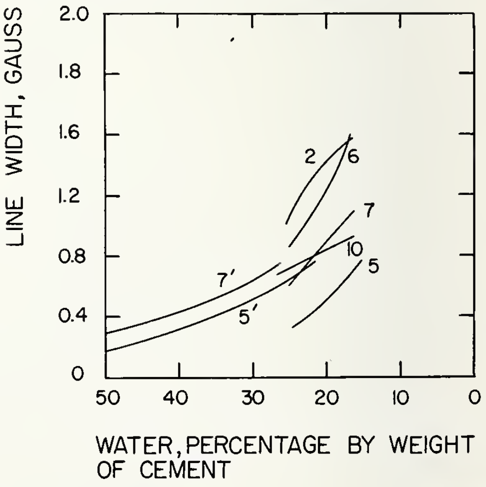

Figure 11. *Line widths of different cements hydrated for 28 days at 23 °C and evacuated to different moisture contents versus the water content expressed as percentage by weight of cement.*

Cement pastes were made with a w/c of 0.25 except cements 5′ and 7′ which were made with a w/c of 0.50. The cement numbers are indicated on the chart.

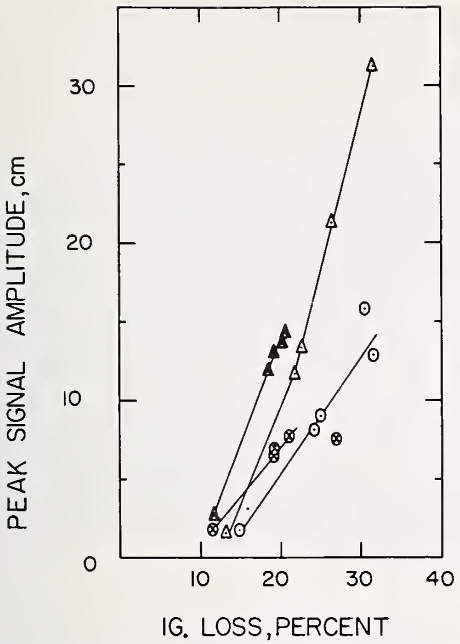

FIGURE *12*. *Peak signal amplitude of cements 2 and 5 versus ignition loss of ½ × 2-in cylinders stored at various relative humidities for 3 months.*

○ Cement 2 w/c 0.50; ⊗ Cement 2 w/c 0.25; △ Cement 5 w/c 0.50; ▲ Cement 5 w/c 0.25.

The derivative curves obtained with most of the cements, hydrated in the autoclave at 295 psi steam pressure were similar to those obtained under normal curing conditions as shown in figure 5. Other autoclaved cements, such as No. 5, presented an additional pair of peaks with a line width of about 4 gauss, as shown in figure 13. Differential thermal analysis curves of these oven-dried samples are presented in figure 14. Whereas the endothermic peak at about 550 °C appears normal for most of the hydrated cements studied, the endothermic peak at 470 °C was observed on the DTA curves only on those autoclaved cements which exhibited the 4-gauss line width on PMR curves.

A hydrated cement with 0.25 w/c which was frozen in liquid nitrogen in a Dewar and permitted to thaw in the apparatus indicated a line width of 10.6 gauss up to a temperature of about −70 °C. Between −70 and −50 °C the curve changed, a second peak of approximately 1.4-gauss width appearing. The peak signal amplitude of this narrow peak increased as the temperature rose further. As mentioned earlier the temperature measured may be somewhat different from that of the portion of the sample actually responsible for the narrow line.

TABLE 3. *Peak-signal-amplitude and line-width values of ½ × 2-in neat cement cylinders after storage at different relative humidities*

Cement number	Water/cement ratio	Relative humidity	Weight of sample	Ignition loss	Peak signal amplitude	Peak signal amplitude per gram water	Line width (ΔH)
		percent	*g*	*percent*	*cm*	*cm*	*gauss*
2	0.25	93	43.0	21.2	78	8.5	1.2
	.25	75	42.7	27.6	77	6.5	1.2
	.25	53	42.0	19.4	68	8.3	1.2
	.25	33	42.0	19.4	65	8.0	1.3
	.25	0	38.5	11.5	19	4.4	1.5
5	0.25	93	42.5	20.4	137	15.8	0.40
	.25	75	42.7	20.5	143	16.3	.44
	.25	53	42.5	19.3	130	15.9	.40
	.25	33	41.6	18.6	119	15.4	.40
	.25	0	38.8	11.7	27	5.9	1.1
6	0.27	93	39.9	22.5	65	7.2	1.2
	.27	75	34.4	21.7	68	8.0	1.1
	.27	53	39.1	21.0	62	7.5	1.1
	.27	33	39.6	20.0	62	7.8	1.1
	.27	0	36.3	12.9	19	4.0	1.7
7	0.28	93	41.9	23.6	120	12.2	0.66
	.28	75	41.7	22.6	121	12.8	.62
	.28	53	40.7	21.5	108	12.4	.62
	.28	33	41.3	21.0	100	11.6	.66
	.28	0	37.6	13.6	27	5.4	1.2
2	0.50	93	35.4	30.3	157	14.6	0.75
	.50	75	35.0	31.6	127	11.5	.82
	.50	53	31.9	25.1	91	11.3	.92
	.50	33	30.1	24.3	82	11.2	.85
	.50	0	28.2	14.9	18	4.3	1.5
5	0.50	93	35.1	31.6	313	28.2	0.20
	.50	75	33.0	26.6	214	24.5	.26
	.50	53	30.9	23.0	134	15.2	.31
	.50	33	30.6	22.0	116	17.3	.31
	.50	0	27.8	13.5	20	5.2	1.2
6	0.50	93	34.8	33.6	149	12.8	0.71
	.50	75	31.4	31.6	134	13.5	.71
	.50	53	31.8	28.7	104	11.4	.81
	.50	33	31.6	27.7	98	11.2	.78
	.50	0	26.8	16.2	16	3.5	1.5

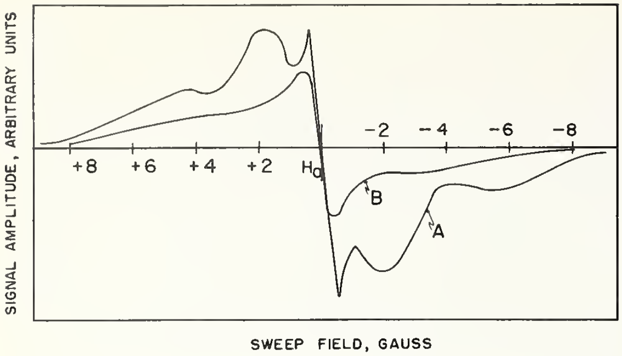

FIGURE 13. *Derivatives of energy-absorption curves of oven-dried samples of cement No. 5.*

Curve A for cement autoclaved at 295 psi for 3 hrs after 24 hrs moist curing and curve B for cement cured at 23 °C for 24 hrs.

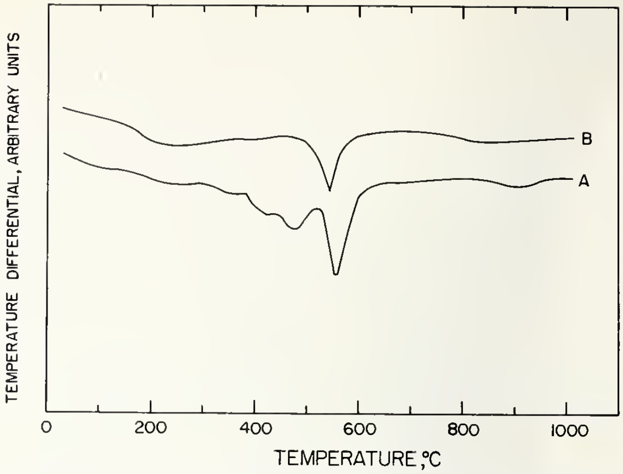

FIGURE 14. *Differential-thermal-analyses curves of oven-dried samples of cement 5, autoclaved "A" and 23 °C-cured "B" oven-dried at 110 °C.*

Summary

Exploratory studies were made at room temperature of the proton magnetic resonance line widths of hydrated cement compounds and of commercial hydraulic cements made with different water-cement ratios and hydrated at different temperatures.

The hydrated dicalcium silicate as well as tobermorite and xonotlite exhibited line widths in the range of 0.33 to 1.2 gauss with no apparent signal in the range of broad widths. Similar values for line widths have previously been obtained for laminar clays such as montmorillonite and illite. These results appear to suggest that the water in the hydration products may not be present as water of crystallization, but as adsorbed water, although further work is needed to confirm this conclusion. The predominant energy absorption of the hydrated tricalcium silicate exhibited a line width of 0.36 gauss with less absorption in the 10-gauss line-width range. The line-width values of hydrated tricalcium aluminate, gibbsite, and boehmite were in the 12- to 13-gauss range, whereas, $Al_2O_3 \cdot (0.8H_2O)$ exhibited a line width of less than 7 gauss.

The curves of hydrated cements exhibited strong absorption near the resonance magnetic field associated with adsorbed water together with some absorption in the 10-gauss range. The absorption in the 10-gauss range, normally associated with water of crystallization or hydroxides, was greatly reduced by carbonation of the hydrated cement.

The peak signal amplitude of cements sealed in vials decreased with time of hydration. However, characteristic amplitudes were obtained for each cement indicating either a difference in bonding of the water to the cement particles or the effect of minor constituents. The signal amplitude of any cement mixed with water appeared to be related to the non-evaporable water content of that cement, but different cements and different water-cement ratios resulted in different curves.

The ½×2-in. specimens stored for 3 months at a relative humidity of 33 percent or higher gave curves which suggest the possibility that most of the protons present were highly mobile and were not bonded as water of crystallization.

Some autoclaved neat cement pastes exhibited curves which were different from those obtained with other autoclaved cements or from those hydrated at normal temperatures. The autoclaved cement pastes which exhibited a line width in the 4-gauss range also had an endothermic peak at about 470 °C in differential thermal analysis measurements.

A hydrated cement frozen in liquid nitrogen exhibited a line width of 10.6 gauss up to temperatures, as measured by our procedure, of about −70 °C and a line width of only 1.5 gauss when the sample attained a temperature, as similarly measured, of −50 °C.

It is not intended that the data presented shall be construed as final quantitative evaluation of parameters involving the structure or the hydrogen bonding in hydrated cements or cement compounds. It is concluded that the study confirms the utility of the NMR techniques for better understanding of these materials.

Appreciation is expressed to Dr. George L. Kalousek of Owens-Corning Fiberglass Corporation for samples of tobermorite and xonotlite, and to various members of the National Bureau of Standards including C. M. Hunt and A. Woolf for preparation of C_2S, C_3S, and C_3A hydrates and determining nonevaporable water contents;

to E. T. Carlson for samples of gibbsite, boehmite, and $Al_2O_3 \cdot 0.8H_2O$; to M. R. DeFore and E. Trattner for preparation of cement samples; to E. S. Newman for differential thermal analyses and to others who have assisted in performing the measurements.

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Paper IV–S6. Infrared Spectroscopy Studies on the Hydration of Clinker Minerals and Cements*

H. Lehmann and H. Dutz

Synopsis

The infrared spectra of the dry minerals γ-C_2S, β-C_2S, C_3S, alite, CA, $C_{12}A_7$, C_3A, one portland cement, and one aluminous cement were studied. The spectra can serve as a basis for qualitative and quantitative analysis. The substances were hydrated and examined after 1 hr, 1 day, and 7 days. Progress of hydration, fixation of water, absorption of carbon dioxide, and the nature of the hydration products are discussed.

Résumé

L'exposé étudie les spectres infra-rouges des minéraux secs γ-C_2S, β-C_2S, C_3S, alite, CA, $C_{12}A_7$, C_3A, un ciment portland et un ciment alumineux. Les spectres peuvent servir de base à des analyses qualitatives et quantitatives. Les substances étaient hydratées et examinées après une heure, un jour, et sept jours. Discussion est faite des progrès de l'hydratation, de la fixation de l'eau, de l'absorption du gaz carbonique et de la nature des produits d'hydratation.

Zusammenfassung

Die trockenen Minerale γ-C_2S, β-C_2S, C_3S, Alit, CA, $C_{12}A_7$, C_3A, ein Portlandzement und ein Tonerdeschmelzzement werden ultrarotspektroskopisch untersucht. Die Spektren können als Grundlage für die qualitative und quantitative Analyse dienen. Die Substanzen wurden hydratisiert und nach einer Stunde, einem Tag und sieben Tagen untersucht. Der Hydratationsfortschritt, die Bindung des Wassers, die Aufnahme von Kohlendioxid und die Art der gebildeten Hydratationsprodukte werden diskutiert.

Introduction

Few papers are as yet available on the use of infrared (IR) spectroscopy in cement research, In a doctoral dissertation C. M. Hunt [1][1] reported in investigations of certain silicates, aluminates, and other compounds that are of interest in portland cement chemistry. Unfortunately this work was not available to us. In joint studies, H. Lehmann and H. Dutz [2] established among other things the rate of hydration of some clinker minerals, one portland cement, one aluminous cement, and one blast-furnace slag. D. M. Roy [5] presented spectra of β- and γ-C_2S. G. L. Kalousek and R. Roy [4] studied certain minerals and indicate a possible method of determining interlayer water. H. E. Petch, N. Sheppard, and H. D. Megaw [5] used IR spectroscopy to check the accepted positions of hydrogen in afwillite.

It was the purpose of our studies to follow, in time, the reaction of clinker minerals with water. Relatively small quantities of water were used, and measurements followed within a short time.

Experimental Procedure

The clinker minerals were synthesized in the usual manner and were checked for purity by chemical and roentgenographic methods. The compositions of the cements are given in table 1.

All substances were subjected to sedimentation analysis with isopropyl alcohol, the $<2\mu$ fraction was separated, and the alcohol driven off at 120 °C. Only particles of this size group were used in the investigations, in order to insure that the absorption spectra would not be affected by light scattering. A 40-mg sample of the substance was mixed with water to produce hydration (silicates and portland cement, w/c 0.5; aluminates and aluminous cement, w/c 1.0) and stored in a tightly sealed glass tube at a room temperature of 22 °C.

Before measurement, the substances were freed from adsorbed water by heating for 15 min at 105 °C. The potassium-bromide-pellet method was used. A 0.9 mg portion of the substance (1.8 mg for portland cement) was mixed with 1 g of potassium bromide and pressed in the form of a transparent disk. This method of preparation has the advantage of being quick. For more extensive studies of hydrogen bonds (H-bridging), experiments should be repeated in a suspension medium of lesser polarity than potassium bromide.

The spectra were determined with a Leitz IR spectrograph, working in the 1–15-μ range with a NaCl prism, and in the 15–24-μ range with a KBr prism. The exact position of the bands in the 1.9–3.8-μ range was measured with a LiF prism.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Institut für Steine und Erden der Bergakademie Clausthal, Clausthal-Zellerfeld, Germany.

[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Composition of cements*

	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	SO_3	S″	MnO	Mn_2O_3	P_2O_5	Insoluble residue	Loss on ignition
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Portland cement	17.22	8.72	2.63	--------	63.15	4.07	0.22	0.18	1.33	--------	0.35	0.30	0.21	0.54	2.20
Aluminous cement	6.87	45.45	2.45	1.44	39.30	1.04	0.46	0.25	0.30	1.04	--------	--------	--------	1.32	--------

Results and Discussion

Each substance has a characteristic IR spectrum. It can serve as a basis for qualitative and quantitative analysis and for a determination of structure. From our standpoint, the method was of advantage because it permits direct observation of the binding of water, CO_2 absorption, and changes of the structure of silicates and aluminates during hydration.

Before discussing the individual spectra, we will briefly review the fundamental principles of IR spectroscopy.

The frequency of vibration is given in cm^{-1}. The relation to the micron is given by the equation

$$\nu[cm^{-1}]=\frac{10,000}{\lambda[\mu]}$$

The frequency or position of molecular vibration is determined by the number of atoms in the vibrating structure, the mass of the atoms which form the vibrating structure, its symmetry, the bond between the atoms, and the surroundings of the vibrating structure.

In the calcium silicates, the absorption by the SiO_4 tetrahedron appears in the accessible portion of the IR spectrum. The vibrations, in which the O atoms vibrate along the lines connecting them with the central Si atom, are called valency vibrations; they lie at around 11μ. Vibrations in which the bonds undergo flexural stress are called deformation vibrations; they lie at around 19μ.

When the tetrahedra are connected into chains, layers, or lattices, the valency vibrations become displaced toward lower wavelengths, or higher wave numbers, i.e., the structure vibrates more rapidly. Deformation vibrations are displaced only slightly toward shorter wavelengths [2].

Water vapor has a deformation vibration band at 6.27μ and a valency vibration band at 2.66μ. H-bonds affect vibrations according to their strength. For this reason the deformation vibration band of water lies at 6.10μ and the valency vibration band at 2.95μ. From the magnitude of the displacement, the half width and change in intensity of the band one can draw conclusions regarding the strength of H bonds, interatomic spacings, etc.

The carbonate bands lie at 14.16, 11.40, with the strongest at 7.00μ.

γ-C_2S (figure 1)

The absorption bands between 10.0 and 12.5μ are the result of SiO_4 valency vibrations; between 17 and 22μ we find the deformation vibration bands.

Upon completion of hydration no evaporable water or carbonate could be detected in the substance. It has been known for some time that γ-C_2S has no hydraulic properties.

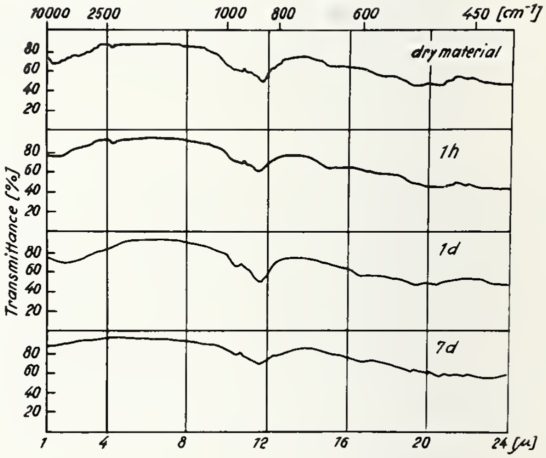

FIGURE 1. *Infrared spectra.*
Hydration of γ-C_2S.

β-C_2S (figure 2)

The spectrum of the β-modification is definitely different from that of the γ-form. Although the valency vibrations still lie in the same range, the β-modification exhibits four maxima, while the γ-form has only two; aside from this difference the band at 11.75μ is weakest in the β-modification and strongest in the γ-form.

The deformation vibrations of the β-modification lie between 18 and 20μ; those of the γ-form between 17 and 21μ.

The progress of hydration can be very satisfactorily followed by the loss of intensity in the SiO_4 valency vibration band. The intensities of the individual maxima of the valency vibration band decrease at different rates; maximum extinction at 11.75μ drops from 0.22 to 0.15; at 11.2μ

from 0.44 to 0.22; at 10.8μ from 0.48 to 0.24 and at 10.05μ from 0.48 to 0.30; on the first and last there become superimposed the absorptions of the newly formed phases, whose spectrum is better revealed in hydrated C_3S and will be discussed in that connection. Half of β-C_2S has reacted at 7 days. Increase of the nonevaporable water, read at 2.95μ, is not very significant. Carbon dioxide absorption can be followed from 6.7 to 7.0μ.

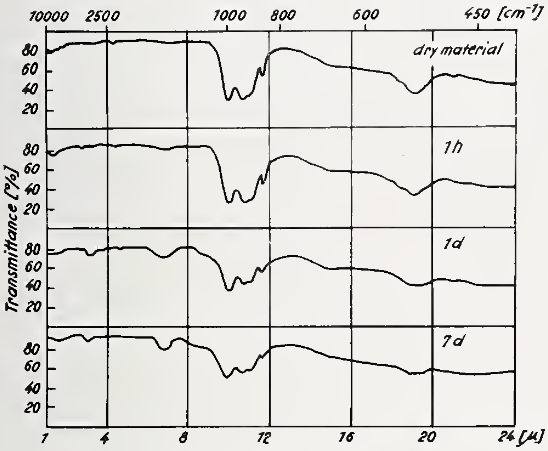

FIGURE 2. *Infrared spectra.*
Hydration of β-C_2S.

C_3S (figure 3)

The valency vibration bands of this mineral are located at lower wave numbers, or higher wavelengths, than for β-C_2S, namely between 10.0 and 12.3μ. Two deformation bands appear at 19.0μ and 22μ. The higher number of calcium ions in C_3S tends to screen the SiO_4 tetrahedra more strongly from each other, the frequencies becoming lower than in β-C_2S.

The reaction with water takes place very rapidly. At the end of 1 day practically all of the C_3S has undergone reaction. The maxima at 10.6μ and 11.2μ disappear and are replaced by a broad maximum at 10.4μ, which migrates to 10.3μ after 7 days. It is produced by the newly formed phase. From the above one may conclude that during hydration of C_3S the SiO_4 tetrahedra combine into larger structures, chains, and layers. The effect can have no other explanation, as water absorption alone during formation of hydrates causes a lowering of frequency and thus a displacement toward greater wavelengths [6]. Numerous other investigations have already shown that calcium silicate hydrates form with continuous molecule growth. The magnitude of the newly formed particles, however, can not yet have attained the order of a few microns in our case, as otherwise light scattering would have been produced at the beginning of the spectrum, i.e., absorption would have become evident. This, however, is not the case.

From the broad and flat shape of the bands of new formations it may be concluded that the molecules are of low crystallinity. This conclusion is also in agreement with the results of other studies.

The water uptake of C_3S is greater than that of β-C_2S. The band shoulder at 2.75μ indicates valency vibrations of free OH-groups, which in all probability belong to calcium hydroxide.

Carbonate formation is more pronounced than for β-C_2S.

