

The System Lime-Alumina-Water at 1°C

Elmer T. Carlson

A study was made of phase equilibria in the system $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ at 1° C. The stable phases are believed to be gibbsite, tetracalcium aluminate hydrate, and $\text{Ca}(\text{OH})_2$, but no solubility curve was established for gibbsite because of extreme slowness of reaction. The compound $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ appears to be metastable, being very slowly transformed to one or the other of the hexagonal hydrates. Metastable equilibrium curves were established for $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ and $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$. The concentration at their intersection (a metastable invariant point) is about 0.10 g of Al_2O_3 and 0.38 g of CaO per liter. The dicalcium compound can readily be dried to a $6\text{H}_2\text{O}$ stage, giving a characteristic X-ray pattern. During the long storage period required to approach equilibrium, most of the reaction mixtures picked up a little CO_2 , apparently by absorption through the polyethylene containers, with formation of a carboaluminate, probably $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$.

1. Introduction

The system lime-alumina-water, largely because of its relation to the setting and hardening of hydraulic cements, is a field in which there has been a great deal of research over a period of many years. The literature on the subject has been thoroughly reviewed by Steinour (1951) [1],¹ by Bogue (1955) [2], and by Lea (1956) [3]. Extensive studies of phase equilibria in the system at room temperature have been reported by Bessey (25° C) [4], by Wells, Clarke, and McMurdie (21° C) [5], and by D'Ans and Eick (20° C) [6]. Equilibrium studies at temperatures from 50° to 250° C have been reported by Peppler and Wells [7] and at 100° to 1,000° C by Majumdar and Roy [8].

The phase diagrams given in the reports of the three investigations at room temperature are in fair agreement, in general; but all three are admittedly incomplete or uncertain in some respects, and on a few points there is direct conflict of opinion. Among the questions left unsettled are the following: (1) The existence of a hexagonal tricalcium aluminate hydrate, usually formulated $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O}$. By many authorities such a compound is considered "well-established", and D'Ans and Eick [6] agreed with this view, though they did not attempt to show an equilibrium curve for it in their phase diagram. On the other hand, Wells, Clarke, and McMurdie [5] concluded that the supposed compound was actually a mixture of the dicalcium and tetracalcium aluminate hydrates. (2) The existence of more than one form of tetracalcium aluminate hydrate. This idea was first put forth by Assarsson [9], who concluded, on the basis of slight differences in index of refraction and X-ray pattern, that two very similar forms, which he termed α and β , existed at room temperature. D'Ans and Eick show widely different metastability areas for the two forms in their phase diagram, whereas Wells, Clarke, and McMurdie report only one form. (3) The area of stability, or metastability, of monocalcium aluminate hydrate. Although Assarsson [9] reported the formation of such a compound many years ago, its existence has been confirmed only recently, and none of the published phase diagrams shows any stability area for it.

The present study was undertaken in the hope of shedding some further light on the above questions, among others. The temperature, 1° C, was selected because Assarsson [9] had indicated that the formation of the monocalcium aluminate hydrate was favored by low temperature. Insofar as the information gained may be related to the practical problems of hydraulic cements, there is the further consideration that temperatures near the freezing point occasionally are encountered during the placing and hardening of such materials.

2. Experimental Work

2.1. Procedures and Materials

An ordinary household refrigerator, equipped with a special control device and a blower, served as a cold cabinet for storage of the reaction mixtures. The temperature was kept at $1^\circ \pm 1^\circ \text{C}$, the relatively wide range being chiefly due to variations from point to point within the chamber rather than to the cycling interval. This range of temperature was acceptable because the solubilities change very little with temperature.

The primary starting materials were reagent-grade calcium carbonate, crystalline hydrated alumina (gibbsite), and distilled water. For most of the experiments the water was freshly boiled to expel carbon dioxide. Secondary starting materials, namely, calcium aluminates, were prepared by heating mixtures of calcium carbonate and gibbsite in the desired proportions. For the greater part of the subsequent work, a monocalcium aluminate preparation was desired that would yield a calcium aluminate solution of high concentration. This was obtained by heating the mix at 1,300° C. since preliminary experiments showed that the use of higher temperature, to effect complete combination, resulted in a comparatively unreactive product. In the preparation of calcium hydroxide solutions, calcium carbonate was converted to the oxide, slaked, shaken with water, and the mixture allowed to stand until it had settled clear.