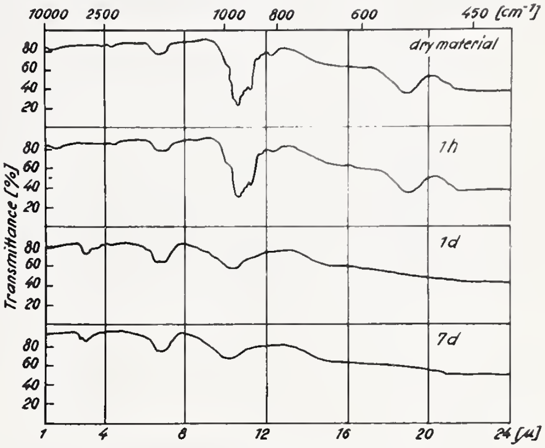

FIGURE 3. *Infrared spectra.*
Hydration of C_3S.

Alite (figure 4)

The alite spectrum is, as expected, very similar to that of C_3S. The valency vibration band is possibly less well defined, and the principal maximum lies at 10.7μ instead of 10.6μ as for C_3S. Aluminum is not present as C_3A, for its typical bands are lacking.

When alite is heated in a glazed porcelain crucible at 800 °C, two double bands appear thereafter, at 8.7–8.9μ and at 16.35–16.8μ (figure 10). These bands are typical for the substances in which an AlO_4 coordination is suspected, e.g., albite, orthoclase, sillimanite, mullite. This is not

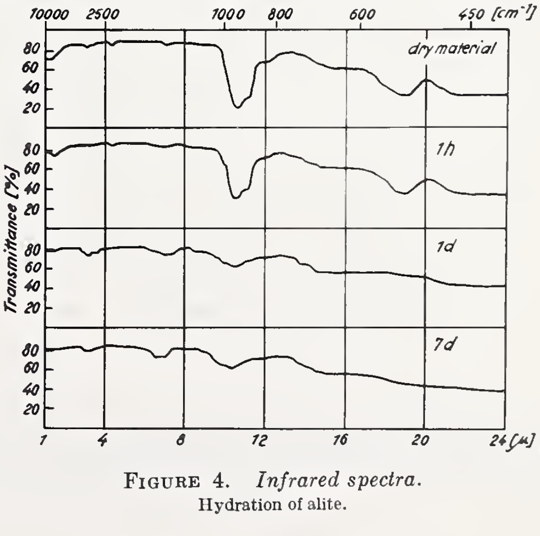

FIGURE 4. *Infrared spectra.*
Hydration of alite.

to say that the above bands actually result from AlO_4 groups. Aluminum can also cause a strengthening of the Si–O bond, which would produce vibrations at higher frequencies. These bands were also observed with portland cement and aluminous cement.

The reaction with water takes place even somewhat more rapidly than for C_3S. Here also the bands of the newly formed mineral phases are broad and flat, and lie at smaller wave lengths than for the dry mineral phase.

Portland Cement (figure 5)

The cement consists essentially of β-C_2S, which can be identified by bands at 10.1 and 11.8μ. Bands at 10.9 and 11.25μ have the same intensity in β-C_2S as that at 10.05μ. In portland cement, however, they are somewhat better revealed, an indication that alite is present, whose bands are superimposed on those of β-C_2S at 10.9 and 11.2μ. All maxima are displaced by 0.05 to 0.1μ in the direction of longer waves as compared with pure minerals. Flat absorption at 13.35 to 14.0μ is attributable to vibration of AlO_6 octahedra.

During hydration the double band at 10.9 and 11.2μ is reduced most rapidly, which points to a rapid reaction of alite. After 1 day the intensities of the three bands at 10.05, 10.85, and 11.25μ are equal; after 7 days the band at 10.05μ is more intense than the two others, as absorption of calcium silicate hydrates adds its effect.

The intensities of nonevaporable water and carbonate are considerably more marked than in hydrated alite or β-C_2S.

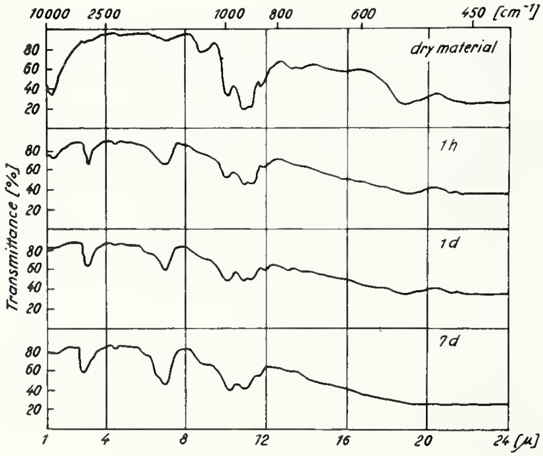

FIGURE 5. *Infrared spectra.*
Hydration of portland cement.

CA (figure 6)

The AlO valency vibrations have lower frequencies than the corresponding SiO vibrations; the deformation vibrations are both lower and higher.

In CA the vibrations have a range from 10.5 to 24.0μ; one could assume that the group from 10.0 to 13.7μ is to be regarded as valency vibrations and the rest as deformation vibrations.

Hydration proceeds quickly, so that at the end of 1 day the greater part of the mineral has undergone reaction. After 7 days one encounters a very broad absorption band, which reaches from 9.0μ to the end of the measurement range and exhibits a larger number of small maxima.

Water absorption is greater than in the silicates; the OH-valency vibration band lies somewhat higher, at 2.90μ. The effect of H bonds is smaller than in silicates; carbonate formation is weaker.

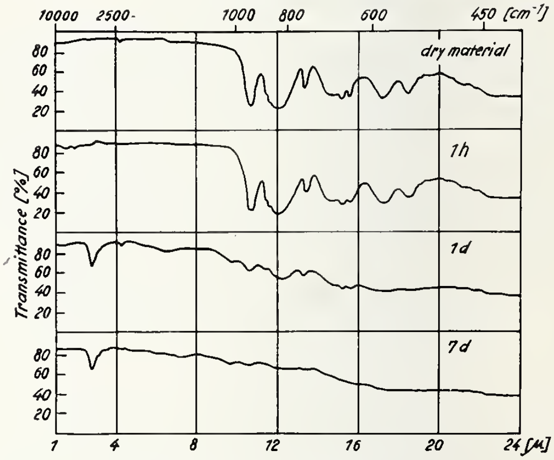

FIGURE 6. *Infrared spectra.*
Hydration of CA

$C_{12}A_7$ (figure 7)

The spectrum of this mineral differs decidedly from the preceding, the number of bands being smaller. The valency vibration band extends from 10.5 to 13.6μ and has a shoulder at 11.1μ, a very intensive maximum at 11.75μ and two smaller maxima at 12.7 and 13.4μ. At 17.25 and

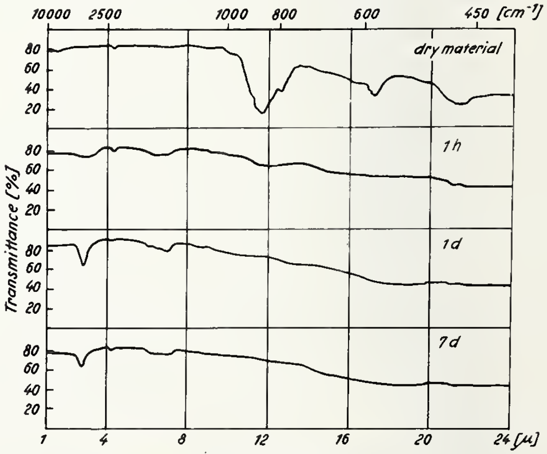

FIGURE 7. *Infrared spectra.*
Hydration of $C_{12}A_7$.

21.6μ we find maxima of two further bands which are probably attributable to deformation vibrations.

Hydration takes place at a rapid rate, so that almost the entire quantity of the mineral has undergone reaction after 1 hr. As in CA a broad absorption band is formed with a maximum at 7 days between 18.3 and 19.9μ.

Water absorption and carbonate formation are about the same as for CA.

C_3A (figure 8)

In the range of valency vibrations from 10.7 to 14.4μ we find four larger and four smaller maxima. The deformation vibration bands are relatively flat and have two maxima at 19.2 and 19.8μ; a further broad maximum begins at 21.4 μ and extends to beyond 24μ.

Hydration is faster than for any of the other minerals; after 1 hr all of the mineral has undergone reaction. A broad band with a maximum at 19.1μ makes its appearance, the peak becoming displaced at 7 days of hydration to 18.8μ, and a second one is added at 12.8μ.

After 1 hr the OH groups vibrate over a wide range. The band extends from 2.75 to 3.0μ; free as well as H-bonded OH groups are present. After 1 day the greater part of the water taken up is present as free OH groups; after 7 days the band maximum has moved to 2.74μ; and two band shoulders appear at 2.77 and 2.79μ. The broad, not very intensive maximum which extends from 2.80 to 2.94μ is attributable to water, whose H bonds are however weaker than is normal for water. Carbonate formation is slight.

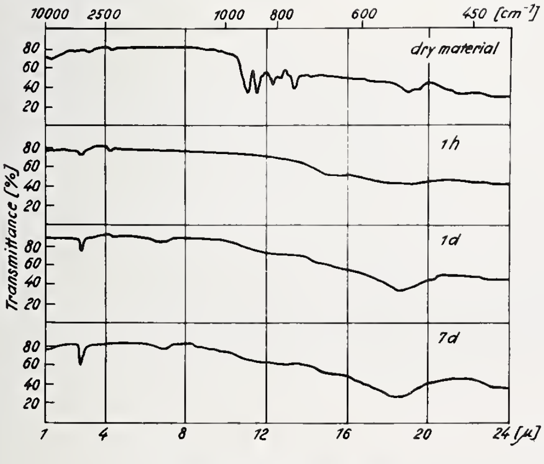

Figure 8. *Infrared spectra.*
Hydration of C_3A.

Aluminous Cement (figure 9)

The spectrum is closest to that of CA, although the bands at 10.8, 13.4, 17.3, and 18.5μ are lacking. The double bands at 8.75 and 8.9μ, 9.95 and 10.3μ, and 16.3 and 16.8μ do not appear in pure calcium aluminates. The first and last are typical for substances in which AlO_4 groups are suspected.

Hydration proceeds even faster than in CA, the intense maximum of the dry cement at 12μ disappearing more rapidly than the double bands at 8.75–8.9μ and 9.9–10.3μ. Three quite flat maxima in the hydrated material from 11.6 to 12.9μ, from 17.3–19.8μ, and from 21.1 to 25μ are rather well covered by the absorptions of calcium aluminate hydrates forming from CA.

The water is taken up primarily as H_2O, identified by a broad band whose maximum extends from 2.84 to 2.97μ. Free OH groups scarcely occur. Carbonate formation is very small.

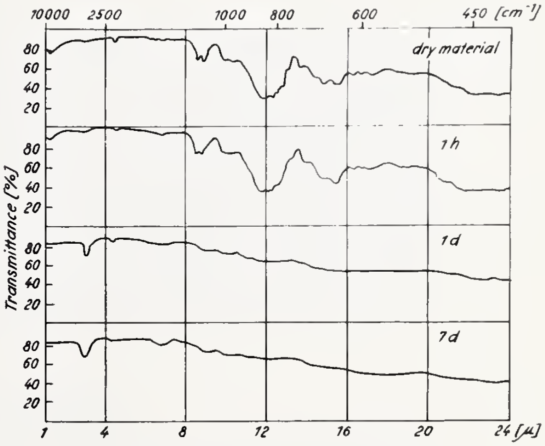

Figure 9. *Infrared spectra.*
Hydration of aluminous cement.

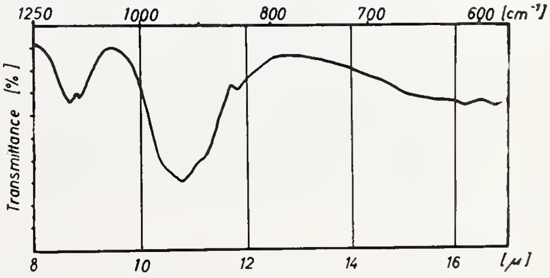

Figure 10. *Infrared spectrum.*
Alite, heated for 15 min in a porcelain crucible at 800 °C.

Summary

Clinker mineral phases can be identified and distinguished from one another with the aid of their characteristic IR spectra; β-C_2S can be distinguished from γ-C_2S in this manner. The spectra may be used as a basis for qualitative and quantitative analysis.

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Paper IV–S7. Heat of Hydration of Cement as Affected by Water-Cement Ratio*

Ulf Danielsson

Synopsis

The influence of the water-cement ratio on the heat evolution accompanying the chemical reactions between a portland cement and water has been investigated using a conduction calorimeter. The experiments, which have been carried out at 20 °C and with water-cement ratios ranging from 0.25 to 0.50, show for later ages the well-established direct relation between total heat of hydration per unit weight cement and water-cement ratio. For early ages, up to about 9 hr, the rate of heat of hydration was found to vary inversely with the water-cement ratio. This observed effect can be explained to some extent by temperature differences between the various pastes, both during mixing and while in the calorimeter. The results indicate, however, that in the early stages of hydration the major part of the measured change in rate of hydration with water-cement ratio is of a chemical nature. According to a hypothesis put forward in this paper, this rate dependence is attributable to the presence of alkali in the cement and is explained in terms of the alkali concentration in the fluid phase.

Résumé

L'influence du rapport eau/ciment sur l'évolution thermique concommittante aux réactions chimiques entre un ciment Portland et l'eau est étudiée à l'aide d'un calorimètre à conduction. Les expériences qui ont été effectuées à 20 °C et avec des rapports eau/ciment allant de 0,25 à 0,50 montrent, pour les phases tardives, une relation directe bien établie entre la chaleur d'hydratation totale par unité de poids de ciment et le rapport eau/ciment. Aux phases initiales, jusqu'à environ 9 heures, la rapidité du dégagement de chaleur d'hydratation s'avéra varier en sens inverse du rapport eau/ciment. Ce phénomène ayant été observé peut dans une certaine mesure être expliqué par des différences de température entre les différentes pâtes, aussi bien au cours du mélange que dans le calorimètre. Les résultats indiquent cependant qu'aux premières phases de l'hydratation la majeure partie de la variation mesurée de la rapidité d'hydratation en fonction du rapport eau/ciment est de nature chimique. Selon une hypothèse émise dans le présent compte-rendu, cette subordination de la rapidité peut être attribuée à la présence d'alcali dans le ciment et est expliquée par la concentration d'alcali dans la phase fluide.

Zusammenfassung

Der Einfluss des Wasserzementwertes auf die Wärmeentwicklung, die die chemischen Reaktionen zwischen ein Portlandzement und Wasser begleitet, wurde mittels eines Leitungskalorimeters untersucht. Die Versuche, die bei 20 °C und mit Wasserzementwerten von 0,25 bis 0,50 ausgeführt wurden, weisen ein für spätere Zeitpunkte früher festgestellte direkte Beziehung zwischen der gesamten Hydratationswärme pro Zementgewichteinhelt und dem Wasserzementwert auf. Für die ersten Zeitpunkte, bis zu etwa neun Stunden, konnte festgestellt werden, dass sich die Geschwindigkeit der Hydratationswärmeabgabe umgekehrt zum Wasserzementwert ändert. Diese beobachtete Wirkung kann aber gewissermassen durch die Temperaturunterschiede zwischen den verschiedenen Massen, sowohl während der Vermischung als auch im Kalorimeter, erklärt werden. Die Ergebnisse deuten jedoch an, dass bei Beginn der Hydratation der Hauptteil der gemessenen Hydratationsgeschwindigkeitsveränderung bei Variation des Wasserzementwertes von chemischer Art ist. Laut einer in diesem Bericht vorgelegten Hypotese ist diese Geschwindigkeitsabhängigkeit auf das Vorhandensein von Alkali im Zement zurückzuführen, und sie wird durch die Alkalikonzentration der flüssigen Phase erklärt.

Introduction

At the Swedish Cement and Concrete Research Institute, Stockholm, we have carried out an investigation of the kinetics of cement hydration, which is now completed and under publication. Part of this work has been described earlier [1][1]. Another section, concerning the effect of different water-cement ratios on the heat of hydration of an ordinary portland cement, is presented briefly here in advance of publication, because the results supplement the discussion on this point in the paper, "Kinetics of the Hydration of Portland Cement" [2].

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Swedish Cement and Concrete Research Institute, Stockholm, Sweden.

[1] Figures in brackets indicate the literature references at the end of this paper.

Experimental

Materials

The cement used was a normal portland cement with the following oxide composition:

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Ignition loss
Percent	20.9	4.2	2.6	63.7	3.9	2.5	0.4	0.4	1.3

The uncombined CaO was 1.1 percent.

Using the formulae given by Bogue [3], the calculated mineralogical composition was:

Compound	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$
Percent	56.7	17.2	6.7	7.9	4.3

The specific surface of the cement, determined by the Lea and Nurse air-permeability method, was 3,120 cm^2/g. The density, determined with a pycnometer filled with kerosene, was 3.12 g/cm^3.

Distilled water was used for mixing.

Mixing

The investigation comprises four experiments carried out on pure cement paste with the water-cement ratios: 0.25, 0.30, 0.40, and 0.50. The amounts of cement and water required to give each batch a volume of approximately 2.5 liters, were weighed out. Cement and water, both originally at 20 °C, were mixed together in an ordinary household mixer, in a constant-temperature room set for 20 °C. The mixing time was 10 min, and the temperature of the cement paste was taken during the mixing.

Measurements

Test tubes were filled with paste and sealed with rubber stoppers. Twenty min after mixing began, one of these test tubes was placed in a thermos flask containing water at 20 °C. Ten min later, it was transferred to a conduction calorimeter, shown in figures 1 and 2.

Due to the exothermal reactions between cement and water, the temperature of the inner calorimeter tube rose slightly above the temperature of the outer tube. This temperature difference was measured accurately by means of 30 thermocouples arranged in series, connected to a precision potentiometer. The temperature of the outer wall of the calorimeter was constant, and the calorimeter thus worked under almost isothermal conditions. To keep this outer wall at as constant a temperature as possible (for these experiments, 20 °C), which is important if reliable results are to be obtained, the calorimeter was immersed in the oil bath of an elaborate thermostat, specially designed for the purpose. Submerged in the oil bath as a sensing element was a thermistor, coupled to a Wheatstone bridge, the output of which was connected to a servo system turning a Variac. This fed heating elements in the oil bath. In this way continuous, sensitive temperature control was achieved, and the temperature in the oil bath could be kept constant to within ±0.001 °C even for long periods. A view of the whole apparatus is shown in figure 3.

The other test tubes were placed directly in the oil bath, and removed one at a time at predetermined ages, whereupon the total heat of hydration of the paste was measured, using the familiar heat-of-solution method.

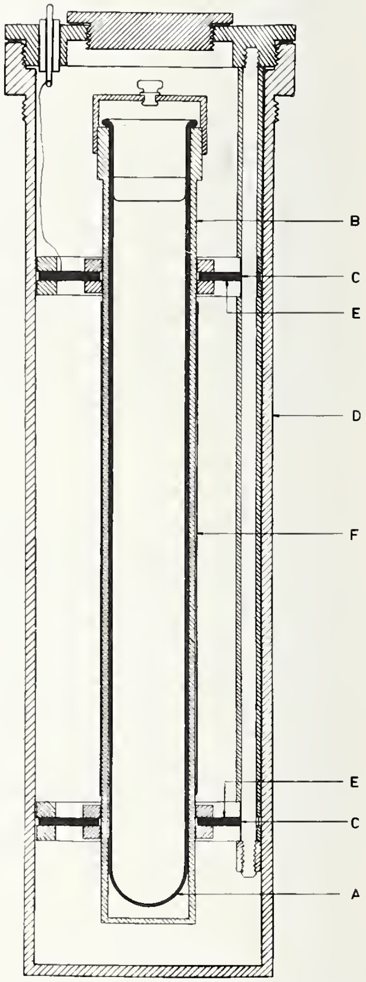

Figure 1. *Cross section of the conduction calorimeter.*

A: glass test tube (6 in × 5/8 in) containing cement paste undergoing testing, fitting tightly into inner calorimeter tube (B).
B: inner calorimeter tube of brass, held in central position in calorimeter by means of two rings (C).
C: two rings of bakelized paper.
D: outer calorimeter tube, kept at constant temperature in thermostat.
E: 30 thermocouples in series to measure temperature differences between inner and outer tubes.
F: heating winding for calibration.

Figure 2. *Calorimeter.*

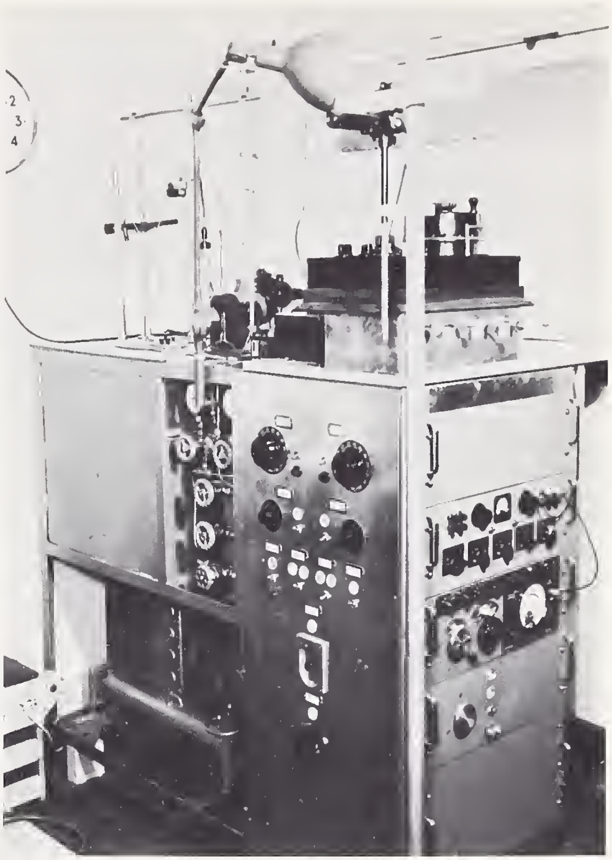

Figure 3. *Apparatus for measuring the rate of heat of hydration.*

Results and Discussion

The rate of heat of hydration values obtained with the conduction calorimeter are shown in figure 4, the rate per gram of ignited cement [2] being plotted as a function of time. The estimated errors in the measured rates amount to ±1 percent and ±0.1 cal/g and day, except at the beginning of an experiment, when the errors may be considerably greater due to temperature disturbances in the thermostat as the test tubes are being transferred. These additional measuring errors decrease rapidly and have vanished after 2 hr.

Figure 5 gives the total heat of hydration versus time. The total heat of hydration has been obtained by integration of the measured rates, the constant of integration being established by comparison with the results from the heat-of-solution determinations. It can be seen from this diagram that for later ages the heat of hydration varies directly with the water-cement ratio. Others have found the same, and the usual explanation is that for low water-cement ratios, after some hydration has taken place, there is insufficient water present to keep the reactions going (self-desiccation). Furthermore, when the water-cement ratio is low, the cement paste becomes so dense that the diffusion of water to, and new hydration products from, the reaction zones is difficult. The retardation of the hydration for low water-cement ratios is more clearly shown in figure 6, where the rate of heat of hydration is plotted against the total heat of hydration.

From these diagrams it may also be seen that up to an age of about 2 days, the deviations between the curves are comparatively small. However, taking the accuracy of measurements into account, it is evident from figure 4 that for early ages (that is from 2 hr at the latest, up to about 9 hr), the measured rates of heat of hydration vary inversely with the water-cement ratio. This unexpected finding agrees with the results of Taplin [4], who, in studying the amount of bound water, also found that for the pastes with the lowest water-cement ratios, the rate of hydration during the first hours was higher than for pastes with a high water-cement ratio. Copeland and

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[2] Throughout this paper all values for heat of hydration have been calculated for ignited cement.

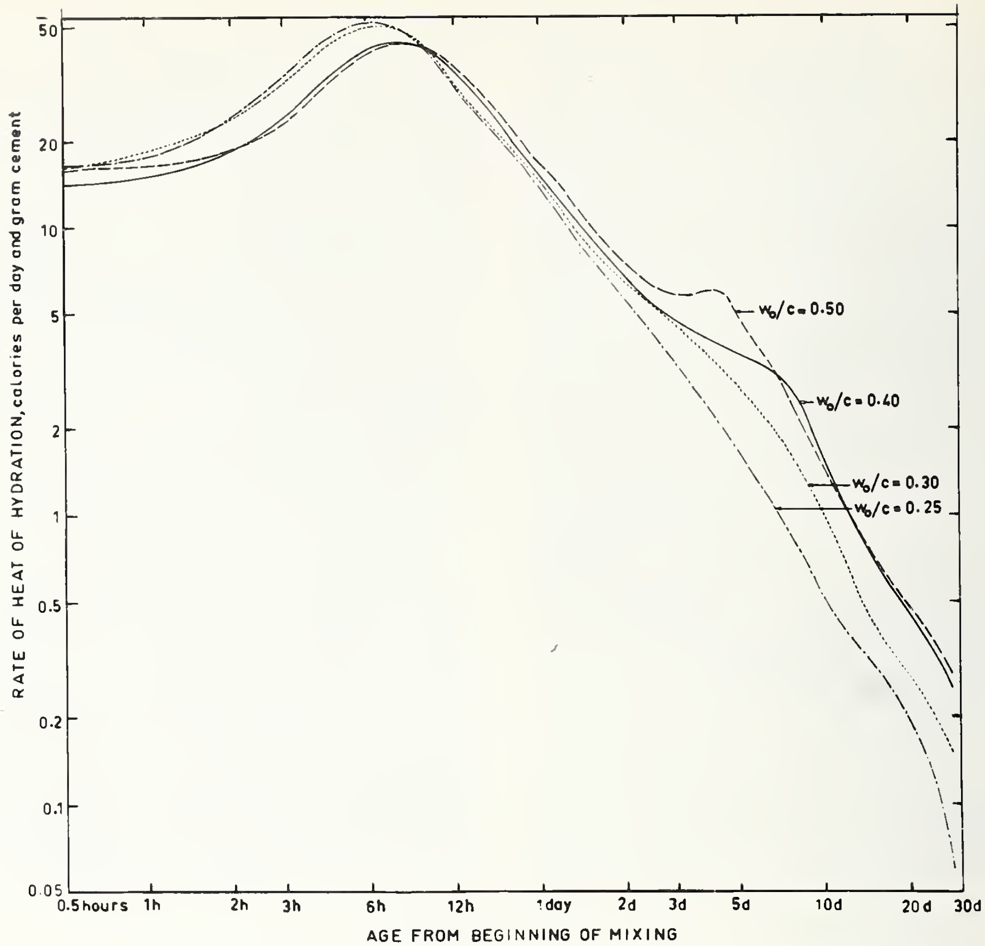

FIGURE 4. *Effect of water-cement ratio on the rate of heat of hydration.*

Kantro [2], when discussing the results of Taplin, have offered as the probable explanation of this result, the suggestion that the observed differences in the rate of hydration are due to the greater temperature rise above the ambient temperature for paste specimens with low water-cement ratios.

Also in the case of our investigation, there have been dissimilar rises in temperature for the different pastes, as figure 7 shows. Here, to the left in the diagram is recorded the temperature of the paste during mixing, and to the right, the calculated temperature of the inner calorimeter tube. With the X-axis at 20 °C, as in the diagram, the values for the mean temperature of the cement paste while in the calorimeter are correspondingly higher, by a factor of approximately 6 percent, calculated from the thermal conductivities of the various materials. The temperature curves between 10 and 40 min are only schematically drawn to give a rough indication of the temperature course during this interval.

The effect of temperature on the rate of heat of hydration has been studied earlier [1] for the same cement and with a water-cement ratio 0.4. These experiments show that in the early stages of hydration at a temperature of approximately 20 °C the rate increases by about 7 percent per degree centigrade. This figure is not likely to vary much with changes in the water-cement ratio. Because the temperature of the paste specimens deviates from 20 °C while they are in the calorimeter, the measured values for the rate should be corrected before being compared. From figure 7 it can be seen that these corrections reach their greatest values at an age between 7 and 9 hr. The estimated maximum correction is 9 percent for water-cement ratio 0 25, and 5 percent for water-cement ratio 0.50, which should be subtracted from the measured values. But the differences between the measured rates reach considerably higher values, as is demonstrated in figure 8, where the rates of heat of hydration relative to that for a water-cement ratio 0.40 are plotted against time for the early ages considered here. The greatest deviation in rate occurs at an age of approximately 3½ hr and is as much as 40 percent higher for water-cement ratio 0.25 than for 0.40. The correction discussed is thus far from sufficient to explain the observed differences.

When comparing the rates of heat of hydration for pastes of the same age, it is not only the temperature of the cement paste at the moment of

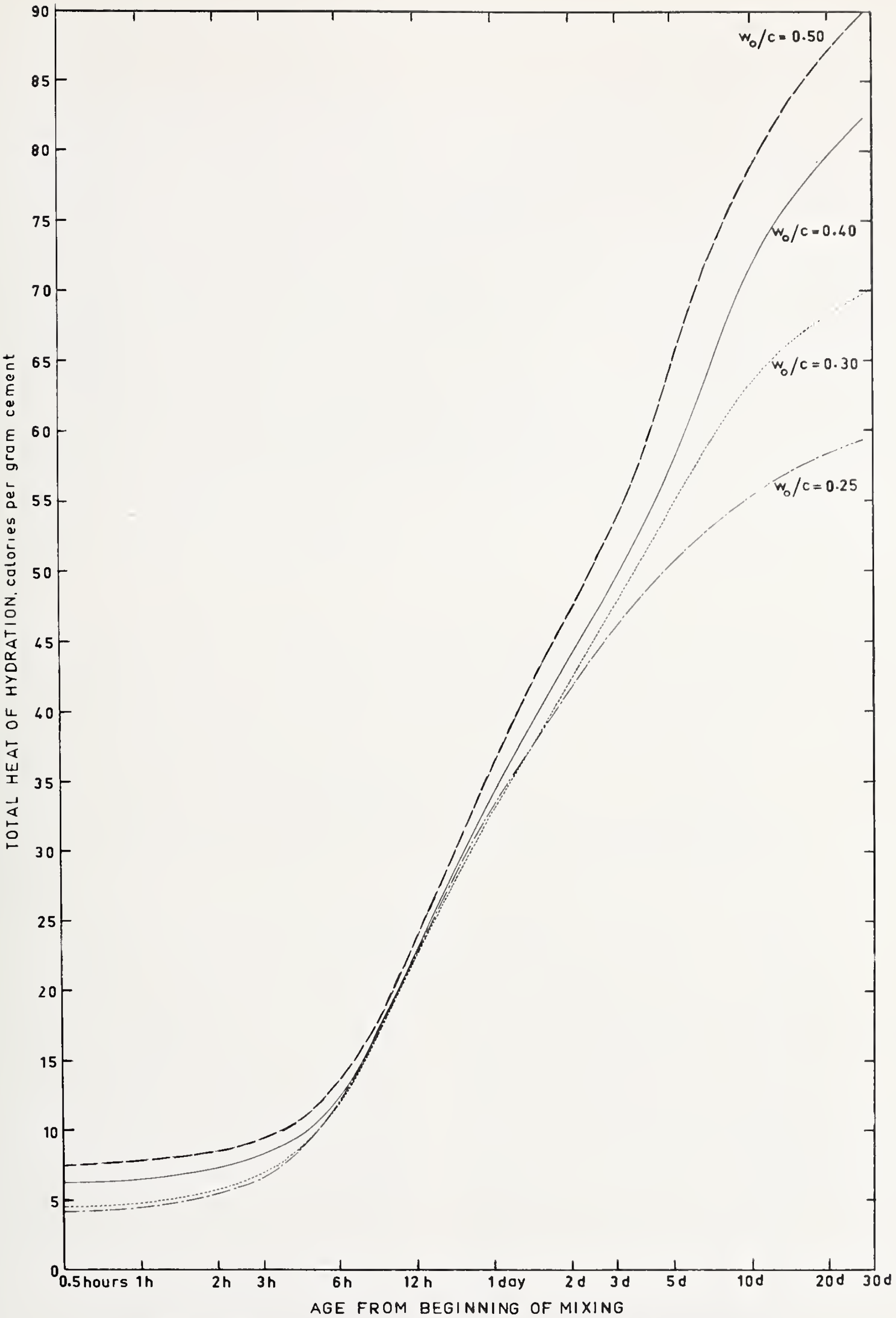

FIGURE 5. *Effect of water-cement ratio on the total heat of hydration.*

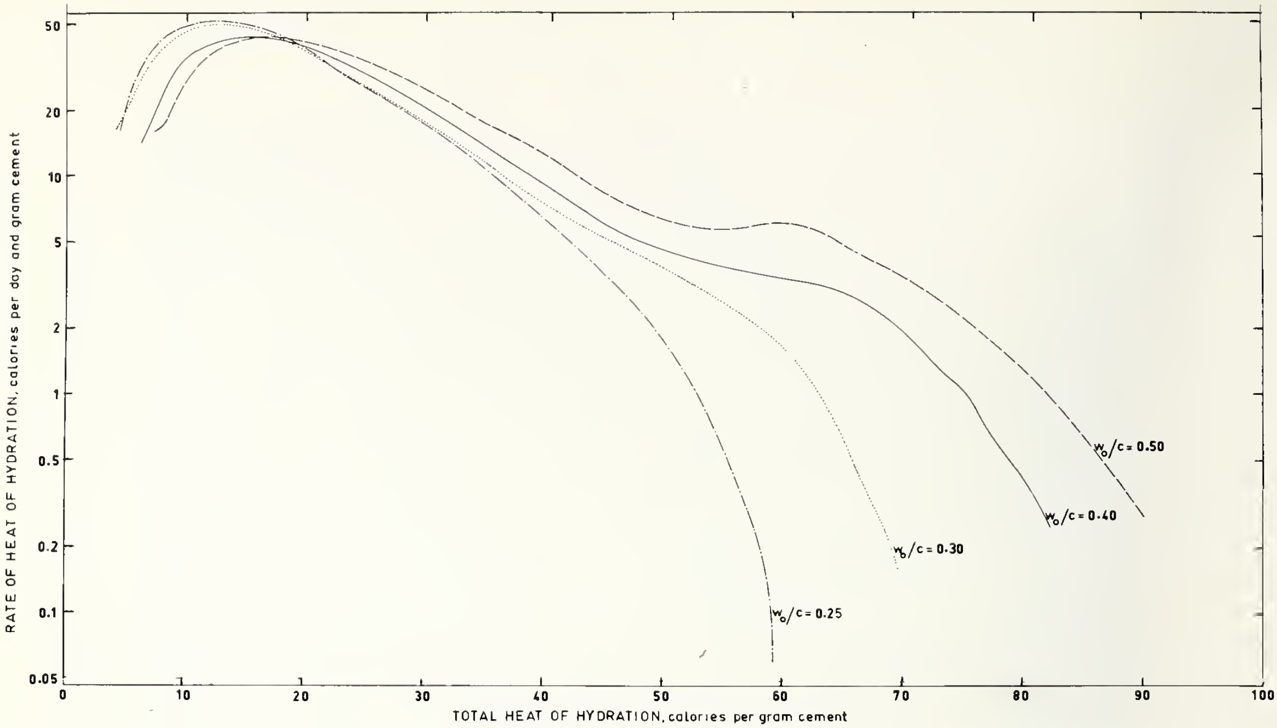

Figure 6. *Rate of heat of hydration plotted against the total heat of hydration for different water-cement ratios.*

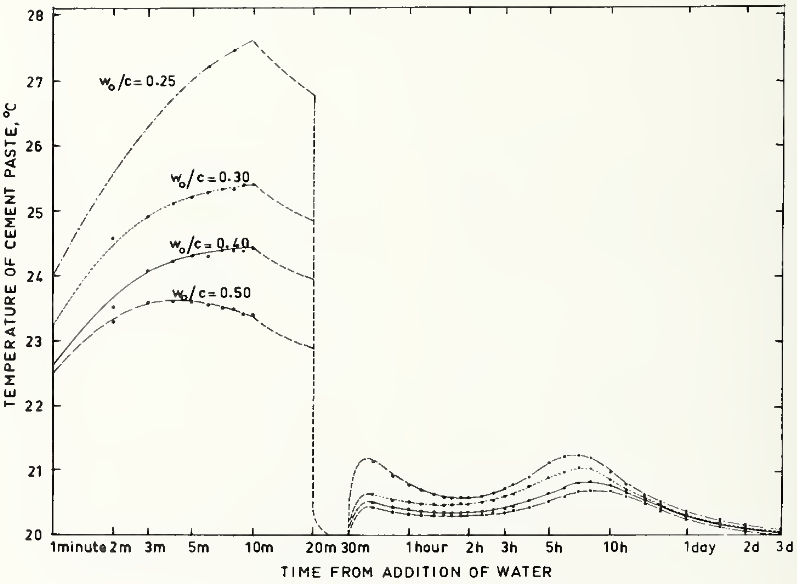

Figure 7. *Temperature of the pastes.*

The curves are in the same order, top to bottom, on the right side of the diagram as on the left.

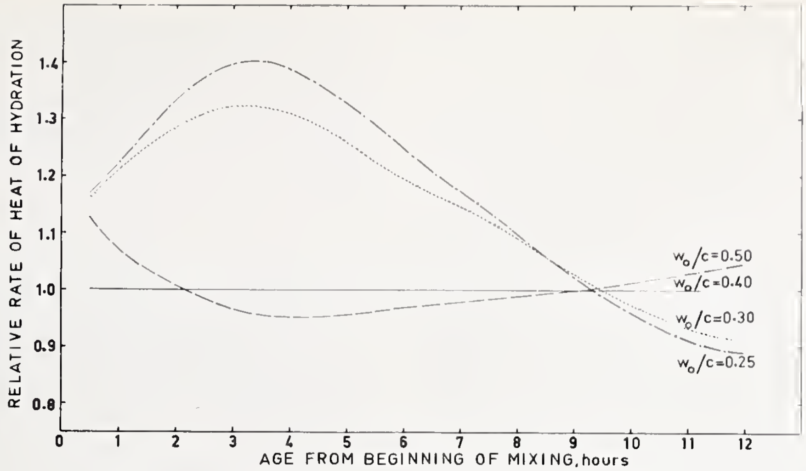

FIGURE 8. *Relative rate of heat of hydration versus time.*

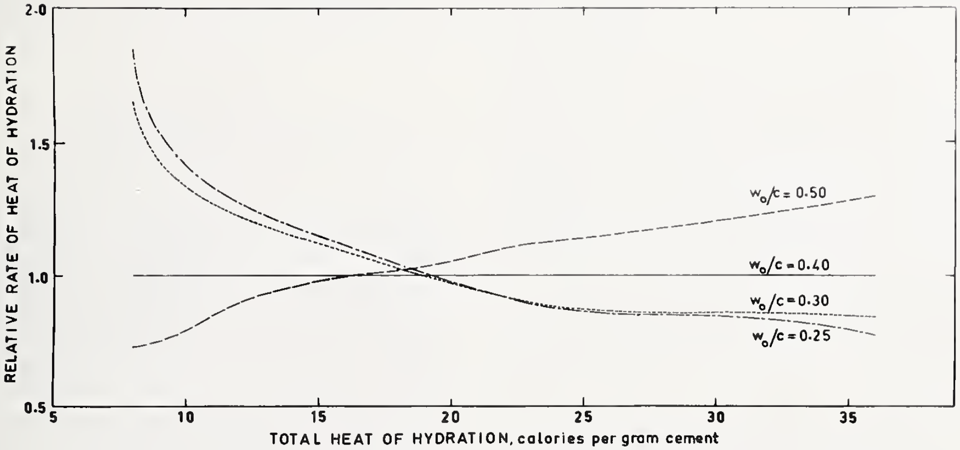

FIGURE 9. *Relative rate of heat of hydration as a function of the total heat of hydration.*

measuring that is important, but the whole temperature history up to the moment of measuring, because the pastes may have reached different degrees of hydration. This difficulty can be avoided by making the comparison when the pastes have developed the same total heat of hydration instead. From the diagram in figure 6 we have determined graphically the rates of heat of hydration for the different water-cement ratios for given values of the total heat of hydration. In figure 9 the rates of heat of hydration relative to that for water-cement ratio 0.40 are plotted against total heat of hydration. When we now compare the rates for the pastes when they have reached the same degree of hydration, the influence on the degree of hydration of the temperature differences during mixing and up to the moment of measuring has been taken care of. We see, however, that when the total heat of hydration has reached for example the value 10 cal/g of cement, which for none of the pastes is earlier than 3 hr, and the measuring errors present at the beginning have disappeared, there still remain differences which amount to more than 40 percent between pastes with water-cement ratios 0.25 and 0.40.

The temperature differences between the pastes, which are comparatively high during mixing, can also cause still other deviations in the measured rates of heat of hydration. We have found earlier [1] that the hydration products formed at different temperatures differ with regard to their influence on further reactivity. If a paste is prehydrated at 20 °C, its rate of heat of hydration measured at 1 °C may be only half that for a paste hydrated to the same degree, but kept at 1 °C all the time. Although the temperature of the paste with a water-cement ratio of 0.25 has exceeded the one for water-cement ratio 0.40 by a full 3 °C during mixing, as seen from figure 7, this can hardly explain the difference in the measured rates, which, even after the previously-mentioned corrections have been taken into account, amount to at least 35 percent.

The results indicate that the rate of heat of hydration would vary inversely with water-cement ratio during the first hours of hydration, even if the measurements could be carried out at constant temperature. Calculations have shown that an explanation based on the assumption that the cement grain boundaries have a higher temperature than the paste as a whole can be ruled out. The reason for this rate dependence must probably be sought in the chemical processes taking place.

When cement and water are brought into contact with each other, the material in the cement grain boundaries passes into solution. Most of the constituents of a portland cement are only slightly soluble in water, and the fluid phase will quickly become saturated. During the process of mixing, the concentrations of the ions these compounds form will have reached fixed values, independent of the water-cement ratio and determined by their solubilities. In the early stages of hydration, the rates of the different reactions must be influenced by the composition and concentration of the fluid phase but not by the solution-cement proportions. However, most portland cements also contain small quantities of sodium and potassium salts. As the solubility of alkalis in water is high, the alkali concentration in the solution will not reach saturation and thus will depend on the water-cement ratio of the paste.

As a hypothesis to explain the observed increase in the rate of heat of hydration with decreasing water-cement ratio during the first hours of hydration, the author suggests that it is due to the alkali salts in the cement accelerating the hydration reactions, and that this acceleration becomes stronger when their concentration in the fluid phase increases with decreasing values for the water-cement ratio.

Many alkali salts have been found to accelerate the hydration when used as admixtures. In cement the alkalis occur mainly in the form of sulfates, but besides these, small amounts of sodium may be present in the calcium aluminates, and potassium in the calcium silicates [5]. In order to verify the hypothesis, we have compared rates of heat of hydration for two prepared pastes, with the same water-cement ratio, the one made with pure water, the other with a sodium sulfate solution. The concentration of this solution was chosen as the difference between the calculated sodium sulfate concentrations one would obtain in two imaginary pastes with water-cement ratios of 0.25 and 0.40, respectively. For these pastes both the amount of potassium oxide converted to the equivalent amount in sodium oxide and of actual sodium oxide, as given in the analysis, have been assumed to exist in the form of sodium sulfate and to dissolve completely.

The experiments showed that the addition of this alkali salt accelerated the reactions during the first hours of hydration to an extent which suggests that the hypothesis can be accepted as the explanation of the dependence, at early ages, of the rate of heat of hydration upon water-cement ratio.

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Discussion

W. C. Hansen

The author suggests that increasing the alkali content of the liquid phase of a cement paste increases the rate of hydration at early ages. This seems logical on the basis that $Ca(OH)_2$ is the compound that retards the rates at which C_3A and aluminoferrites react with water and sulfate. The data by Hansen and Pressler [1] show that, as the alkali content of the liquid phase of a cement increases, the SO_3 content should increase and the CaO content should decrease. If the degree of retardation is a function of the amount of $Ca(OH)_2$ in the solution, then the rate of reaction of the aluminates should increase as the concentration of $Ca(OH)_2$ decreases or as the concentration of alkali increases.