When pulverized monocalcium aluminate is shaken with water it dissolves in amounts up to 2 g per liter or more, forming a solution slightly richer in lime than

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

the parent solid, because of hydrolysis [10]. The solution thus formed is highly supersaturated with respect to certain hydrated compounds, but the initial rate of precipitation is slow, so that if the mixture is filtered after being shaken 30 to 60 minutes, the resulting filtrate will remain clear for several minutes or even hours. The same result can be attained somewhat more conveniently by substituting an aluminous cement for the monocalcium aluminate. In the present study, however, the idea of using aluminous cement was abandoned when it was found that the cement at hand produced solutions containing an appreciable amount of sulfur as sulfide.

Supersaturated calcium aluminate solutions were prepared as described above, cooled in the refrigerator, and then mixed with varying proportions of previously cooled calcium hydroxide solution in 1-liter polyethylene bottles. These were stored in the cold-cabinet, shaken at intervals, and examined from time to time.

By similar methods the various hydrated calcium aluminates were prepared, filtered off, and used in subsequent experiments on solubility in water and in various concentrations of calcium hydroxide. Thus equilibrium was approached on the one hand from supersaturation, and on the other, from undersaturation. Additional solubility experiments were performed with $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ and $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$. These compounds were prepared hydrothermally, the first by heating a mixture of $\text{Ca}(\text{OH})_2$ and gibbsite at 200° in the presence of water, the second similarly from $\text{Ca}(\text{OH})_2$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3$ at 250° .

Two methods of sampling the solutions for analysis were employed. If the solution was clear, the sample was taken directly with a pipet, usually 50-ml. If any turbidity was noted, the liquid was first filtered with the aid of a suction flask and a fritted glass crucible, fitted with a stopper and a tube that extended into the reaction vessel. Contamination with carbon dioxide thus was held to a minimum. (Filtration of lime solutions through fritted glass introduces a small error, apparently because of adsorption of lime on the glass. This error was disregarded, as in no case did it appreciably affect the position of the equilibrium curves.)

Aluminum and calcium oxides were determined by conventional methods. Because of the low concentrations, especially in the case of Al_2O_3 , the errors were relatively high in the analyses of 50-ml samples; however, the final analysis in each case was done on a sample of 100 to 400 ml.

When portions of the solid were filtered off for analysis or examination they were not washed with water. Dissolution of the precipitate was thus avoided, and the minute amount of dissolved matter adhering to the precipitate was considered negligible. Usually the precipitates were dried in a desiccator containing calcium chloride and a CO_2 absorbent. More rapid drying, when desired, was accomplished by washing with alcohol and ether.

Precise determination of the optical properties of the hydrated calcium aluminate usually is difficult because of the minute size of the crystals, especially

in the case of the plate-form phases. The crystals formed at 1°C were much smaller than those obtained under similar conditions at 25°C , so that identification by microscopic means often was impossible. X-ray diffraction, however, proved to be a very useful method for identification, even when several phases were present. The apparatus used was a Geiger-counter diffractometer, with copper $\text{K}\alpha$ radiation. The platy phases ordinarily were strongly oriented, and gave very strong reflections at the lower angles. With certain precipitates containing $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ it was found essential to obtain the X-ray pattern while the material was still damp, as important phase changes occurred on drying.