This finding, it seems, is very significant in connection with early reactions. I pointed out in the closure to the paper on false set in portland cement pastes that aeration of a cement may decrease the rate at which the cement minerals release $Ca(OH)_2$ to the liquid phase and that this, in turn, may cause the cement to develop flash-setting tendencies. Heat of hydration studies on cements aerated under controlled conditions might furnish valuable data on the reactions that occur during the handling and storage of cement.

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Paper IV–S8. The Influence of False Setting on Some Properties of Hardening Cement Paste and Mortar*

Jerzy P. Sulikowski

Synopsis

Two normal-setting cements and one false-setting cement were investigated. Both normal-setting cements became false-setting on heating to 200 °C. Samples of the false-setting cements thus obtained were then kept in a moist chamber, whereby they again became normal setting. The third cement, false setting when obtained, became normal setting on storage in a moist atmosphere. A portion of this normal-setting sample was again changed to false setting by heating. Each of the three original samples thus was subjected to a cycle of operations, resulting in nine cement samples, five normal and four false-setting. Each of the nine samples was investigated for bleeding and initial shrinkage.

It was established quantitatively and with good reproducibility that false set, brought about artificially by heating, is connected with appreciable reduction of bleeding and increase in initial shrinkage. A reversibility of the phenomena was also established, as the artificially obtained false-setting cement after storage in moist atmosphere again becomes normal setting, and thereby again expels greater amounts of water and exhibits less initial shrinkage.

Résumé

Deux ciments à prise normale et un ciment présentant le phénomène de fausse prise sont les matériaux utilisés dans cette étude.

Les deux ciments à prise normale furent transformés en ciments à fausse prise sous l'effet de la chaleur. Ces ciments à fausse prise retrouvèrent une prise normale après séjour dans une chambre humide.

Le troisième ciment, qui présentait le phénomène de fausse prise au moment de la livraison, fut soumis à un séjour en atmosphère humide et acquit une prise normale. Une partie de ce ciment à prise normale fut de nouveau transformé en ciment à fausse prise par l'effet de la chaleur.

Ainsi chacun des trois échantillons initiaux fut soumis à un traitement cyclique et en tout ils produisirent neuf échantillons de ciment: cinq présentant une prise normale, et quatre une fausse prise.

Chacun des neuf échantillons fut examiné pour déterminer le ressuage et le retrait du début.

On établit quantitativement, et les résultats se reproduisaient bien, que la fausse prise artificiellement produite par la chaleur est liée à un décroissement visible du ressuage et à un accroissement du retrait du début.

On put également établir que les phénomènes sont réversibles, puisque les ciments à prise artificiellement rendue fausse retrouvaient une prise normale après un séjour en atmosphère humide et de nouveau remontaient de plus grandes quantités d'eau, et indiquaient un retrait du début moins grand.

Zusammenfassung

Als Untersuchungsmaterial wurden zwei normalbindende Zemente und ein falschbindender Zement benutzt.

Beide normalbindende Zemente wurden durch Erwärmen in Falschbinder umgewandelt. Die so entstandene falschbindende Zementproben wurden durch Aufbewahren in feuchtem Raum wieder normalbindend gemacht.

Der dritte, schon im Lieferzustande falschbindender Zement wurde durch Aufbewahren in feuchter Atmosphäre beruhigt, und band normal ab. Ein Teil dieser normalbindender Probe wurde durch Erwärmen wieder in Falschbinder umgewandelt.

Jede der drei Ausgangsproben wurde also einem Bearbeitungszyklus unterworfen, und infolgedessen entstanden 9 Zementproben, und zwar 5 Normalbinder, und 4 Falschbinder.

Jede der 9 Proben wurde auf Bleeding und Anfangsschwindung untersucht.

Es wurde quantitativ und mit guter Wiederholbarkeit der Resultate festgestellt, dass künstlich durch Erwärmen hervorgerufenes falsches Abbinden mit merklicher Verkleinerung der Bleeding und mit Vergrösserung von Anfangsschwindung verbunden ist.

Man hat dabei auch eine Reversibilität der Erscheinungen festgestellt, weil die künstlich erhaltene Falschbinder nach dem Aufbewahren in feuchter Atmosphäre wieder normalbindend werden und stossen dabei wieder grössere Mengen von Wasser ab, und weisen kleinere Anfangsschwindung auf.

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* Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Institute for Mining and Metallurgy, Krakow, Poland.

Introduction

The false setting of cement not only makes more difficult the mixing of concrete, its transport and placing, but probably is also the cause of some defects in buildings and constructions made of concrete. Thus for example during production of large concrete slabs, which are the basic element of highways and runways, often numerous surface cracks appear; they are 300–500 mm long and about 30 mm deep. Such cracks are usually situated parallel to each other and occur in rows over the whole surface of the slab.

It should be pointed out that such cracks appear repeatedly some hours after placing the concrete, therefore before its final setting.

The author is acquainted with a case of the appearance of such cracks on large slabs of a runway some hours after placing the concrete, although it was protected against surface drying by a cover of wet sand and plastic foil.

The cause of this phenomenon has been sought in false setting of cement, although the characteristic premature stiffening of concrete has been, seemingly, ultimately suppressed by means of more vigorous and prolonged mixing of the concrete.

The observations described allow one to assume that the calcium sulfate hemihydrate, present in false-setting cement, affects permanently and specifically the structure of the gels which are the basic constituents of the setting cement paste.

It may be assumed at the same time that the more vigorous mixing of the concrete, although it allows the suppression of the premature stiffening, characteristic of false setting, and makes possible the regaining of the initial consistency of the mixture, does not liquidate the mentioned permanent influence on the structure of the gel.

It is the structure of the gel that undoubtedly determines the properties of hardening and hardened cement, and therefore, any changes in it should in turn cause measurable changes of these properties.

The present work aims at the determination of the influence of false setting on bleeding and on the course and extent of the initial shrinkage of the hardening cement.

Materials

In the investigations three brands of portland cement, delivered by three different cement plants, were used. The characteristics of these cements are presented in table 1. The initial and final setting of these cements were in complete accordance with the standard specifications. Two of them, viz., cements *R* and *S*, do not display false setting, while the third one, cement $W_{(f)}$ is a typical false-setting one.

Cement $W_{(f)}$ contains a scant addition of granulated blast-furnace slag. Because of this in table 1 neither its moduli nor its mineralogical composition are presented.

A portion of the samples of cements *R* and *S* received from the cement plants was subjected to heating to 200 °C during 20 min; thus samples R_f and S_f, with artificially developed false setting were obtained.

Then a part of these false-setting portions of both cements was spread as a layer about 25 mm thick above a water surface in a closed chamber for a period of 24 hr at a temperature about 20 °C.

The cements thus treated lost the false setting acquired by heating, and came back to their initial setting behavior without any disturbances. These cements were designated *R′* and *S′*.

TABLE 1. *Characteristics of cements*

	Cement *R*	Cement *S*	Cement $W_{(f)}$
Loss on ign	1.85	2.60	2.74
SiO_2	23.40	21.76	24.20
Fe_2O_3	2.13	3.35	2.50
Al_2O_3	4.33	6.05	6.78
CaO	64.88	62.00	59.20
MgO	1.12	2.02	2.27
SO_3	2.44	1.92	2.26
Insoluble	0.43	0.42	0.38
Hydraulic modulus	2.16	1.96	------------
SiO_2/R_2O_3	3.62	2.31	------------
Al_2O_3/Fe_2O_3	2.03	1.80	------------
C_3S	46.93	35.94	------------
C_2S	31.76	35.34	------------
C_3A	7.87	10.36	------------
C_4AF	6.47	10.18	------------
$CaSO_4$	4.14	3.26	------------

TABLE 2. *Origin and preparation of cement samples*

Symbol of sample	Origin or preparation	Setting characteristics
R	Cement plant *R*	Normal setting.
R_f	Heating of cement *R*	False setting.
R′	Humidifying of R_f	Normal setting.
S	Cement plant *S*	Normal setting.
S_f	Heating of cement *S*	False setting.
S′	Humidifying of S_f	Normal setting.
$W_{(f)}$	Cement plant *W*	False setting.
W′	Humidifying of $W_{(f)}$	Normal setting.
W_f	Heating of cement *W′*	False setting.

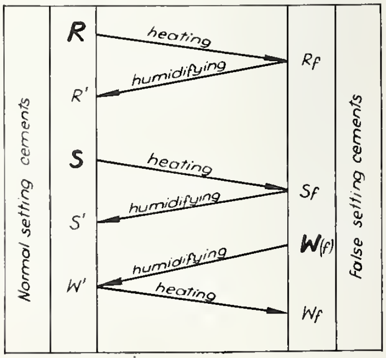

FIGURE 1. *Scheme of sample preparation.*

(Cement samples as received from plants are designated by bold-face letters.)

Cement $W_{(f)}$ which, as mentioned above, displayed false setting on delivery from the cement-works, was treated in the same manner, though in different order. A part of that cement was subjected for a 24-hr period to the action of atmospheric moisture, thus making it lose its natural property of false setting.

The sample thus obtained was marked as cement **W′**. A part of it was heated for 20 min at 200 °C, thus acquiring again the property of false setting (cement W_f).

As the result of the above described treatment, from three kinds of cement of different origin, nine samples were obtained. Their symbols, characteristics, and origin or means of preparation are presented in table 2.

In the scheme presented in figure 1 the means of preparation of the samples from the initial three cements, marked by bold-face letters, are given.

Apparatus and Procedure

The cement samples, prepared in the manner described above, were investigated for bleeding. In addition the course and extent of the initial shrinkage of the cement paste were determined.

False Setting

For the detection of false setting a method, the principle of which is based on ASTM C359–56 T, was used. Previous investigations [1][1] have shown the applicability of this method and the good agreement of results obtained by its use.

Bleeding

For the determination of the rate and capacity of bleeding the method and apparatus recommended by ASTM C243–58 T, were used. This method also affords concordant results, as has been found during previous studies.

Initial Shrinkage

The study of the influence of false setting on the shrinkage of cement paste and mortar has been the subject of previous papers [2]. These have dealt, however, with shrinkage after 3, 7, and 28 days, and have shown that the false setting considerably increases the shrinkage of the hardened cement paste and mortar after 28 days.

The investigations described in this paper have been limited to observations of the course of shrinkage during the initial stage of setting, before the final hardening of the cement. Observations have been carried out only during 480 min from the moment of the preparation of the cement paste.

The shrinkage was measured using an ordinary microscope by means of a method proposed by Lefèvre [4]. The cement paste was placed in a mold made of zinc sheet 1 mm thick. The shape and size of the mold are presented in figure 2. The mold rested on a glass plate and the area along which the mold touched the plate was sealed with molten paraffin. The inner walls of the mold and the area of the plate within them were greased with machine oil.

The mold thus prepared was filled with cement paste. On its surface, smoothed with a knife, at a distance of 90 mm from the diagonal, closing wall of the mold, a fragment of steel plate, suitable for microscopic observations, was placed.

The device was put on the stage of the microscope provided with an eyepiece calibrated previously by means of a stage micrometer with a section 1 mm long, divided into 100 parts. Observations were carried out at 80 times magnification and the length of one division of the eyepiece scale corresponded to 10.7μ. The temperature of the surroundings fluctuated from 18 to 20 °C and the relative humidity from 50 to 60 percent.

The sample was placed on the microscope stage so that the metal mark made on the surface of the paste was covered by the first mark of the eyepiece scale. The translocations of the mark in the field of vision were noted each 15 min.

The unpublished preliminary investigations resulted in finding that the measurements of the initial shrinkage made by means of the above-described method are in very good agreement, provided of course that the temperature and humidity of the surroundings are kept constant.

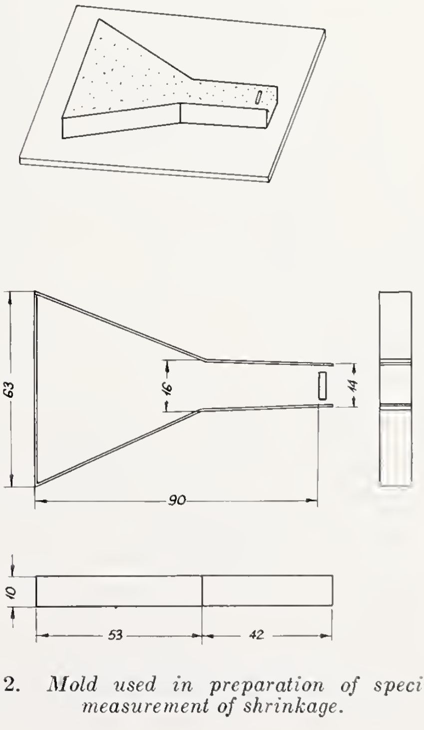

Figure 2. *Mold used in preparation of specimens for measurement of shrinkage.*

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[1] Figures in brackets indicate the literature references at the end of this paper.

Results

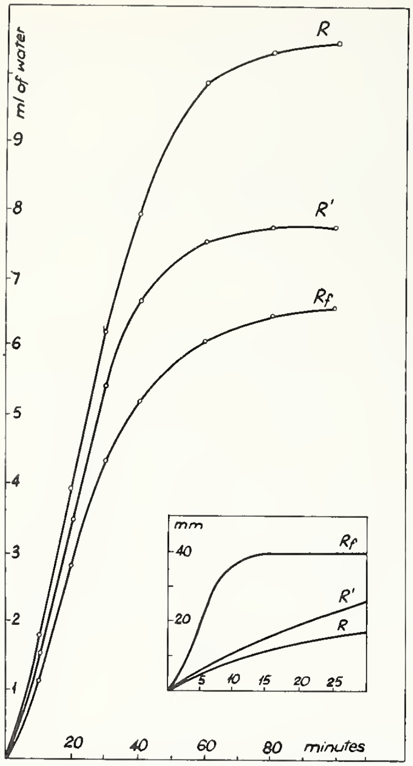

FIGURE 3. *Amount of bleeding exhibited by samples* R, R_f, *and* R′.
Inset shows penetration in test for false setting.

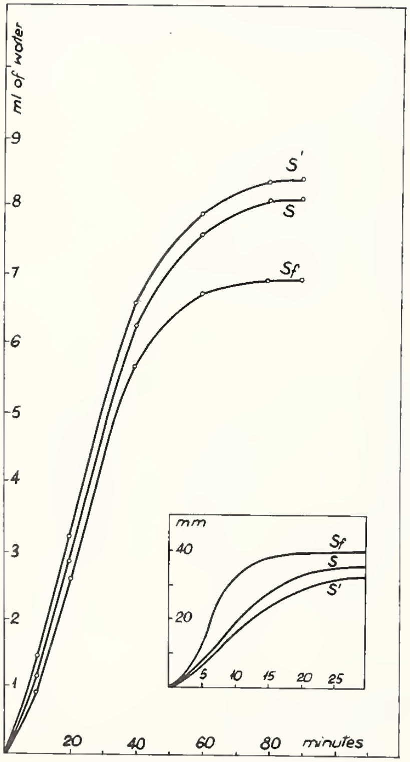

FIGURE 4. *Amount of bleeding exhibited by samples* S, S_f, *and* S′.
Inset shows penetration in test for false setting.

Since, as had been mentioned in the previous section, the results obtained by means of the methods used are in good agreement, the present paper does not contain tabular representation of numerical values; these are represented graphically only.

The course of bleeding is illustrated by curves in figures 3, 4, and 5. Each of these curves is the mean of six parallel measurements, the results of which differed from the arithmetical mean value by not more than ±7 percent.

In these figures there are auxiliary plots in which each curve is the result of three parallel measurements of false setting.

In table 3 are presented, for each of the nine cements, numerical values of the rate and capacity of bleeding. These values are calculated from the arithmetical mean value of six parallel measurements made for each of the nine cements.

TABLE 3. *Bleeding rate and capacity*

Cement	Bleeding rate cm³/cm²/sec	Bleeding capacity cm³/cm³
R	0.0000761	0.0228
R_f	.0000524	.0142
R'	.0000658	.0166
S	.0000597	.0176
S_f	.0000546	.0152
S'	.0000628	.0183
$W(_f)$	.0000595	.0170
W'	.0000737	.0202
W_f	.0000374	.0115

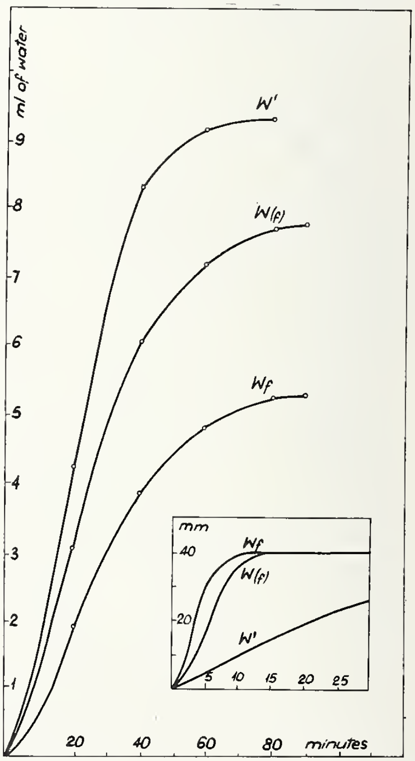

FIGURE 5. *Amount of bleeding exhibited by samples* $W_{(f)}$, W′, *and* W_f.
Inset shows penetration in test for false setting.

The courses of the initial shrinkage of the setting paste are presented in figures 6, 7, and 8. Each of these curves is the mean of six parallel measurements, the results of which differed from the arithmetical mean value by not more than ±5 percent.

Bleeding

The results presented above confirm the assumption put forward in one of our earlier papers [4] that the occurrence of false set is connected with the decrease of the rate and capacity of bleeding.

The investigations described in this paper have allowed in addition to find a reverse phenomenon, viz, that the loss of the natural or artificially acquired property of false setting of cement is connected with the increase of the rate and capacity of bleeding.

This regularity was found during the study of cements subjected to the closed cycle of operations illustrated graphically in figure 1. The course of bleeding was altered each time according to the order of operations of that cycle.

Initial Shrinkage

The changes of length were observed for 7 to 8 hr from the moment of the preparation of the paste and placing it in the form. After that time the initial shrinkage of the setting paste did not increase any more.

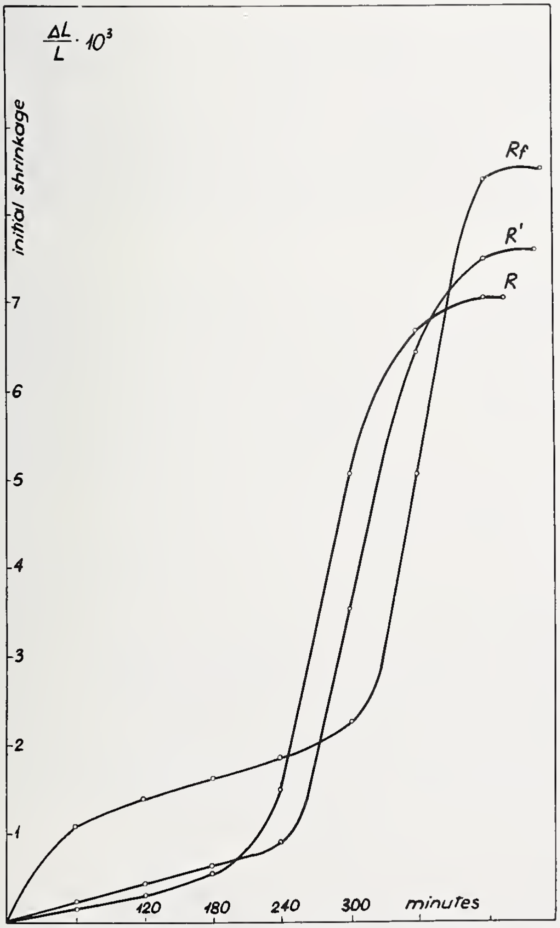

FIGURE 6. *Initial shrinkage of samples* R, R_f, and R'.

By comparison of the plots in figures 6, 7, and 8 it is found that the three original cements differ considerably from each other. The order of the initial shrinkage of the paste, after 7 to 8 hr, is, for each of these cements, quite different. This is caused undoubtedly by the different chemical and mineralogical compositions of these cements and of their different fineness.

Closer comparison of the course of the curves presented in the above mentioned three plots results in finding that the appearance of the phenomenon of false setting or its disappearance influences very distinctly and always in the same manner the course of the initial shrinkage observed during the first 7 to 8 hr after the mixing of cement with water. In the case of each of the nine studied samples the course of the initial shrinkage of the paste may be divided into several characteristic stages. The pastes made of normal-setting cements shrink in three stages while in the case of false-setting cements four definite stages may be distinguished.

Normal-Setting Cements: *R*, *R'*, *S*, *S'*, *W'*

The first stage lasts for 3 to 3½ hrs after preparation of the paste, placing it in the mold and

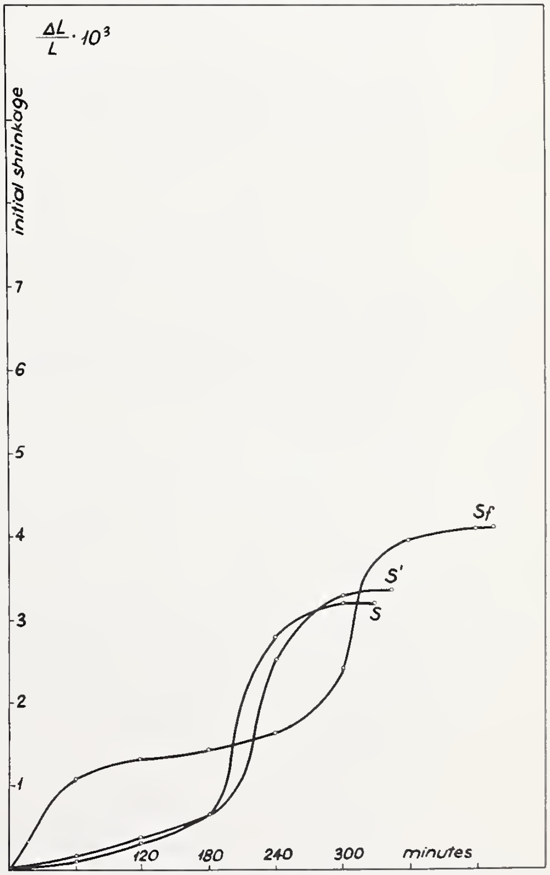

FIGURE 7. *Initial shrinkage of samples* S, S_f, *and* S'.

FIGURE 8. *Initial shrinkage of samples* $W_{(f)}$, W', *and* W_f.

starting the observations. This stage is characterized by slow shrinking of the paste which shows, at the end of this stage, a shrinkage of the order of 0.5–0.8 mm/m.

The second stage lasts for 1½ to 2½ hr. In this stage a rapid and very considerable increase of the shrinkage takes place. In the third and last stage the shrinkage comes to a constant value, characteristic for each original cement.

False-Setting Cements: R_f, S_f, W_f, $W_{(f)}$

The first stage comprises the first hour after the preparation of the paste. This short initial stage is typical for false-setting cements and is characterized by a rapid increase of the shrinkage which, after an hour, reaches the value of 1.0–1.2 mm/m, i.e., several times that shown during the same time by normal-setting cements.

In the second stage, lasting 3 to 4 hr, the shrinkage of false-setting cements increases slowly. This increase lasts for about 1 to 1½ hr longer, counting from the moment of the preparation of the paste, than in the case of normal-setting cement of the same origin. At the end of this stage the shrinkage of the false-setting cements reaches the value of 1.8–2.0 mm/m, thus being then more than twice that of normal-setting cements at the end of the first stage.

The third stage is that of a rapid increase of the shrinkage. This stage is late in relation to the analogous (second) stage of the normal-setting cements by about an hour.

In the fourth, final stage there occurs a decrease of the rate of shrinkage. The length of the sample becomes constant, showing, however, a total shrinkage 10 to 20 percent greater than that of the normal-setting cements.

Discussion

The results presented in this paper show that the phenomenon of false setting influences distinctly the process of bleeding of the cement paste as well as the initial shrinkage of the setting paste. This influence is marked in a regular and repeated manner and the quantitative changes of bleeding and initial shrinkage are measurable and considerable.

In addition, the mentioned influence is in a way reversible since it appears when normally setting cement is remade into a false-setting one as well as when falsely setting cement is remade into a normal-setting one.

Both investigated phenomena, i.e., that of bleeding and that of shrinkage of the cement paste, are related to the colloidal structure of the setting paste. Thus, for example, the course of bleeding depends, as is known, on the size and number of capillary canals constituting the fundamental element of the structure of the gels of which the hardening cement paste consists in the major part.

Thus the fact of the influence of false setting on the process of bleeding and shrinkage of cement paste, found in the course of studies being the subject of this paper, proves the decisive and distinct influence of false setting on the structure of the gels which are the main component of the hardening cement paste.

Further studies aiming at learning the influence of false setting on the practical properties of cement are being carried out at the Department of Technology of Binding Materials of the High School of Mining and Metallurgy, Kraków. It is to be expected that these studies will allow the whole-range interpretation of the observed phenomena and regularities, and, first of all, will enable us to know to a greater extent the influence of various forms of calcium sulfate on the structure of hardened cement paste.

References

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Paper IV–S9. Thermodynamics of the Hardening Processes of Cement*

O. P. Mchedlov-Petrosyan and W. I. Babushkin

Synopsis

To define the energetics of binding properties the authors have used the thermodynamic research method which allowed them to examine theoretically without complex experiments the energetics of hardening processes of binders and on this basis to outline the mechanism of their reactions.

Previously unknown thermic data (ΔH_{298}, ΔF_{298}, S_{298}, and $C_p=f(T)$) for hydrosilicates and hydroaluminates of Ca and silicic acid ions were obtained by approximate methods of calculation, the accuracy of which, as comparison of calculated and experimental data showed, is within the limits of usual experimental errors (±5%).

According to the data obtained there were calculated the equations $\Delta F=f(T)$ of the reactions in the systems: $Ca(OH)_2$–SiO_2–H_2O, β-$2CaO \cdot SiO_2$–H_2O, and $3CaO \cdot SiO_2$–H_2O under hydrothermal conditions, as well as the hydration reactions of $3CaO \cdot Al_2O_3$, $2CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $CaO \cdot Al_2O_3$, $CaSO_4 \cdot 0.5H_2O$, CaO, and MgO at normal temperature.

The results of the thermodynamic calculations enable one to indicate the conditions for synthesis of various hydrosilicates.

Using the values of average bond energies for Ca-O, Si-O, O-H, etc., and taking β-$2CaO \cdot SiO_2$ as an example, there is shown the possible mechanism of its hardening process, the first stage of which is the solution of β-$2CaO \cdot SiO_2$ in water. This provides conditions for increase of the average bond energy of Ca-O which assures in its turn a considerable supersaturation of the ions of Ca^{++} in the solution and affords the possibility of making them stable. The second stage is the polymerization of the $SiO_3^=$ and $HSiO_3^-$ ions (depending upon the *p*H of the medium in the presence of Ca ions) first into chains $[Si_3O_9]^{6-}$ and then into bands $[Si_6O_{17}]^{10-}$, etc. This process is accompanied by the immediate precipitation of submicroscopic poorly soluble calcium hydrosilicates able to join with each other.

Résumé

Pour définir les énergétiques des propriétés liantes les auteurs ont utilisé la méthode de recherche thermo-dynamique qui leur a permis d'examiner théorétiquement sans expériences complexes les énergétiques des procédés de durcissement des liants et sur cette base d'exposer le mécanisme de leurs réactions.

Des données thermiques inconnues jusqu'à présent (ΔH_{298}, ΔF_{298}, S_{298} et $C_p=f(T)$) pour les hydrosilicates et hydroaluminates de calcium et les ions d'acide silicique furent obtenues par des méthodes de calculation approximative, dont l'exactitude, comme l'indique la comparaison avec les données calculées et expérimentales, est dans les limites des erreurs expérimentales habituelles (±5%).

Suivant les données obtenues les équations $\Delta F=f(T)$ des réactions furent calculées dans les systèmes: $Ca(OH)_2$–SiO_2–H_2O, β-$2CaO \cdot SiO_2$–H_2O, $3CaO \cdot SiO_2$–H_2O sous conditions hydro-thermiques, aussi bien que les réactions d'hydratation de $3CaO \cdot Al_2O_3$, $2CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $CaO \cdot Al_2O_3$, $CaSO_4 \cdot 0.5H_2O$, CaO et MgO à température normale.

Les résultats des calculs thermo-dynamiques nous permettent d'indiquer les conditions pour les synthèses de différents hydrosilicates.

Quand on utilise les valeurs des énergies du lien moyennes pour Ca-O,Si-O,O-H etc., et quand on prend β-$2CaO \cdot SiO_2$ comme exemple, on voit le mécanisme possible de ce procédé de durcissement dont le premier stade est la solution de β-$2CaO \cdot SiO_2$ dans l'eau. Ceci fournit les conditions pour l'augmentation de l'énergie du lien moyenne de Ca-O qui à son tour assure une sursaturation considérable des ions de Ca^{++} dans la solution et offre la possibilité de les rendre stables. Le second stade est la polymérisation des ions de $SiO_3^=$ et de $HSiO_3^-$ (dépendant du *p*H du milieu en présence d'ions de calcium) d'abord en chaînes $[Si_3O_9]^{6-}$ et ensuite en bandes $[Si_6O_{17}]^{10-}$ etc. Ce procédé est accompagné par la précipitation immédiate d'hydro-silicates de calcium peu solubles et sous-microscopique capables de se joindre les uns aux autres.

Zusammenfassung

Für Erforschung der Energetik der Bindeeigenschaften benutzten die Verfasser die thermodynamische Forschungsmethode, die es ohne der Durchführung von komplizierten und mühevollen Versuchen erlaubte die Energetik der Erhärtung von Bindemittel zu untersuchen und auf dieser Grundlage den Mechanismus entsprechender Reactionen zu entwerfen.

Die früher unbekannten thermischen Daten [ΔH_{298}, ΔF_{298}, S_{298} und $C_p=f(T)$] für Hydrosilikate und Hydroaluminate des Calciums und der Siliziumsäureionen wurden mittels Näherungsberechnungsmethoden erhalten, die Genauigkeit welcher, wie ein Vergleich berechneter und Versuchswerte zeigte im Bereich gewöhnlicher Experimentalfehler liegen (±5%).

Zufolge den berechneten Daten wurden Gleichungen $\Delta F=f(T)$ der Reaktionen in Systemen: $Ca(OH)_2$–SiO_2–H_2O, β-$2CaO \cdot SiO_2$–H_2O, $3CaO \cdot SiO_2$–H_2O in hydrothermalen Zuständen, sowie die Reaktionen der Hydratation von $3CaO \cdot Al_2O_3$, $2CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $CaO \cdot Al_2O_3$, $CaSO_4 \cdot 0.5H_2O$, CaO und MgO bei normaler Temperatur betrachtet.

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Die Resultate thermodynamischer Berechnungen erlauben es die Bedingungen der Synthese verschiedener Hydrosilikate zu beurteilen.

Mit der Anwendung der mittleren Bindungsenergien von Ca-O, Si-O, O-H, u.s.w., werden am Beispiel von β-2CaO·SiO$_2$ der mögliche Mechanismus seiner Erhärtung gezeigt, deren erster Akt die Lösung von β-2CaO·SiO$_2$ im Wasser ist, was Möglichkeit für die Vergrösserung der mittleren Bindungsenergie Ca-O, eine Bedingung der empfindlichen Übersättigung der Lösung mit Ca^{++} -ionen bildet, und bietet eine Möglichkeit der Erzielung ihres mehr stabilen energetischen Zustandes.

Als zweiter Akt ist die Polymerization von $SiO_3^{=}$ und $HSiO_3^{-}$ ionen anzusehen, in Abhängigkeit vom pH der Mediums in Anwesenheit der Ca^{++}-ionen zuerst in Metasilikat-ketten $[Si_3O_9]^{6-}$ und dann in Bänder $[Si_6O_{17}]^{10-}$ u.s.w. mit sofortigen Ausscheiden aus der Lösung submikroskopischer schwerlöslicher Calciumhydrosilikate, die zur gegenseitigen Verwachsung miteinander veranlagt sind.

In recent years there has been considerable progress in the study of the hardening processes of mineral binders. Formulation of a reliable theory of cement hardening is necessary for rational control of the technology of concrete and other products made with cements, and to assure the fabrication of products of desired quality.

It should be noted that all the numerous aspects of this problem have up to now been divisible either into the crystallochemical study of structural features of binders and their hydration products, represented in the USSR by the works of acad. N. V. Belov's school [1, 2],[1] N. A. Toropov, Yu. M. Butt, and their co-workers [3, 4], and abroad by J. Bernal [5], J. Jeffery [6], R. Nurse [7], F. Ordway [8], Å. Grudemo [9], H. Megaw [10], H. Taylor [11], E. Thilo [12], and others, or the branch of physical-chemical mechanics involving problems of "strength synthesis" of hardened binders, which was developed first in the USSR by acad. P. A. Rehbinder's school [13, 14].

From our point of view, for further fruitful development, a close and extensive application to these problems of the methods of chemical thermodynamics is necessary.

Apparently no one now would have any doubts about the assumption formerly made by us that inorganic compounds with binding properties have differently activated crystalline structures [15].

The crystallochemical aspect of the instability of those compounds was first explained by E. Brandenberger [16], who assumed that the ability to show binding properties is associated with reduced coordination of active cations of the structure. This opinion is, in our point of view, not far from the truth, because any distortion or irregular coordination will inevitably cause a reduction to the next order.

Therefore, without considering M. Bredig [17] incorrect, we assume that for the explanation of binding properties it is not the formal crystallochemical coordination but the quantity of the nearest neighbors that is important. It is just like the zones of different electronic levels in metals [18], or in other words, everything depends upon the yet unknown connection between the limit values of cation-oxygen distances and the energy coefficients of the structure.

Therefore, to explain the energetics of binding properties, the use of thermodynamic research methods becomes of great importance.

Application of thermodynamic research methods to the study of reactions on which the hardening processes of binders are based has up to now been hindered by a number of factors: first, it has not yet been decided to what degree the classical thermodynamic principles might be applied to real irreversible processes such as the processes causing the hardening of cements; second, there have been no initial thermodynamic data for hydrosilicates and hydroaluminates of calcium, because their experimental determination is associated with great difficulties in the synthesis of pure monocrystals and their unique identification [5, 19, 20, 21, 22, 23, 24].

Chemical processes represent combinations of chemical and phase transformations, mass, and heat transfer.

In this connection, thermodynamic potentials as measures of the driving force of the physical-chemical processes must be of decided importance in determination of relative rates and especially in qualitative estimation of the preferred course under given conditions [25].

Ideas on the significance of thermodynamic potentials in the determination of process rate can be found in some works [25–31].

It should be further noted that the assertion that one cannot use the concepts of time, space, and rate in thermodynamics is unsound, for it is correct only within the framework of classical thermodynamics, whose abstract concepts often fail to satisfy today's wants, and especially our desire to interpret in a concrete way the objective contents of thermodynamic laws.

It can be assumed [25] that for each real irreversible chemical process its exact reversible replica can be imagined; a prototype, passing through the same intermediate states. The amounts of work involved in these two processes are equal, but in the second case the work is connected with the covering of external forces influencing the system, while in the first case it is objective work against real internal resistance forces of a nonequilibrium system.

Summarizing all that is said above, we can conclude that for the analysis of hydraulic binders it is quite possible to use classical thermodynamic methods. The simplicity and convenience of their application consist in the fact that the main principles do not depend upon the correctness of our knowledge of the interatomic structure of materials taking part in the reaction and this enables us without complex and laborious experi-

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[1] Figures in brackets indicate the literature references at the end of this paper.

ments to examine theoretically the reactions of interest in order to predict the possibility of obtaining one or another product, or to predict the impossibility of a synthesis under certain conditions.

In connection with the above, the problem of reliable initial thermal data becomes of great importance; such data are heat of formation (ΔH), isobaric-isothermal potential (ΔF), entropies (S), and temperature dependence of heat capacities ($C_p=f(T)$) for the compounds formed through the hardening of binders as well as for their ions in water solution.

In the present work, to obtain the necessary thermal data for hydrosilicates and hydroaluminates of calcium and ions of silicic acid in water solution we used approximate calculation methods for ΔH, ΔF, S, and $C_p=f(T)$ [32, 33, 34, 35, 36]. The use of such approximate methods is justified in this case by the above-mentioned complexity of experiments and nearly complete absence of thermodynamic constants for hydrosilicates of calcium, since their experimental determination would delay this research for many years. The use of approximate methods without pretending to final decision of all questions concerning the hardening of binders allows us to draw important qualitative conclusions in a comparatively short time.

By the authors' methods, ΔH_{298}, S_{298}, and ΔF_{298} of nine hydrosilicates of calcium were calculated: hillebrandite, afwillite, foshagite, xonotlite, riversideite, tobermorite, plombierite, gyrolite, and okenite. The calculations were also made for three hydroaluminates of calcium: C_3AH_6, C_4AH_{12}, C_2AH_5. For the hydrosilicates, $C_p=f(T)$ was calculated by the method of N. A. Landya [37].

ΔF and ΔH for SiO_3 ions in water solution and the average binding energies for Si—O, Al—O, S—O, O—H, Ca—O, and Mg—O were also calculated for the main types of binders and their hydration products. All these calculated data, as well as those previously known, which were generally taken from the reference book by Rossini and associates [38], are given in table 1.

By use of these data, values of $\Delta F=f(T)$ for hydrothermal reactions in the systems $3CaO$–SiO_2-H_2O, β-$2CaO\cdot SiO_2$–H_2O, $Ca(OH)_2-SiO_2-H_2O$, and for hydration reactions of $3CaO\cdot Al_2O_3$, $2CaO\cdot Al_2O_3$, $12CaO\cdot 7Al_2O_3$, $CaO\cdot Al_2O_3$, $CaSO_4\cdot 0.5H_2O$, CaO, and MgO at room temperature were calculated, and on the basis of the values of average bond energies an energy analysis of binding qualities was made.

TABLE 1

1	2	3	4	5	6
No.	Compound	State	ΔH_{298} *kcal/mole*	ΔF_{298} *kcal/mole*	$C_p=f(T)$
1	CaO	Crystal	-151.90	-144.40	$C_p=11.67+1.08\cdot 10^{-3}T-1.56\cdot 10^{5}T^{-2}$
2	$Ca(OH)_2$	do	-235.80	-214.33	$C_p=19.79+10.45\cdot 10^{-3}T-2.94\cdot 10^{5}T^{-2}$
3	MgO	do	-143.84	-136.13	$C_p=10.18+1.74\cdot 10^{-3}T-1.48\cdot 10^{5}T^{-2}$
4	$Mg(OH)_2$	do	-221.00	-199.27	$C_p=10.4+27.00\cdot 10^{-3}T$
5	$CaSO_4\cdot 0.5H_2O(\beta)$	do	-375.97	-342.78	$C_p=18.8+36.3\cdot 10^{-3}T$
6	$CaSO_4\cdot 2H_2O$	do	-483.06	-429.19	$C_p=27.03+58.6\cdot 10^{-3}T$
7	$CaSO_4$ (anhydrite)	do	-342.42	-315.56	$C_p=18.52+21.97\cdot 10^{-3}T-1.56\cdot 10^{5}T^{-2}$
8	β-$CaO\cdot SiO_2$	do	-378.20	-358.20	$C_p=26.64+3.6\cdot 10^{-3}T-6.52\cdot 10^{5}T^{-2}$
9	β-$2CaO\cdot SiO_2$	do	-538.00	-512.70	$C_p=41.26+5.34\cdot 10^{-3}T$
10	γ-$2CaO\cdot SiO_2$	do	-539.00	-513.7	$C_p=27.16+19.6\cdot 10^{-3}T$
11	$3CaO\cdot SiO_2$	do	-688.10	-653.40	$C_p=49.85+8.621\cdot 0^{-3}T-10.15\cdot 10^{5}T^{-2}$
12	$CaO\cdot Al_2O_3$	do	-554.80	-526.80	$C_p=34.62+6.751\cdot 0^{-3}T-0.76\cdot 10^{5}T^{-2}$
13	$3CaO\cdot Al_2O_3$	do	-850.00	-809.10	$C_p=52.34+15.81\cdot 0^{-3}T+0.55\cdot 10^{5}T^{-2}$
14	$2CaO\cdot Al_2O_3$	do	-704.00		
15	$12CaO\cdot 7Al_2O_3$	do	-4617.00	-4365.72	$C_p=291.32+50.3\cdot 10^{-3}T-5.25\cdot 10^{5}T^{-2}$
16	$3CaO\cdot Al_2O_3\cdot 6H_2O$	do	-1329.00	-1205.18	
17	$2CaO\cdot Al_2O_3\cdot 5H_2O$	do	-1078.00		
18	$4CaO\cdot Al_2O_3\cdot 12H_2O$	do	-1916.40	-1704.20	
19	$2CaO\cdot SiO_2\cdot 1.17H_2O$ (hillebr.)	do	-624.80	-580.55	$C_p=41.04+22.04\cdot 10^{-3}T-7.4\cdot 10^{5}T^{-2}$
20	$3CaO\cdot 2SiO_2\cdot 3H_2O$ (afwill.)	do	-1118.45	-1028.25	$C_p=81.54+45.1\cdot 10^{-3}T-14.67\cdot 10^{5}T^{-2}$
21	$4CaO\cdot 3SiO_2\cdot 1.5H_2O$ (foshag.)	do	-1402.85	-1310.85	$C_p=87.95+39.5\cdot 10^{-3}T-13.48\cdot 10^{5}T^{-2}$
22	$6CaO\cdot 6SiO_2\cdot H_2O$ (xonotl.)	do	-2322.82	-2185.32	$C_p=132.25+65\cdot 20\cdot 10^{-3}T-18\cdot 35\cdot 10^{5}T^{-2}$
23	$5CaO\cdot 6SiO_2\cdot 3H_2O$ (rivers.)	do	-2300.90	-2140.90	$C_p=143.55+74\cdot 7\cdot 10^{-3}T-20\cdot 82\cdot 10^{5}T^{-2}$
24	$5CaO\cdot 6SiO_2\cdot 5.5H_2O$ (toberm.)	do	-2482.15	-2287.35	$C_p=110.6+189\cdot 1\cdot 10^{-3}T$
25	$5CaO\cdot 6SiO_2\cdot 10.5H_2O$ (plomb.)	do	-2837.15	-2573.20	$C_p=132.2+270\cdot 0\cdot 10^{-3}T$
26	$2CaO\cdot 3SiO_2\cdot 2.5H_2O$ (gyrol)	do	-1138.82	-1048.62	$C_p=79.47+36.3\cdot 10^{-3}T-17.55\cdot 10^{5}T^{-2}$
27	$CaO\cdot 2SiO_2\cdot 2H_2O$ (oken.)	do	-725.69	-661.70	$C_p=44.81+18.7\cdot 10^{-3}T-10.35\cdot 10^{5}T^{-2}$
28	H_2O	liquid	-68.32	-56.69	$C_p=7.93+16.95\cdot 10^{-3}T+2.67\cdot 10^{5}T^{-2}$
29	SiO_2(β-quartz)	crystal	-205.40	-192.40	$C_p=11.22+8.20\cdot 10^{-3}T-2.7\cdot 10^{5}T^{-2}$
30	Ca	gas	$+46.04$	$+37.98$	
31	Si	do	$+88.04$	$+77.41$	
32	Al	do	$+75.00$	$+65.30$	
33	H	do	$+52.089$	$+48.575$	
34	O	do	$+59.16$	$+54.99$	
35	S	do	$+53.25$	$+43.57$	
36	Mg	do	$+35.90$	$+27.60$	
37	SiO_3^{--}	solid	-256.00	-219.20	
38	OH^-	do	-54.66	-37.56	
39	Ca^{++}	do	-129.70	-132.18	
40	α-Al_2O_3	crystal	-399.09	-376.77	
41	$Al_2(SO_4)_3$	do	-820.98	-738.99	

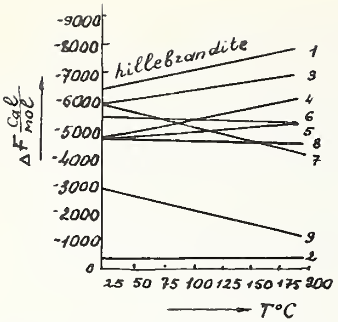

FIGURE 1. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for compositions* C:S=2:1 *and higher.*

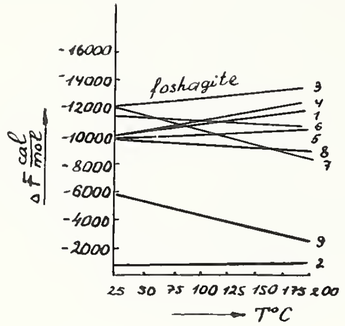

FIGURE 2. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=3:2.