2.2. Solid Phases in the System $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$

a. Hydrated Alumina

Various investigators [5, 6, 7, 10] have found gibbsite, $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, to be the stable form of hydrated alumina in this system at temperatures from 20° to 150°C . In the present study its stability at 1°C is assumed rather than proved. Actually, as suggested by D'Ans and Eick [6], the true stable phase may be anhydrous Al_2O_3 rather than gibbsite, but if so, the transformation does not occur even in geologic time. In the present study, gibbsite was identified in the precipitates from certain reaction mixtures, for example, No. 1 in table 3. In other cases, hydrated alumina in some form was believed present, even though the X-ray patterns gave no evidence of it. Occasionally, after filtration of a mixture, the filtrate would contain a little very fine suspended material, not readily soluble in dilute HCl. This was assumed to be alumina since all the other expected solid phases are readily soluble in acid. Again, the examination of one exceedingly finely divided precipitate (No. 1, table 2) under the electron microscope revealed aggregates of fibers believed to be alumina gel.

b. Calcium Hydroxide

This is a stable phase in the system at room temperature [5]. The solubility of coarsely crystalline $\text{Ca}(\text{OH})_2$ in pure water was reported by Bassett [11] to be 0.130 g of CaO per 100-g solution at 0°C , and 0.128 at 5° . He also reported values of 0.143 and 0.151 for finely crystalline $\text{Ca}(\text{OH})_2$ at 0°C . The marked effect of particle size on the solubility of $\text{Ca}(\text{OH})_2$ at somewhat higher temperatures has been critically studied by Hedin [12]. In the present study no attempt was made to fix the solubility precisely, since the particle size was not subject to control. The value 1.30 g of CaO per liter at 1° has been accepted on the basis of Bassett's data.

c. $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$

The isometric crystalline compound of composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ has been shown to be a stable phase in the system $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ at temperatures from 20° to 200°C [4, 5, 6, 7, 8]. As will be brought out later, it probably is not a stable phase at 1°C .

d. $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$

Hydrated monocalcium aluminate was described, and its composition discussed, in an earlier paper [13]. It exists as a metastable phase in the system at 1° . It was obtained as crystals ranging from about 25μ down to submicroscopic size in different preparations. The larger crystals were well-developed hexagonal prisms with flattened terminal pyramids.

e. $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$

Dicalcium aluminate hydrate, crystallizing in hexagonal plates, is a well-established metastable phase in the system at room temperature, and, with decreasing stability, even as high as 90°C [4, 5, 6, 7]. Whether the crystals really are hexagonal or of lower symmetry is not definitely known [1]. Despite this uncertainty, the phase is generally referred to as hexagonal, and this usage will be followed herein. McMurdie [5] indexed the X-ray lines on the basis of hexagonal symmetry, and his indices of 001 and 002 for the first two reflections will be adopted in the following discussion. Although the formula commonly adopted shows 8 molecules of water, the water of hydration is known to vary somewhat with the degree of drying. According to Salmoni [14] the fully hydrated compound may contain 11 molecules of water, but this can be reduced to 7 by drying the compound over CaCl_2 , and to 5 by heating at 100° , without essential change in the crystal structure. Further drying is said to alter the structure irreversibly.

Although the dehydration of dicalcium aluminate hydrate was not systematically investigated in the present work, certain data were obtained that appear to necessitate a slight modification of the picture presented above. Drying of the precipitate from the moist condition to the octahydrate stage (over a saturated solution of NH_4Cl) resulted in only a very minor change in crystal-cell size. Thus the largest d -spacing (001) dropped from 10.9 or 10.8 Å down to 10.6. The same effect has been noted by others [5]. There was evidence that this continues on further drying, down to $d_{001}=10.4$ Å (approximately), but beyond that point an abrupt change was observed. A specimen dried to constant weight over CaCl_2 , and having an approximate composition $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$, gave an X-ray pattern indicating spacings distinctly different from those of the octahydrate. The largest spacing was 8.8 Å. The only change in appearance under the microscope was a slight increase in refractive indices. Numerous preparations showed both hydrates coexisting in varying proportions.