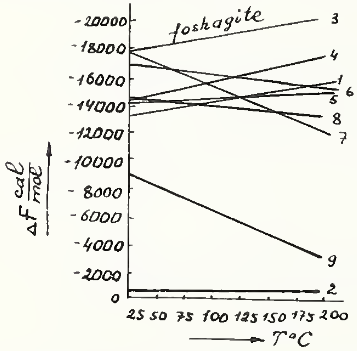

FIGURE 3. *The diagram* ΔF=f(T) *for direct reaction in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=4:3.

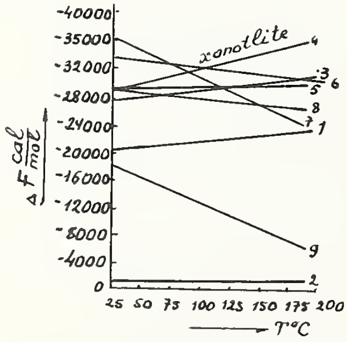

FIGURE 4. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=1:1.

Examination of figures 1 to 7,[2] in which ΔF=*f*(*T*) for reactions in the system $Ca(OH)_2-SiO_2-H_2O$ is given, allows us to draw the following conclusions:

For compositions C:S=2:1 and more basic, 3:1, 4:1, etc., in the whole range of temperatures, primary formation of hillebrandite is thermodynamically most probable (fig.1).

For compositions C:S=3:2 and 4:3 and intermediate values, primary formation of foshagite is most probable (figs. 2, 3).

For the composition C:S=1:1, the primary products may be tobermorites (plombierite and tobermorite), and above 90 to 100 °C formation of xonotlite becomes thermodynamically most probable (fig. 4).

For the composition C:S=5:6, the primary product at low temperatures is indicated to be plombierite; from 50 to 220 °C tobermorite proper is indicated; and above 220 °C, xonotlite (fig. 5).

For compositions C:S=2:3 and 1:2 and the more acid region 1:3, 1:4, 1:5, etc., up to 230 and 240 °C, primary formation of gyrolite is most probable, and above 240 °C, xonotlite (figs. 6, 7).

In the system β-C_2S-H_2O (fig. 8), primary formation of hillebrandite is thermodynamically most probable up to 65 °C, and from 65 to 170°, afwillite.

In the system C_3S-H_2O (fig. 9), primary formation of hillebrandite is most probable over the whole temperature range, but the absence of data for C_3S-H_2O does not allow us to make at present a full analysis of reactions in this system.

The analysis of side reactions in the system $Ca(OH)_2$-SiO_2-H_2O makes it possible to conclude:

1. Stable hydrosilicates in the absence of excess of SiO_2 and $Ca(OH)_2$ are: hillebrandite (fig. 10), foshagite (though its transformation into xonotlite at high temperatures is not excluded, as is indicated by the inclination of curve 4 in figure 15), and xonotlite (but only at temperatures above 100 °C, for at low temperatures it can be transformed into tobermorite in the presence of water, fig. 18, curve 6).

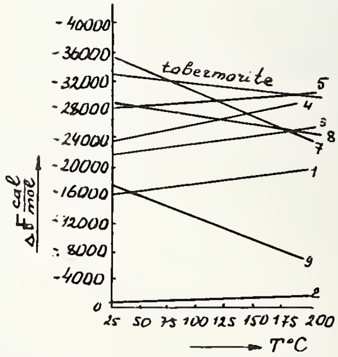

FIGURE 5. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=5:6.

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[2] In figures 1 to 27 the following symbols are used: 1—the formation of hillebrandite, 2—of afwillite, 3—of foshagite, 4—of xonotlite, 5—of riversideite, 6—of tobermorite, 7—of plombierite, 8—of gyrolite, 9—of okenite.

2. Tobermorite and gyrolite are thermodynamically stable at low temperatures but tend to transform into xonotlite at temperatures above 170 to 220 °C (figs. 21 and 24).

3. Afwillite and okenite are thermodynamically unstable over all the temperature range. Afwillite tends to transform into foshagite (fig. 12, curve 3), and okenite into gyrolite and tobermorite (fig. 27, curves 6 and 8).

With excess of $Ca(OH)_2$, all hydrosilicates exhibit a tendency to transform into hillebrandite (figs. 13, 16, 19, 22, 25), and with excess of SiO_2, into gyrolite (figs. 11, 14, 17, 20, 23).

A certain peculiarity characterizes afwillite, which in the presence of SiO_2 tends to transform into gyrolite only at temperatures up to 175 °C. At higher temperatures its transformation into foshagite becomes more probable (fig. 14, curve 3).

The results of calculations correspond very well with the experimental data of numerous scientists: P. P. Budnikov and N. V. Petrovykh [39], Yu. M. Butt, L. N. Rashkovich and others [4], H. F. W. Taylor [40], R. B. Peppler [41] and G. L. Kalousek [42, 43], but require the assumption that all the processes of hydrosilicate formation in the system $Ca(OH)_2$–SiO_2–H_2O take place in solution.

For instance, Peppler has stated that the final products are gyrolite and xonotlite when the initial materials are $Ca(OH)_2$ and silicic acid gel at molar $CaO:SiO_2$ ratios ranging from 0.26 to 0.63 (at 180 °C from 4 to 15 days). According to our data this can be explained in the following way. At 180 °C the concentration of $Ca(OH)_2$ in the solution is ~1.5 mmole/liter [44], while the concentration of SiO_2 is ~12.9 mmole/liter [45] in the case of amorphous SiO_2. Generally for more accurate analysis it is necessary to take into account the mutual influence of Ca and OH ions upon the solubility of SiO_2, and of silicic acid ions upon the solubility of $Ca(OH)_2$ in water; and instead of concentrations the activities of ions in solution should be used. Taking into consideration the approximate character of the initial thermodynamic data and the expectation of only qualitative estimation of the direction of observed reactions, we have taken as a basis the concentrations of $Ca(OH)_2$ and SiO_2 in solution.

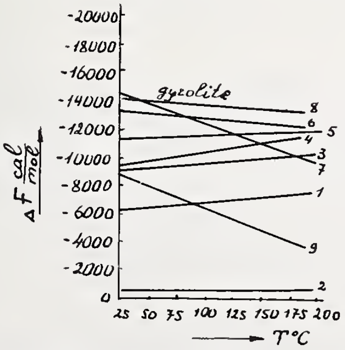

FIGURE 6. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=2:3.

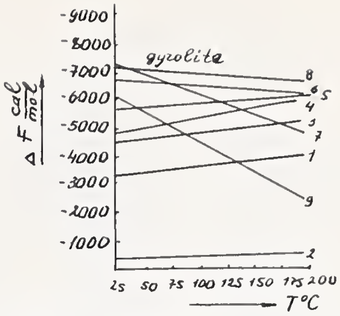

FIGURE 7. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=1:2.

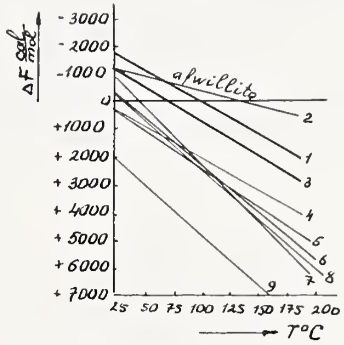

FIGURE 8. *The diagram* ΔF=f(T) *for direct reactions in the system* β-$2CaO{\cdot}SiO_2$-H_2O.

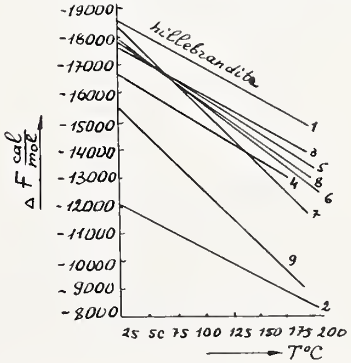

FIGURE 9. *The diagram* ΔF=f(T) *for direct reactions in the system* $3CaO{\cdot}SiO_2$-H_2O.

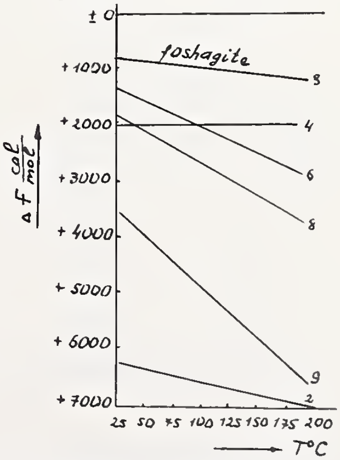

FIGURE 10. *The diagram* ΔF=f(T) *for transformation reactions of hillebrandite.*

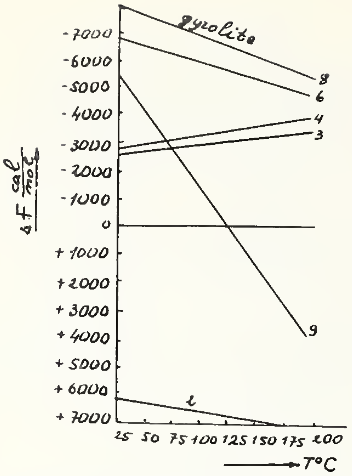

FIGURE 11. *The diagram* ΔF=f(T) *for transformation reactions of hillebrandite with excess* SiO_2.

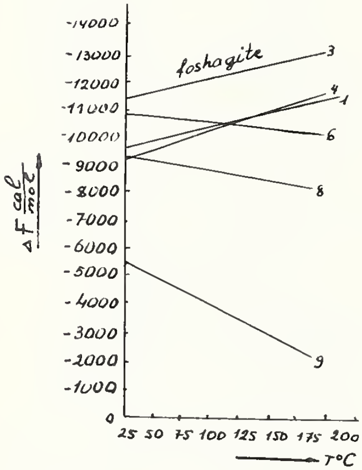

FIGURE 12. *The diagram* ΔF=f(T) *for transformation reactions of afwillite.*

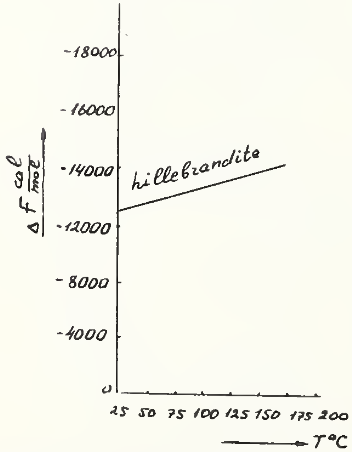

FIGURE 13. *The diagram* ΔF=f(T) *for transformation reactions of afwillite with excess* $Ca(OH)_2$.

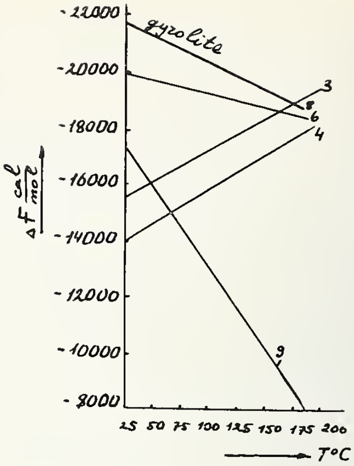

FIGURE 14. *The diagram* ΔF=f(T) *for transformation reactions of afwillite with excess* SiO_2.

Thus, the C:S ratio at 180 °C in this case will be $\frac{1.5}{12.9}=0.12$, or nearly 1:8. For this composition, according to figure 7 (curve 8) the primary product must be gyrolite. But gyrolite at high temperatures is a metastable phase and according to the data of figure 24 (curve 4) is able to transform into xonotlite. The transformation temperature indicated by our data (~225°) differs from Peppler's data by 45 °C, but for qualitative estimation it is quite acceptable. As the period of 4 to 12 days proved insufficient for the full transformation of gyrolite into xonotlite at 180 °C, Peppler found in this case just a mixture of gyrolite and xonotlite. But for the same composition in a second series of experiments continued for 6 months, Peppler found only xonotlite, which completely confirms the correctness of our conclusions. The results of other researchers correspond with them equally well.

We can draw very important conclusions from the examination of the data of figure 18. As we see in the figure (curve 6), xonotlite is a metastable compound at low temperatures and in the presence of water is able to condense into tobermorite according to the equation:

$$6CaO{\cdot}6SiO_2{\cdot}H_2O+5.5H_2O\rightarrow 5CaO{\cdot}6SiO_2{\cdot}5.5H_2O+Ca(OH)_2$$

This condensation leads to the removal of one molecule of $Ca(OH)_2$ from xonotlite, and this is important for preventing the solution of hydrosilicates in water.

The results of theromodynamic calculations allow us also to analyze the possibility of synthesis of various hydrosilicates.

1. Gyrolite may be obtained only when using active forms of SiO_2 at ratios of CaO and SiO_2 in the solution within limits of 2:3 to 1:∞ (corresponding to certain temperatures and states of initial materials), and when taking into account a

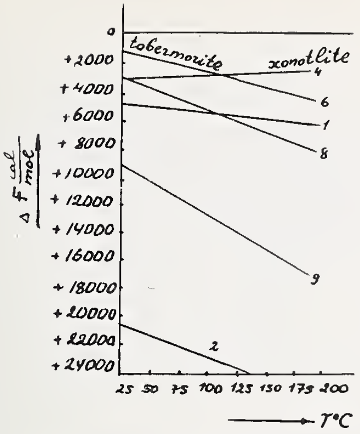

FIGURE 15. *The diagram* ΔF=f(T) *for transformation reactions of foshagite.*

suitable reaction period, because as a metastable phase it can transform fully into xonotlite under long processing.

2. Tobermorites may be synthesized from quartz and lime at such a temperature and with such a physical condition of initial SiO_2 and $Ca(OH)_2$ that the composition of CaO and SiO_2 in solution will be kept near or equal to 5:6 (with initial composition C:S=5:6). If the process is conducted with the initial composition of CaO to SiO_2 differing from C:S=5:6 (that is, with excess of CaO or SiO_2) it will be possible at certain temperatures and particle fineness of materials to obtain tobermorites as primary product, but through long processing they can transform with excess of $Ca(OH)_2$ into hillebrandite, and with excess of SiO_2 into gyrolite. Besides, it should be considered that at high temperatures (>190°) tobermorites are able to transform into xonotlite.

3. Xonotlite is formed when the C:S ratio in solution is nearly 1:1, and the higher the temperature the wider is the composition range near 1:1 for its preferred formation. Besides, xonotlite may be a product of gyrolite and tobermotite transformation at high temperatures.

4. Hillebrandite may be formed in all mixtures of CaO and SiO_2 when the ratios in the solution amount to 2:1 or more. Besides, it should be considered that initial mixtures rich in $Ca(OH)_2$ will consist of hillebrandite as final product after long processing.

5. Foshagite may be obtained as a primary product when the ratio of CaO to SiO_2 in the solution is equal to 3:2 to 4:3. Incidentally, such a composition is difficult to obtain as it lies in a very narrow range of temperatures ($\sim$160 to 165 °C for quartz and $Ca(OH)_2$).

6. Afwillite and okenite are not to be expected as products of synthesis from normal SiO_2 and $Ca(OH)_2$.

As to the hydration reactions of aluminates of calcium, gypsum, CaO, and MgO, the values of ΔH_{298} and ΔF_{298} for these reactions are given in

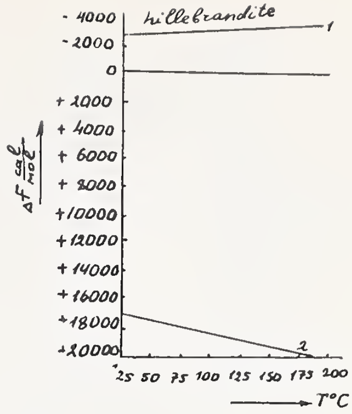

FIGURE 16. *The diagram* ΔF=f(T) *for transformation reactions of foshagite with excess* $Ca(OH)_2$.

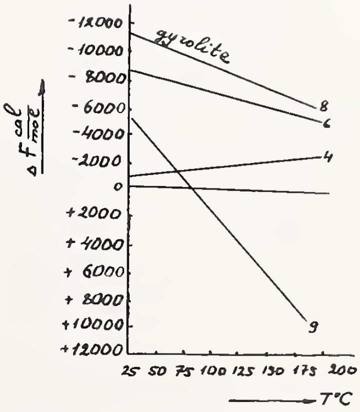

FIGURE 17. *The diagram* ΔF=f(T) *for transformation reactions of foshagite with excess* SiO_2.

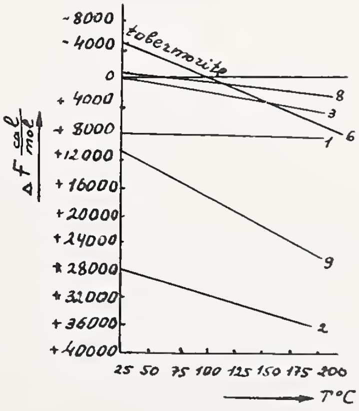

FIGURE 18. *The diagram* ΔF=f(T) *for transformation reactions of xonotlite.*

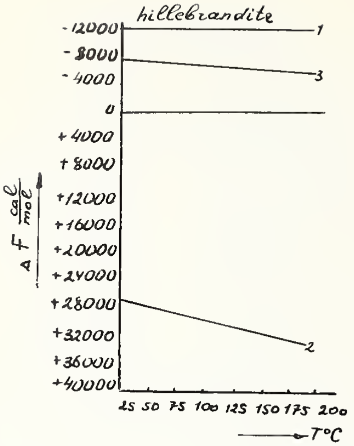

FIGURE 19. *The diagram* ΔF=f(T) *for transformation reactions of xonotlite with excess* $Ca(OH)_2$.

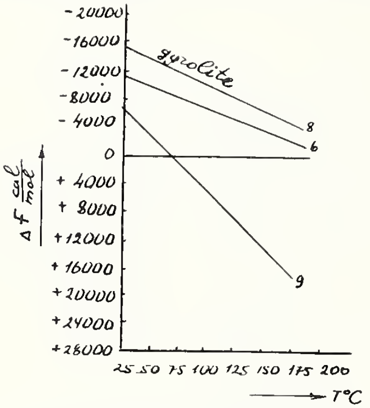

FIGURE 20. *The diagram* ΔF=f(T) *for transformation reactions of xonotlite with excess* SiO_2.

table 2, along with the values of ΔH and ΔF for hydration of CS, C_2S, and C_3S to hillebrandite. Average bond energies of Ca—O and Mg—O for the hydrated and unhydrated forms of these various compounds are given in table 3.

The calculation of the average bond energies of Ca—O and Mg—O, which are the ones that vary

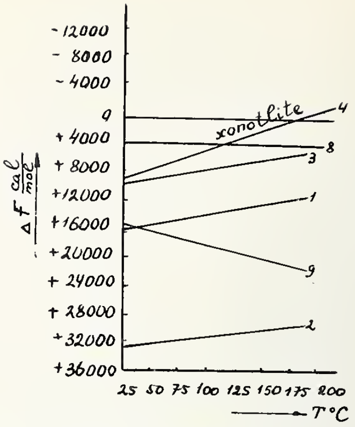

FIGURE 21. *The diagram* ΔF=f(T) *for transformation reactions of tobermorite.*

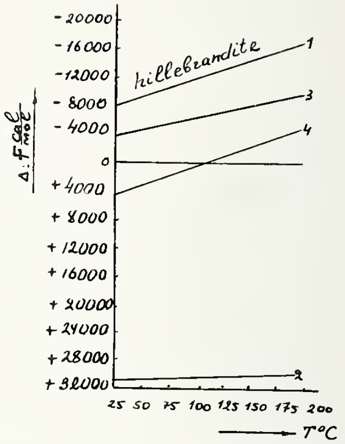

FIGURE 22. *The diagram* ΔF=f(T) *for transformation reactions of tobermorite with excess* $Ca(OH)_2$.

the most as functions of the condition and energy state of the oxygen, can be performed only on the assumption that the *average* energies of Si—O, Al—O, S—O, and O—H, which are common to both unhydrated and hydrated (stable) forms, do not change, and if they do, the difference is so insignificant in comparison with the change of

TABLE 2

No.	Hydration reaction	ΔH of the reaction at 298 °K	ΔF of the reaction at 298 °K
		kcal/mole	*kcal/mole*
1	$CaO+H_2O \rightarrow Ca(OH)_2$	−15.60	−13.21
2	$3CaO \cdot SiO_2+2.17H_2O \rightarrow 2CaO \cdot SiO_2 \cdot 1.17H_2O + Ca(OH)_2$	−24.50	−18.70
3	β-$2CaO \cdot SiO_2+1.17H_2O \rightarrow 2CaO \cdot SiO_2 \cdot 1.17H_2O$	−6.80	−1.72
4	γ-$2CaO \cdot SiO_2+1.17H_2O \rightarrow 2CaO \cdot SiO_2 \cdot 1.17H_2O$	−5.80	−0.72
5	β-$CaO \cdot SiO_2+0.585H_2O \rightarrow \frac{1}{2}(2CaO \cdot SiO_2 \cdot 1.17H_2O)-\frac{1}{2}SiO_2$	+3.47	+4.89
6	$3CaO \cdot Al_2O_3+6H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O$	−69.08	−56.01
7	$2CaO \cdot Al_2O_3+5H_2O \rightarrow 2CaO \cdot Al_2O_3 \cdot 5H_2O$	−32.40	----------
8	$12CaO \cdot 7Al_2O_3+48H_2O \rightarrow 3(4CaO \cdot Al_2O_3 \cdot 12H_2O)+8Al(OH)_3$	−307.08	−199.20
9	$CaO \cdot Al_2O_3+4H_2O \rightarrow \frac{1}{2}(2CaO \cdot Al_2O_3 \cdot 5H_2O) + Al(OH)_3$	−17.77	----------
10	$CaSO_4 \cdot 0.5H_2O+1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O$	−4.61	−1.32
11	$CaSO_4+2H_2O \rightarrow CaSO_4 \cdot 2H_2O$	−4.00	−0.25
12	$MgO+H_2O \rightarrow Mg(OH)_2$	−8.84	−6.45

TABLE 3

No.	Anhydrous compound	Average bond energy of the Ca—O bond	Hydrate	Average bond energy of the Ca—O bond	Energy gain on hydration
		kcal/bond		*kcal/bond*	*kcal/mole*
1	CaO	128.55	$Ca(OH)_2$	141.60	13.05
2	$3CaO \cdot SiO_2$	133.05	$2CaO \cdot SiO_2 \cdot 1.17H_2O$	140.60	7.55
3	β-$2CaO \cdot SiO_2$	135.76	$2CaO \cdot SiO_2 \cdot 1.17H_2O$	140.60	4.84
4	γ-$2CaO \cdot SiO_2$	136.00	$2CaO \cdot SiO_2 \cdot 1.17H_2O$	140.60	4.60
5	β-$CaO \cdot SiO_2$	139.21	$2CaO \cdot SiO_2 \cdot 1.17H_2O$	140.60	1.39
6	$3CaO \cdot Al_2O_3$	127.75	$3CaO \cdot Al_2O_3 \cdot 6H_2O$	149.78	22.03
7	$2CaO \cdot Al_2O_3$	128.82	$2CaO \cdot Al_2O_3 \cdot 5H_2O$	150.07	21.25
8	$12CaO \cdot 7Al_2O_3$	128.56	$4CaO \cdot Al_2O_3 \cdot 12H_2O$	155.56	27.00
9	$CaO \cdot Al_2O_3$	130.44	$2CaO \cdot Al_2O_3 \cdot 5H_2O$	150.07	19.63
10	$CaSO_4 \cdot 0.5H_2O$	155.80	$CaSO_4 \cdot 2H_2O$	166.00	10.20
11	$CaSO_4$ (anhydrite).	153.40	$CaSO_4 \cdot 2H_2O$	166.00	12.60
12	MgO	[a] 119.45	$Mg(OH)_2$	129.13	9.68

[a] For MgO and $Mg(OH)_2$ the value of average bond energy is for the Mg—O bond.

average energy of Ca—O and Mg—O that it may be neglected.

This is understandable because the average energies of Si—O, Al—O, S—O, and O—H are the basis of formation of complex oxygen-anions: SiO_4^{4-}, AlO_2^-, SO_4^{2-}, and OH^-, stability of which is large enough, since the radii of Si^{4+} (0.39 A), Al^{3+} (0.57 A) and S^{6+} (0.34 A) ions, compared with the radius of O^{2-} (1.32 A), are very small and will not distort the close packing of oxygen-anions even for considerable energy changes. The influence of these anions on Ca and Mg cations depends in great degree upon the differences of their energy condition, determined mostly by temperature and medium. At high temperatures, the polarization of anions causes decrease of the bond energy of Ca^{2+} with the free bonds of the oxygen of SiO_4^{4-}, SO_4^{2-}, and AlO_2^- anions; at low temperature this bond can return into its normal state.

The bond energy for Si—O was determined from β-quartz, for Al—O from corundum, for S—O from $Al_2(SO_4)_3$, and for O—H from water, in accordance with the methods described by T. Cottrell [46].

As may be seen in table 3, the calculated energy gain for one bond of Ca—O for hydration of CaO is 13.05 kcal. It is quite natural that under

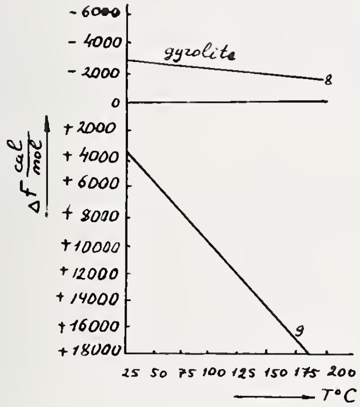

FIGURE 23. *The diagram* ΔF=f(T) *for transformation reactions of tobermorite with excess* SiO_2.

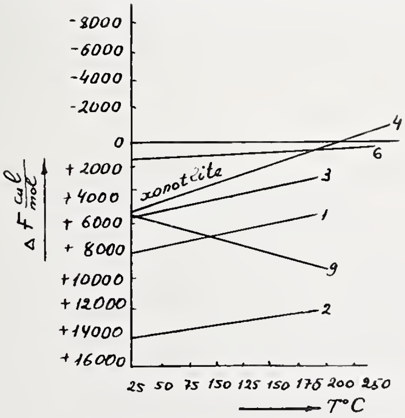

FIGURE 24. *The diagram* ΔF=f(T) *for transformation reactions of gyrolite.*

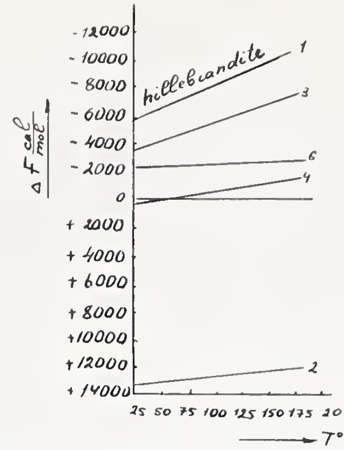

FIGURE 25. *The diagram* ΔF=f(T) *for transformation reactions of gyrolite with excess* $Ca(OH)_2$.

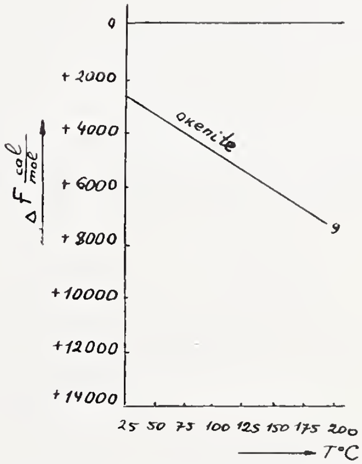

FIGURE 26. *The diagram* ΔF=f(T) *for transformation reactions of gyrolite with excess* SiO_2.

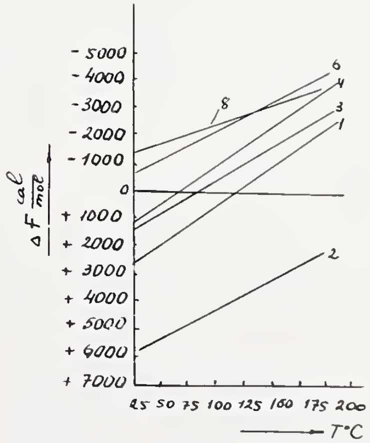

FIGURE 27. *The diagram* ΔF=f(T) *for transformation reactions of okenite.*

certain kinetic conditions, which could make it possible to overcome the activation energy, there would be immediately produced in lime a corresponding rearrangement leading to a lower level of free energy of the system.

The same may be said with respect to C_3S (energy gain 7.5 kcal/Ca—O bond), β-C_2S (energy gain 4.84 kcal/Ca—O bond), C_3A (energy gain 20.15 kcal/Ca—O bond), C_2A (energy gain 21.25 kcal/Ca—O bond), $C_{12}A_7$ (energy gain 27.0 kcal/Ca—O bond), CA (energy gain 19.63 kcal/CaO bond), $CaSO_4 \cdot 0.5H_2O$ (energy gain 10.2 kcal/Ca—O bond) and MgO (energy gain 9.68 kcal/Mg—O bond).

It is interesting to note that ΔF_{298} of these reactions has considerable negative value (table 2), which characterizes the great motive forces of those processes, assuring the spontaneous nature of the transformation.

Such compounds as γ-C_2S, β-CS, and $CaSO_4$ (anhydrite) are in a peculiar position. As table 3 indicates, the average bond energies of Ca—O in them are such that there is a gain of energy during hydration, but ΔF values of these processes (table 2) are found to be either nearly zero (γ-C_2S and $CaSO_4$) or positive (β-CS). Hence the activation energy of hydration processes for them is considerable, and therefore in the presence of water these processes cannot occur spontaneously. Either hydrothermal conditions (for γ-C_2S) or very fine grinding and the use of additions that increase the solubility (for anhydrite) are necessary.

Binders are composed of compounds that are able to harden into stonelike solids. This means not only that the binders must form hydrates stable in water, but a strong concretion of these hydrates must occur as well; therefore supersaturation in water solutions during hardening is necessary for binders [14, 47].

It may also happen that under usual conditions a compound does not give supersaturation, whereas under hydrothermal conditions, or with the help of additions or fine grinding, supersaturation can be secured.

Therefore conditions must be taken into account when defining binders. For most binders these conditions are easily met, as the hardening process is thermodynamically possible for them under normal conditions ($t=25$ °C, $p=1$ atm). To this group belong CaO, β-C_2S, C_3S, C_3A, C_2A, $C_{12}A_7$, CA, $CaSO_4 \cdot 0.5H_2O$, and MgO.

Since the main minerals of cement clinker are silicates of calcium, we take them as a model for analysis of the hardening mechanism of binders.

Hardening processes may be divided into the stage of interaction of a binder with water (hydration and supersaturation) and the stage of the formation of crystalline concretion (crystallization, recrystallization, contact formation).

Thermodynamically, the hydration can occur both in the solid phase and through solution [48], since the total energy of the process does not depend upon its path. The formation of hydrates in the solid phase does not provide the attainment of thermodynamically stable hydrate forms, and they, having some supply of free energy, will thus be converted through solution into more stable, well-formed hydrates, but this only over a longer period of time and under conditions of insignificant supersaturation which will not provide a strong concretion.

Hydration of binders through solution presents quite another picture. First of all, solution of the binder will not be hindered by hydrate films. It will be governed by the energy of the crystalline structure of the initial binder and by the properties of the solvent [49].

The activation energy of reactions between saturated molecules amounts to some tens of kcal/mole, and between ions is practically zero. This decides the kinetics of the process.

Therefore, in this case kinetic factors determine that the predominant development of the process is through solution, which was experimentally confirmed by V. B. Ratinov's researches [47].

From the average bond energies calculated by us we can indicate the mechanism of hydration of β-$2CaO \cdot SiO_2$ as follows.

The influence of polar molecules of H_2O weakens the bonds between atoms in C_2S, and heat movement is enough to make the elements of its structure pass into solution. We stated that the average bond energy of O—H in water is 110.57 kcal/bond, Si-O in β-C_2S—102.93 kcal/bond, Ca–O in β-C_2S—139.21 and Ca–O in hillebrandite—140.6 kcal/bond.

As the bond energy of Ca–O in β-C_2S is weaker than in hillebrandite, the Ca ion passing into solution (it will be manifested most probably only by the increase of mobility of Ca^{++} towards oxygen) will try to decrease its free energy, which will be manifested by development of a stronger bond with oxygen. The energy gain will be, as table 3 shows, 4.84 kcal/bond. Though this is not ΔF, it may be used as a measure for qualitative conclusions only.

From the comparison of values of bond energies of Si—O and Ca—O in β-C_2S (102.93 and 135.76 respectively), it is evident that the Ca ion passing into solution does not lose its oxygen, since 135.76 is greater than 102.93. Therefore the Ca ion, occupying a certain thermodynamically most advantageous position in oxygen packing, will assure stability.

In this case far different conditions will arise for silicon. Remaining without surroundings, since all four oxygen ions will pass to Ca^{++}, silicon (Si^{4+}) will immediately try to neutralize its charges. But this is not so easy to do, as oxygen in water is bound with protons by stronger bond (110.57 kcal/bond) than Si with O (102.93 kcal/bond). In this case, silicon can either join with existing OH^- groups, provided ones are in solution, or form double bonds with oxygen (then it will be easy to take oxygen from water, since $2x102.93 >> 110.57$).

Apparently those processes will depend in great degree upon the *p*H of the medium. Since pure water is but little dissociated, basic additives will be of great use for stimulating interaction of β-C_2S with water. The initial *p*H value will influence the primary formation of $Si(OH)_4$ (when all four bonds of silicon are bound with OH^-) or H_2SiO_3 (when two silicon bonds belong to OH while two others belong to oxygen).

Since there are experimental data on dissociation constants of H_2SiO_3 [50], while for $Si(OH)_4$ there are not, it is more reliable in this case to examine formation of metasilicic acid.

In connection with this, it is desirable to know the influence of the *p*H values upon the form of silicic acid in solution. It is easy to show this by calculations based on known values of the first and second dissociation constants of H_2SiO_3 [50].

$$K_1=\frac{[H^+]\,[HSiO_3{}^-]}{[H_2SiO_3]}\cong 10^{-10}$$

$$K_2=\frac{[H^+]\,[SiO_3{}^{--}]}{[HSiO_3{}^-]}\cong 10^{-12}$$

Denoting by ΣSiO_2 the collective content of all the forms of silicic acid, we can obtain the equations for determination of the percentage contents of H_2SiO_3, $HSiO_3^-$, and SiO_3^{--} in solution corresponding to the hydrogen-ion concentration in solution and K_1 and K_2:

$$\%H_2SiO_3=\Sigma SiO_2\,\frac{[H^+]^2}{[H^+]^2+K_1[H^+]+K_1K_2}$$

$$\%HSiO_3^-=\Sigma SiO_2\,\frac{K_1[H^+]}{[H^+]^2+K_1[H^+]+K_1K_2}$$

$$\%SiO_3^{--}=\Sigma SiO_2\,\frac{K_1K_2}{[H^+]^2+K_1[H^+]+K_1K_2}$$

The results of calculations by means of these equations are given in table 4.

Thus the main form of silicic acid at $pH<8.0$ is the undissociated H_2SiO_3. At $pH>12.0$, H_2SiO_3 is practically absent.

TABLE 4

Form of silicic acid	*p*H						
	4	6	8	10	12	13	14
H_2SiO_3	~100.0	~100.0	99.00	49.995	0.01	0.001	--------
$HSiO_3^-$	--------	--------	0.995	49.995	49.995	9.099	0.99
SiO_3^{--}	--------	--------	0.005	0.01	49.995	90.90	99.01

The existence of $HSiO_3^-$ ion is limited to the range $pH=8$–13. At $pH>13$ the main form is SiO_3^{--} ion.

SiO_3^{--} ions thus formed will undoubtedly try to be preserved in solution. The only way is by polymerization. The polymerization is aided by the unsaturated character of the double bond. In an acid medium the polymerization process will go with final formation of framework structures of silica which are practically insoluble in water under normal conditions and therefore quite stable.

In a basic medium, SiO_3^{--} ions will form complex radicals of polysilicic acids, the size and form of which will to a certain degree be governed by the character and properties of the cation of the base introduced into solution (Ca, Mg, Na, K, etc.). And, as is stated in the works of acad. N. V. Belov [1, 2], in the presence of Ca^{++} ions in solution, SiO_3^{--} polymerizes with the formation of bands $(Si_6O_{17})^{10-}$, crimps $(Si_{12}O_{31})^{14-}$, and networks $(Si_6O_{15})^{6-}$, at the basis of all of which lie wollastonite chains, Si_3O_9.

With a certain degree of reliability, this scheme may be transferred to the hydration processes of C_3S and the processes of the formation of calcium hydrosilicates from lime and sand under hydrothermal conditions.

Thus, binders are salts and oxides with lowered active coordinations of cations of the second group of D. I. Mendeleev's periodic system: Ca, Mg, etc., capable through this thermodynamic instability, or under conditions promoting the rise of free energy of the system to create supersaturations under the influence of water. The supersaturations permit crystallization through solution of a considerable mass of an initial binder, with the formation of stonelike solid strengthened by its hydrate forms.

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Paper IV–S10. Contribution to the Determination of the Heat of Hydration of Clinker Minerals*

H. E. Schwiete and A. Tan Tik-Ien

Synopsis

The heats of hydration of C_3S and β-C_2S were determined by means of the solution calorimeter as a function of time. The results were compared with those of identified hydration products.

The preparation of the tobermorite-like phase was studied as a function of temperature, pressure and time. The minimum CaO/SiO_2 molar ratio of the clinker hydrates was determined from the measured heats of hydration.

These studies led to the conclusion that hydration in a shaking machine, with a water factor of 50, results in a minimum CaO/SiO_2 molar ratio of 1.6 (C_3S hydrate) and 1.7 (β-C_2S hydrate), respectively.

Also studied was the effect of foreign oxides on the heat of solution of clinker minerals. This effect was particularly marked for incorporation of Al_2O_3 and MgO. Furthermore, when 2.5 weight-percent Al_2O_3 and 1 weight-percent MgO were incorporated in C_3S, thus giving the chemical composition of alite, the heat of solution rose by 14.2 percent. When these quantities of Al_2O_3 and MgO were added to the clinker as impurities a rise of 1.2 percent in the heat of solution was observed.

Incorporation of C_3A, and C_3A and MgO, in C_3S was also investigated. From the totality of the intercalation experiments, there could be determined the variation in the free enthalpy of the system and the quantities which represent maximum inclusion of foreign oxides in the individual clinker minerals. This yields a conclusive proof, that in determining the heat of solution of clinker minerals the nature and quantity of the impurities present should be taken into account.

Résumé

Les chaleurs d'hydratation de C_3S et β-C_2S ont été déterminées au moyen du calorimètre de solution en fonction du temps. Les résultats ont été comparés à ceux des produits d'hydratation identifiés.

La préparation de la phase semblable au tobermorite a été étudiée en fonction de la température, de la pression et du temps. Le rapport moleculaire minimum CaO/SiO_2 des hydrates du clinker a été déterminé à partir des chaleurs d'hydratation mesurées.

Ces études menèrent les auteurs à la conclusion que l'hydratation dans une secoueuse, avec un facteur d'eau de 50, résulte en un rapport moleculaire minimum CaO/SiO_2 de respectivement 1.6 (C_3S-hydrate) et 1.7 (β-C_2S-hydrate).

On a étudié également l'effet des oxydes étrangers sur la chaleur de solution des minéraux du clinker. Cet effet était particulièrement marqué pour l'incorporation de Al_2O_3 et MgO. De plus, quand 2.5 poids-% Al_2O_3 et 1 poids-% MgO étaient incorporés dans C_3S, donnant ainsi la composition chimique de l'alite, la chaleur de solution s'éleva à 14.2%. Lorsque ces quantités de Al_2O_3 et MgO étaient ajoutées au clinker comme des impuretés une élévation de 1.2% fut observée dans la chaleur de solution.

Des recherches furent faites également sur l'incorporation de C_3A, et de C_3A et MgO, dans C_3S. De la totalité des expériences d'intercalation on a pu déterminer la variation dans l'enthalpie libre du système et des quantités qui représentent l'inclusion maximum des oxydes étrangers dans les minéraux individuels du clinker. Ceci donne la preuve concluante que lorsqu'on détermine la chaleur de solution des minéraux du clinker il faut tenir compte de la nature et de la quantité des impuretés présentes.

Zusammenfassung

Die Hydratationswärme von C_3S und β-C_2S wurde unter Verwendung des Lösungskalorimeters in Abhängigkeit von der Zeit bestimmt. Die Ergebnisse wurden verglichen mit denen von definierten Hydratationsprodukten.

Die Herstellung der tobermoritähnlichen Phase wurde in Abhängigkeit von Temperatur, Druck und Zeit untersucht. Das minimale CaO/SiO_2-Molverhältnis der Klinkerhydrate wurde aus den Meßergebneissen der Hydratationswärmen ermittelt.

Bei diesen Untersuchungen konnte festgestellt werden, daß bei der Hydratation in der Schüttelmaschine und bei einem Wasserfaktor von 50 ein minimales CaO/SiO_2-Molverhältnis von 1.6 (C_3S-Hydrat) bzw. 1.7 (β-C_2S-Hydrat) entsteht.

Ferner wurde der Einfluß der Fremdoxide auf die Lösungswärme der Klinkermineralien untersucht. Der Einfluß war besonders stark bei Einlagerung von Al_2O_3 und MgO, weiterhin wurden 2.5 Gewicht-% Al_2O_3 und 1 Gewicht-% MgO in C_3S eingelagert, so daß sich die chemische Zusammensetzung von Alit ergab, dann stieg die Lösungswärme um 14.2%. Diese Mengen Al_2O_3 und MgO wurden als Verunreinigungen dem Klinker beigegeben, hierbei wurde nur ein Anstieg der Lösungswärme von 1.2% beobachtet.

Ausserdem wurde die Einlagerung von C_3A, und von C_3A und MgO, in C_3S untersucht. Aus der Gesamtheit dieser Einlagerungsversuche konnte die Änderung der freien Enthalpie des Systems und die Menge, die maximal an Fremdoxiden in den einzelnen Klinkermineralien eingelagert sind, bestimmt werden. Daraus ergibt sich der eindeutige Beweis, daß bei der Bestimmung der Lösungswärme von Klinkermineralien auf die Art und auf die Menge der vorhandenen Verunreinigungen Rücksicht genommen werden muß.

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Introduction

The determination of the heat of hydration of C_3S and β-C_2S, respectively, was based on the first law of thermodynamics, so that the heats of solution of the substances participating in the reaction could also be determined.

Determinations were also made of the heats of solution of MgO, Al_2O_3, and C_3A, which may become incorporated in the C_3S lattice, as well as the heats of solution of C_3S containing such inclusions of foreign substances. The heats of solution were determined using an acid concentration of $4N$ HF and $11N$ HNO_3 in a ratio of 1:1.