An X-ray pattern of the lower hydrate is given in table 1, along with one of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$. The octahydrate pattern is included merely for comparison; the relative intensities given indicate a high degree of orientation of the mounted sample. No doubt this factor likewise affected the relative intensities in the second pattern, though to a smaller extent. Certain similarities between the two patterns are evident. On the basis of McMurdie's

indexing, the pattern of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ [5], together with the fact that the crystals do not lose their platy habit on dehydration to the $6\text{H}_2\text{O}$ stage, it appears likely that the lattice remains essentially unchanged except for shortening along the c -axis. This suggests that the water thus removed may have been present in loosely bound layers within the structure. The change from 8 to $6\text{H}_2\text{O}$ is completely reversible and occurs rather rapidly. Thus certain samples actually went from the higher to the lower hydrate while on the X-ray diffractometer, during a period of less than 1 hour.

The amount of water in the lower hydrate is known only approximately. The material used for the X-ray pattern (table 1) had the composition $2.10\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6.14\text{H}_2\text{O}$. Another preparation had the composition $1.95\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 5.22\text{H}_2\text{O}$, but this was shown to contain a small percentage of the cubic $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ (which would also necessitate the presence of some form of Al_2O_3); the latter figure is therefore less reliable. The value, $6\text{H}_2\text{O}$, appears most probable from the data at hand.

TABLE 1. X-ray diffraction lines of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ and $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$

$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$		$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$	
Spacing	Relative intensity	Spacing	Relative intensity
λ		λ	
10.6	100	8.8	100
5.27	80	4.80	13
3.49	20	4.36	65
2.88	14	3.80	5
2.67	4	3.60	2
2.62	7	2.86	22
2.53	5	2.72	11
2.49	7	2.57	8
2.44	5	2.47	12
2.39	3	2.39	8
2.22	3	2.32	8
2.12	2	2.29	3
2.03	2	2.23	9
1.954	2	2.14	2
1.935	3	2.04	11
1.740	2	1.802	4
1.662	7	1.742	4
1.528	2	1.653	8
1.440	3	1.623	7
1.424	1	1.441	3
		1.352	4
		1.292	4
		1.289	3
		1.260	2

f. $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$

Tetracalcium aluminate hydrate crystallizes in hexagonal plates, almost indistinguishable under the microscope from those of dicalcium aluminate hydrate. Like the latter compound its existence is well established, as a result of numerous investigations [1, 4, 5, 6, 9]. The comments given above concerning the symmetry of the dicalcium aluminate hydrate apply equally to the tetracalcium. Just as with the dicalcium compound the amount of water of crystallization is in some doubt. Most of the compositions reported in the literature range from 12 to $14\text{H}_2\text{O}$ [5]. The formula with $13\text{H}_2\text{O}$ has been generally adopted, but certain work of the

Building Research Station in England as reported by Lea [3] indicates that the fully hydrated compound may contain $19\text{H}_2\text{O}$. Some investigators, led by Assarsson [9], believe there are two forms, designated α and β , with the same degree of hydration but slightly different degrees of stability in the system; also perhaps a third form with one less molecule of water.

In the present study only one form of tetracalcium aluminate hydrate was produced, judging from the X-ray diffraction patterns. (Certain apparently contradictory evidence will be discussed below.) No special study was made of the amount of water of hydration. A slight shift in the X-ray diffraction lines with increased drying was noted.

g. $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$

This compound obviously falls outside the system $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$; nevertheless, it may appropriately be considered here. During the study of X-ray diffraction patterns of numerous preparations in the high-lime region of the system, a series of lines was frequently noted very close to those of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$. The maximum spacing averaged about 7.7 Å, as compared with 8.2 for the tetracalcium compound. At first the new phase was tentatively considered to be the β -form of this compound, but when it later appeared in the low-lime region of the system as well, another explanation was sought. To ascertain whether it might be a carboaluminate such as that reported by Bessey [4], an attempt was made to prepare such a compound. From a mixture of calcium aluminate, calcium hydroxide, and ammonium carbonate solutions a precipitate was obtained, consisting of minute platy crystals having indices and birefringence somewhat higher than those of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$. The X-ray pattern agreed perfectly with the series of lines in question. Although the amount of material was insufficient for a precise analysis, the composition was reasonably close to the formula $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 11\text{H}_2\text{O}$ suggested by Bessey. Further confirmation was deemed unnecessary, because just at that time a publication by Turriziani and Schippa [15] appeared describing the preparation of a carboaluminate of composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot \text{CaCO}_3\cdot 10.8\text{H}_2\text{O}$ and reporting an X-ray pattern in good agreement with those under consideration.