Change in the Heat of Solution of C_3S With Incorporation of Foreign Substances

In accordance with a chemical formula for alite ($C_{54}S_{16}AM$, established by Jeffery [1] [1] and confirmed by Müller-Hesse and Schwiete [2] as well as other authors, the C_3S lattice can contain 0.97 percent (by wt) of MgO and 2.5 percent (by wt) of Al_2O_3. The present part of this investigation concerns the effect of increasing quantities of MgO and Al_2O_3 in the C_3S lattice on the magnitude of the heat of solution of pure C_3S.

The authors' tests have shown that a temperature of 1,350 °C and a temperature duration of 20 hr are needed to incorporate the above mentioned maximum percentages by weight of MgO and Al_2O_3 completely into the C_3S lattice. Figure 1 shows the changes in heat of solution with increasing incorporation of MgO and Al_2O_3 in the C_3S lattice. Curve 1 shows changes in heat of solution with constant admixture of 2.5 percent (by wt) of Al_2O_3 and additions of MgO increasing from 0.2 to 1.0 percent (by wt); curve 2 shows variation with constant admixture of 1.0 percent (by wt) of MgO and additions of Al_2O_3 increasing from 0.27 to 2.5 percent, curve 3 shows variation in heat of solution with an increasing admixture of MgO and Al_2O_3 in equal mole ratio.

A comparision of the three curves shows that, in spite of quantitatively larger additions of foreign oxides in the mixes shown in curves 1 and 2, the heat of solution is lower than that shown in curve 3 for additions of foreign oxides that are gravimetrically smaller but have the mix ratio of 1:1. This means that electron neutrality is not attained with mixing proportions represented by curves 1 and 2, i.e., the added foreign oxides are not completely built into the C_3S lattice.

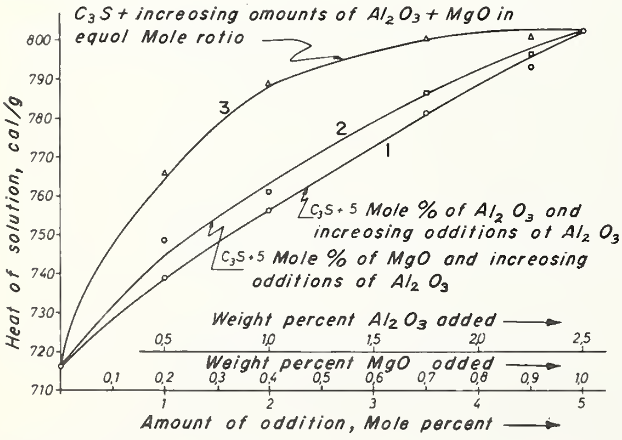

FIGURE 1. *Heat of solution of* C_3S *as affected by increasing additions of* Al_2O_3 *and* MgO.

The values for heat of solution shown in figure 1 can be used in the equation below to compute the heat of formation of alite. This computation gives 83.1 cal/g, and the reaction is endothermic.

$$18\ C_3S+A+M \rightarrow C_{54}S_{16}AM+2S-\Delta H$$

Incorporation of Al_2O_3 and MgO in the C_3S lattice produces an abrupt increase in the heat of solution:

Heat of solution of	cal/g
C_3S	716. 4
Alite	802. 4

This change amounts to 14.2 percent. This result shows that the heats of solution of the MgO and Al_2O_3 in the C_3S lattice can not be interpreted as additive. By adding the heats of solution of MgO, Al_2O_3, and C_3S for the percentages present in alite, an increase of only 1.4 percent would be obtained.

This sudden change in the heat of solution can also be negative, as seen in tempering C_3S with C_3A. In tests with mixes of 0.5 to 5 mole percent of C_3A with C_3S a drop in the heat of solution from 7.0 to 6.4 percent was observed after heating at 1,450 °C for 8 hr. With a 1-mole-percent admixture of C_3A in C_3S the heat of solution is lowered from 716.4 to 660.9 cal/g, i.e, there is a drop of 7.7 percent. Figure 2 shows the course of the heat of solution curve as a function of C_3A-admixture in C_3S.

With additions of more than one mole-percent of C_3A a rise in enthalpy of 1.5 cal/g per mole-percent of C_3A was obtained.

Addition of the heats of solution of C_3S (716.4 cal/g) and 1.5 percent of C_3A results in an *increase* in the heat of solution of 1.2 percent. However, the tests (see above) disclosed a drop. The heat of solution of C_3A at the above acid concentration is 813.6 cal/g.

The maximum incorporation of C_3A in C_3S amounts to 1.5 percent. This value was deter-

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[1] Figures in brackets indicate the literature references at the end of this paper.

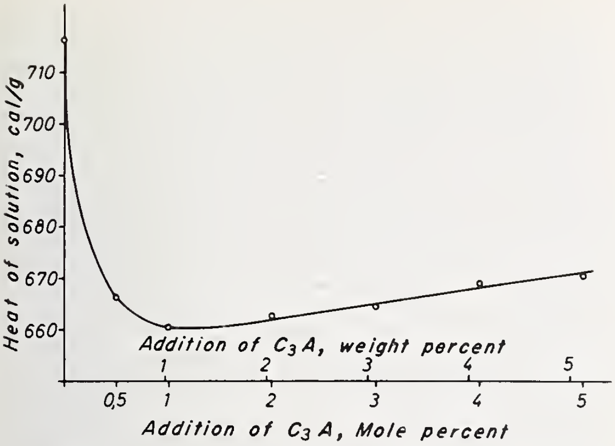

Figure 2. *Relation of heat of solution of* C_3S *to incorporated* C_3A *admixture.*

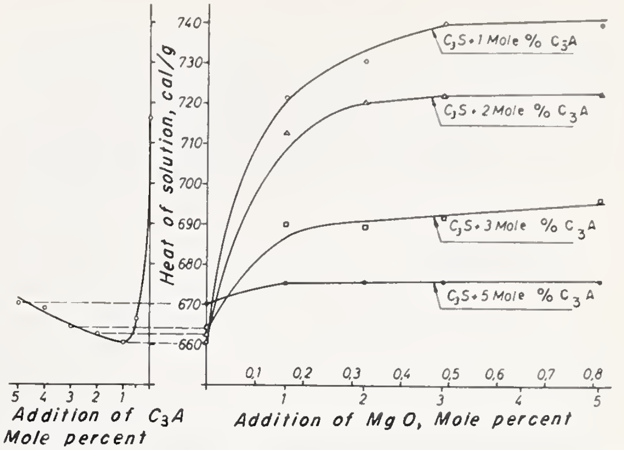

Figure 3. *Effect of* C_3A *and* MgO *on the heat of solution* of C_3S.

mined by plotting the algebraic sum of the enthalpies against composition.

Further computations showed that the heat change for incorporation of C_3A in C_3S is exothermic. It amounts to 57.9 cal/g.

The fact that the measured change in enthalpy can be different, as found in the incorporation of Al_2O_3 and MgO or C_3A in C_3S cannot be interpreted for C_3A (in contrast to Al_2O_3 + MgO) on the basis of substitution in the lattice, since in this case the change in enthalpy is negative. From the statistical mole volumes we find that the C_3A lattice must be larger than the C_3S lattice. From this fact we can conclude that C_3A and C_3S combine to form a mixed crystal (solid solution).

The X-ray patterns of alite and C_3S with incorporation of C_3A show no differences. The typical interference of alite at d=1.49 A found by Midgley [3], was also observed when C_3A was incorporated in C_3S.

When MgO was also incorporated in these C_3S–C_3A mixed crystals, the heat of solution began to rise again. The maximum was reached with a mixed crystal of C_3S with 1 mole percent of C_3A and 2.5 mole-percent of MgO. With greater addition of C_3A, the heat of solution again decreases (fig. 3).

This observation led to the conclusion that only small additions produce sudden changes (deviations) in the heat of solution, i.e., form a mixed crystal. Further additions remain present as original components along with the mixed crystal. In this case the heat of solution is additive. From the above reasoning, it can be seen that the solution-calorimeter values used heretofore in computing the percentage composition of clinker minerals are not suitable. In determining the clinker minerals in cements one cannot start with the heats of solution of pure clinker minerals. Rather computation of cement components should be based on such substituted clinker minerals as contain the quantities of foreign substances corresponding to those present in the cement.

Preparation of Calcium Silicate Hydrates

Calcium silicate hydrates can be produced by the following methods: (1) through a reaction of calcium hydroxide on an aero-silica, or calcium hydroxide and soluble silicic acid salts, such as alkali silicates; (2) through the hydration of tricalcium silicate or β-C_2S.

Preparation of Calcium Silicate Hydrates From $Ca(OH)_2$ and an Aero-Silica or Alkali Silica, Respectively

The heretofore known methods of producing calcium silicate hydrates from $Ca(OH)_2$ and an aero-silica or soluble silicic acid salts do not yield crystals without hydrothermal treatment of the specimens. To be sure, a white precipitate forms when $Ca(OH)_2$ solution and an aero-silica solution or sodium silicate solution are combined or come in contact with each other; however, it is not crystalline but X-ray amorphous. Hydrothermal treatment of this precipitate requires 2 months, as reported by McMurdie and co-workers [4] and Taylor [5]. A temperature increase is needed to accelerate crystallization. This temperature increase, however, is limited by the following conditions: (1) the stability of the calcium silicate hydrate products is a function of temperature; (2) at temperatures above 400 °C the calcium silicate hydrate formed is dehydrated into wollastonite. The latter cannot hydrate.

To avoid these difficulties and yet achieve rapid crystallization, the X-ray-amorphous precipitate was subjected to hydrothermal treatment in a nitrogen atmosphere at a constant pressure of 100 atm and for a constant time. This method resulted in the production of tobermorite in 10 days. By simultaneously increasing the temperature systematically, various phases of tobermorite were produced, which finally became converted into xonotlite at 310 °C. The crystalline substances obtained in this manner were studied using solution calorimetry and X-ray methods. As shown in figure 4, a conversion of the X-ray-amorphous substance into the crystalline state is accompanied by a stepwise change in the heat of solution, i.e., each jump corresponds to a new formation, as indicated by the X-ray charts (figure 5). From the fact that no crystalline calcium silicate hydrate can be obtained from a lime solution and sodium silicate, and from the general trend of the hydration of C_3S, one might suspect that hydration of C_3S proceeds topochemically. In further study of the course of hydration, C_3S was hydrated while maintaining a CO_2 pressure of one atm. All of the lime was changed into calcium carbonate in 12 hr. This test leads to the following conclusions:

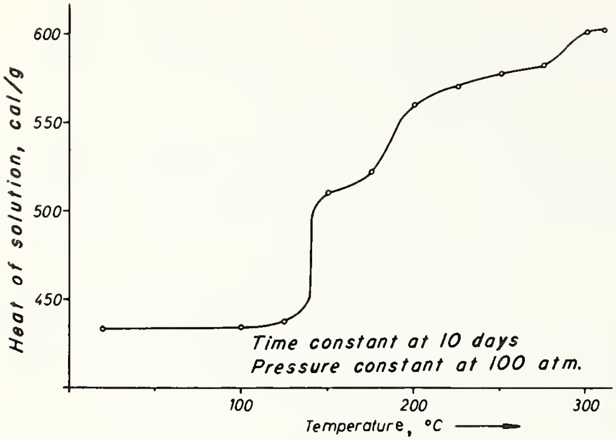

Figure 4. *The heat of solution of* CSH *produced hydrothermally at constant pressure (100 atm) and constant time (10 days) as a function of temperature of treatment.*

Had C_3S hydrated topochemically, carbonation should have lasted longer and calcium silicate hydrate should still have been present after 12 hr. However, as no calcium silicate hydrate was found after this time, the test shows that hydration proceeds by ionic reaction, and, in such manner that calcium ions are appropriated by HCO_3 ions, thus preventing the formation of calcium silicate hydrate by the active calcium and silicic acid ions. One must take into consideration that calcium and silicate ions, directly ionized out of C_3S, remain active only for a very short time, during which calcium silicate hydrate is formed if no foreign ions

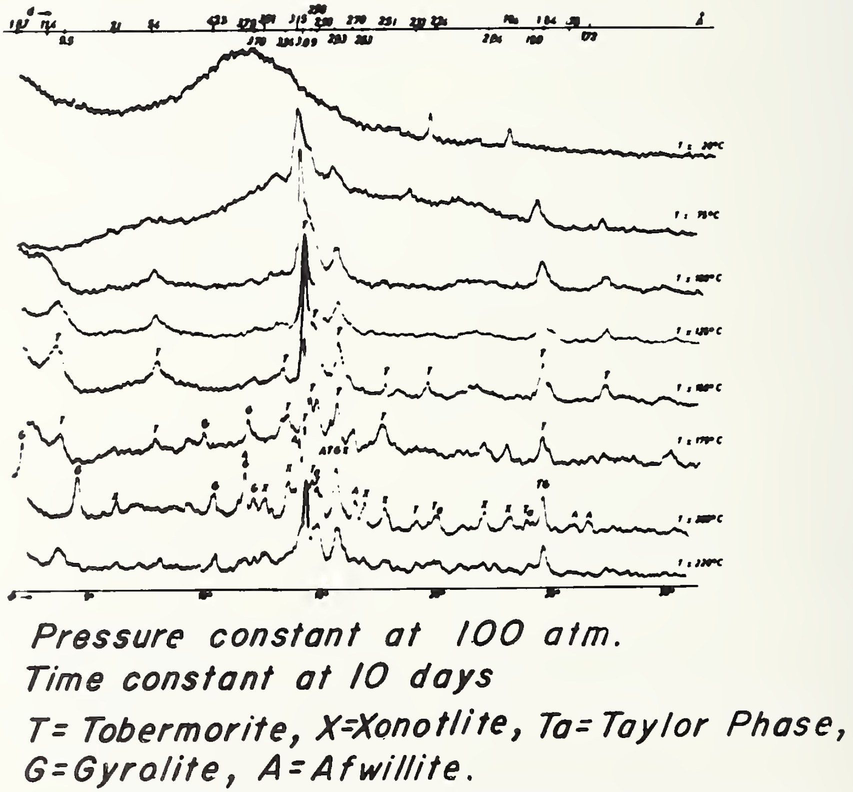

Figure 5. *X-ray charts of calcium silicate hydrates produced hydrothermally at constant pressure (100 atm) and constant time (10 days) as a function of temperature of treatment.*

Bottom scale, angle θ, to 30°. Top scale, *d*-spacing, from 18.7 A to 1.72 A. Top curve, T=20 °C; others, T=75 to 225 °C (bottom curve) by 25° increments.

are present with a greater affinity for calcium ions than the silicate ions.

Also to be noted is the presence of adsorbed water in the calcium silicate hydrate, which causes an endothermic effect on the DDC-curve at 160 °C (dynamic differential calorimeter developed by Schwiete and Ziegler, fig. 6, curve 2).

Curve 1 shows the dehydration curve of moistened $CaCO_3$. This curve indicates that water was not adsorbed in the lattice. This curve was used as a calibration curve in evaluating dehydration results at temperatures of about 100 °C. The water which is driven off at 100 °C is designated as "moisture" water. The double effect at 100 and 160 °C, respectively, is retained when calcium silicate hydrate is dried with acetone and ether prior to test (curve 2). Curve 3 shows the same specimen after 1½ hr of preliminary drying at 75 °C. One recognizes that this drying removed all of the moisture water and part of the adsorptive water. A similar specimen was first completely dehydrated, then wetted, and examined (DDC-curve 4). Curve 5 shows a dehydrated, wetted, dehydrated, and again wetted calcium silicate hydrate. With preliminary drying of calcium silicate hydrate at 110 °C, the adsorptive water appears to be completely driven off; the DDC-curve becomes a straight line.

The above tests indicate that the adsorptive water removed at 160 °C is only loosely bound. The binding forces of the crystal-adsorptive water are greater than the binding forces between adsorptive water and moisture water. It is further revealed that adsorption of water takes place slowly and is endothermic, in contrast to clay minerals. Repeated dehydration renders the surface of calcium silicate hydrates inactive, i.e., it no longer adsorbs water. The heat of adsorption amounted to 4.31 kcal/mole H_2O. After a single dehydration and a single wetting it amounted to 1.39 kcal/mole H_2O.

These dehydration phenomena were observed with hydrothermally produced calcium silicate hydrates as well as with C_3S specimens hydrated in water. In contradiction to this observation is Taylor's [7] experience that this effect occurs only in hydrothermally produced calcium silicate hydrates. One can conclude that the properties of calcium silicate hydrates are dependent on the method used in their preparation.

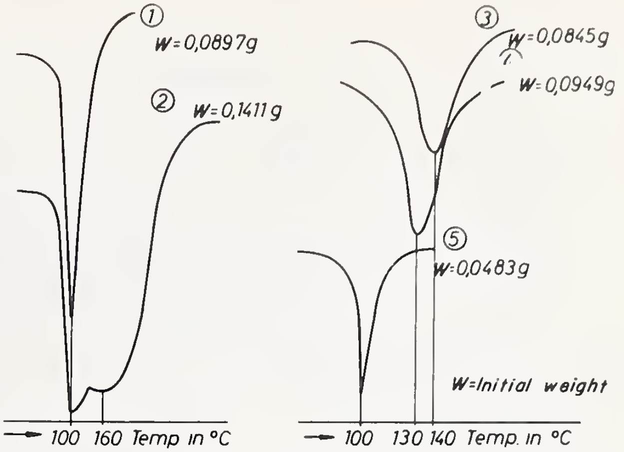

FIGURE 6. *Dynamic-differential-calorimeter curve of water loss in calcium silicate hydrate.*

Preparation of Calcium Silicate Hydrates Through Hydration of C_3S or β-C_2S

In preparing calcium silicate hydrates excess water was used in order to accelerate the reaction. The water-silicate ratio was 50:1. The preparation was energetically shaken during the reaction. Care was taken that no carbonation could take place. To measure the progress of the reaction the hydrated products were analyzed and the liberated $Ca(OH)_2$ determined. In addition, the calcium hydroxide was removed from the solution at constant time intervals to permit completion of the reaction. This removal was necessary because hydration of C_3S with a definite water-silicate ratio results in an equilibrium becoming established after a certain time. Thus, Verbeck and Foster [8] could observe no further rise in the heat of hydration after 1 or 6½ yr.

It was the purpose of these investigations to determine the heat of hydration of C_3S. This determination was to be carried out during progressive hydration, i.e., the liberation of $Ca(OH)_2$ was to progress until a calcium silicate hydrate with lowest CaO/SiO_2 mole ratio was obtained, and finally decomposed into its original components $Ca(OH)_2$ and silica. In this way the heat of hydration of C_3S or β-C_2S was to be determined as a function of the CaO/SiO_2 mole ratio of the calcium silicate hydrates.

Heat of Hydration of Clinker Minerals

The heat of hydration was determined from the results of solution calorimetry. When the heat of hydration is plotted as ordinate and the degree of hydration (course-of-reaction factor) as abscissa, i.e., the CaO/SiO_2 mole ratio, the curve shows a maximum (fig. 7).

The maximum occurs for calcium silicate hydrates at a CaO/SiO_2 mole ratio of 1.6. The heat of hydration amounts to 120 cal/g. If hydration continues, the heat of hydration becomes lower and ends in a decomposition of the components into $Ca(OH)_2$ and silica. The heat of decomposition was established here as 62 cal/g. The maximum indicates that calcium silicate hydrate is most stable, in other words, that free enthalpy is highest, when the entropy of the solid substances is about the same. To confirm this discovery $Ca(OH)_2$ and a silicic acid solution were mixed. The CaO/SiO_2 mole ratio was varied. It was observed that a mix-

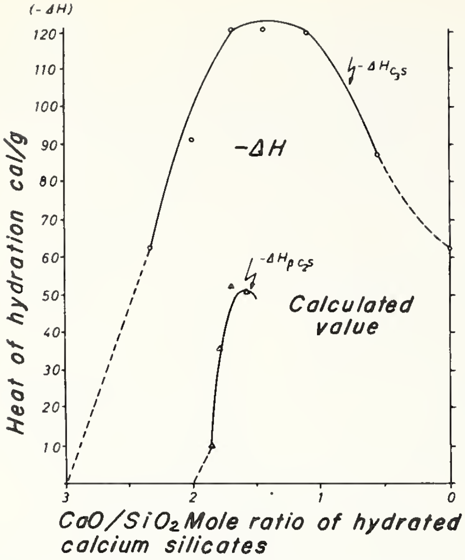

FIGURE 7. *Heat of hydration of* C_3S *and* β–C_2S, *respectively, as a function of* CaO/SiO$_2$ *mole ratio of the precipitate (with removal of* Ca(OH)$_2$ *during the reaction, and employment of a water-silicate ratio of 50:1).*

ture with a CaO/SiO$_2$ mole ratio less than 1.6 forms no calcium carbonate after 2-yr in free air and at room temperature. Above 1.6 the residual calcium was converted by the CO$_2$ of the air into calcium carbonate. Similar observations were reported by Steinour [9]. This test leads to the conclusion that C_3S cannot hydrate to calcium silicate hydrate when the CaO/SiO$_2$ mole ratio is below 1.6. In the hydration of β-C_2S this limiting value was reached at a CaO/SiO$_2$ mole ratio of 1.7. The heat of hydration amounts to 52.7 cal/g.

Our values of the heats of solution agree with those of Verbeck and Foster [8]. No comparison can be made with corresponding test results obtained by Brunauer [10], as he did not hydrate his clinker minerals completely.

The heat of hydration of C_3S with establishment of a CaO/SiO$_2$ mole ratio of 0.81 amounts to 69.9 cal/g of C_3S for hydrothermally synthesized calcium silicate hydrate, and 115 cal/g of C_3S for normally hydrated C_3S. The corresponding values for β-C_2S are 22.7 cal/g of C_2S. This difference in the values for normally hydrated and hydrothermally produced calcium silicate hydrate is inherent in the greater calcium-ion adsorption in the interlayers of calcium silicate hydrate produced by hydrothermal treatment.

The different heats of hydration of C_3S or β-C_2S show that the magnitude of the heat of hydration depends not only on the degree of hydration, but also on the CaO/SiO$_2$ mole ratio of the calcium silicate hydrate formed. The results of measurements are also dependent on the hydration method used.

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