In only one of the preparations (No. 13, table 2) were the carboaluminate crystals of sufficient size to permit a determination of their indices of refraction, and even in this it was difficult because of the masking effect of the other phases. The high and low indices were 1.554 and 1.527, respectively.

The question as to the source of the CO_2 naturally arises. Although there was undoubtedly a little entry of atmospheric CO_2 when the bottles were opened for removal of samples, it seems likely that a more important factor was the passage of CO_2 through the walls of the polyethylene bottles. Polyethylene is known to be somewhat permeable to CO_2 [16], although the effect apparently was rather slow under the conditions of the present study. In

most cases the amount was barely enough to be shown by the X-ray patterns. In a few it was much higher, possibly indicating that the bottle cap did not form a perfect seal.

h. Other Aluminates

Certain other hydrated calcium aluminates that have been reported by various investigators may also be mentioned. No evidence of a hexagonal tricalcium aluminate hydrate was found in this study. Compositions having approximately this ratio invariably gave X-ray patterns indicating mixtures of di- and tetracalcium aluminate hydrates. This negative evidence supports the view of Wells, Clarke, and McMurdie [5] that the alleged tricalcium compound does not occur.

Another tricalcium aluminate hydrate, in acicular form, and assigned the formula $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 18$ to $21\text{H}_2\text{O}$, has been reported by several investigators [2]. It was not found in the present study. However, the author has previously prepared a compound of this general description and approximate composition. It was found only in aqueous extracts of an aluminous cement, and then only as a transitory phase. The solutions contained a trace of sulfide, which may or may not be significant.

The more basic aluminates that have been reported were not considered in this study, since they probably do not possess a field even of metastability in the system. There remains the compound $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, which is formed under hydrothermal conditions but is unstable below 200°C . Although it has no place in the system at 1°C , a pair of experiments were conducted to study the course of its reactions.

2.3. Precipitation Experiments

A series of 10 supersaturated calcium aluminate solutions were prepared as described above, by diluting a master solution with various amounts of saturated lime water. They were then stored in the cold-cabinet. These are designated by numbers 1 to 10 in table 2. From time to time, samples of the solutions were taken for analysis, and small portions of the precipitates for examination. Data obtained at intermediate periods have been omitted from the table, except when needed to show the course of the reaction. The figures given for initial concentrations (columns 2 and 3) were calculated from the measured volumes of the analyzed master solutions. Concentrations at later periods (columns 5 and 6) were obtained by analysis, and the composition of the precipitate (column 7) was calculated from the difference. In the last column, the solid phase present in greatest amount is given first.

The change in concentration during precipitation may be visualized better by reference to figure 1, in which the concentration data for solutions 1 to 10, table 2, are plotted on rectangular coordinates. Initial concentrations are represented by the row of circles at the right. The lines extending downward to the left represent the changing concentrations.

TABLE 2. Data showing changes in concentration and solid phases present during precipitation from calcium aluminate solutions at 1°C

Experiment	Initial concentration		Reaction period	Concentration after reaction period		Molar ratio CaO:Al ₂ O ₃ in precipitate (calculated)	Solid phases present ^a
	Al ₂ O ₃	CaO		Al ₂ O ₃	CaO		
1	1.278	0.833	1 day	1.266	0.828	1.03	CaO·Al ₂ O ₃ ·10H ₂ O; probably a little Al ₂ O ₃ hyd.; trace of 2CaO·Al ₂ O ₃ ·8H ₂ O.
			11 days	0.144	.190	1.06	
			13 mo.	.112	.152	1.06	
2	1.150	.879	1 day	.436	.393	1.24	CaO·Al ₂ O ₃ ·10H ₂ O; trace of 2CaO·Al ₂ O ₃ ·8H ₂ O. Same, plus trace of 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O.
			11 days	.162	.316	1.04	
			75 days	.104	.300	1.01	
3	1.022	.925	1 day	.572	.412	2.07	2CaO·Al ₂ O ₃ ·8H ₂ O; traces of CaO·Al ₂ O ₃ ·10H ₂ O, 4CaO·Al ₂ O ₃ ·13H ₂ O, and 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O. 2CaO·Al ₂ O ₃ ·8H ₂ O; CaO·Al ₂ O ₃ ·10H ₂ O; 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O.
			7 days	.422	.402	1.58	
			11 days	.332	.330	1.57	
			13 mo.	.112	.388	1.07	
4	0.895	.970	1 day	.480	.499	2.06	2CaO·Al ₂ O ₃ ·8H ₂ O; trace of 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O. 2CaO·Al ₂ O ₃ ·8H ₂ O; CaO·Al ₂ O ₃ ·10H ₂ O; 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O.
			11 days	.314	.329	2.01	
			1 mo.	.316	.333	2.00	
			15 mo.	.120	.394	1.35	
5	.767	1.014	1 day	.230	.412	2.04	2CaO·Al ₂ O ₃ ·8H ₂ O; trace of 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O. Same.
			11 days	.174	.345	2.05	
			9 mo.	.203	.366	2.09	
6	.639	1.058	1 day	.168	.512	2.11	2CaO·Al ₂ O ₃ ·8H ₂ O; 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O. Same.
			11 days	.110	.442	2.12	
			9 mo.	.085	.384	2.21	
7	.511	1.108	1 day	.106	.543	2.54	2CaO·Al ₂ O ₃ ·8H ₂ O; 4CaO·Al ₂ O ₃ ·13H ₂ O. Same.
			11 days	.096	.556	2.42	
			11 mo.	.078	.503	2.54	
8	.383	1.154	1 day	.140	.670	3.62	4CaO·Al ₂ O ₃ ·13H ₂ O; 2CaO·Al ₂ O ₃ ·8H ₂ O. Same, plus 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O.
			11 days	.098	.570	3.73	
			11 mo.	.072	.499	3.83	
9	.256	1.191	1 day	.090	.870	3.52	4CaO·Al ₂ O ₃ ·13H ₂ O; 2CaO·Al ₂ O ₃ ·8H ₂ O. 4CaO·Al ₂ O ₃ ·13H ₂ O; 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O.
			11 days	.026	.726	3.67	
			11 mo.	.016	.695	3.76	
10	.128	1.246	1 day	.046	1.111	2.99	4CaO·Al ₂ O ₃ ·13H ₂ O. Same.
			11 days	.004	1.018	3.34	
			9 mo.	.004	0.963	4.15	
11	1.310	0.970	3 hr.	.570	.908	1.81	2CaO·Al ₂ O ₃ ·8H ₂ O; CaO·Al ₂ O ₃ ·10H ₂ O. Same.
			1 day	.208	.322	1.07	
			7 mo.	.092	.260	1.06	
12	0.916	1.066	3 hr.	.328	.366	2.16	2CaO·Al ₂ O ₃ ·8H ₂ O; trace of 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O. Same.
			2 days	.312	.364	2.12	
			5 mo.	.240	.332	1.97	
			10 mo.	.153	.372	1.65	
13 ^b	.466	0.327	1 mo.	.449	.317	0.27	Gibbsite; CaO·Al ₂ O ₃ ·10H ₂ O; 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O. Same.
			2 mo.	.364	.312	.57	
			6 mo.	.152	.229	.54	
			13 mo.	.100	.209	.54	
14 ^b	.466	.327	1 mo.	.386	.269	1.32	Gibbsite; CaO·Al ₂ O ₃ ·10H ₂ O; 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O.
			3 mo.	.320	.266	0.76	
			14 mo.	.085	.200	.61	
15 ^b	.310	.610	1 mo.	.104	.410	1.77	Gibbsite; few hexagonal plates. Gibbsite; 2CaO·Al ₂ O ₃ ·8H ₂ O; 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O.
			11 mo.	.103	.399	1.85	
16 ^b	.155	.893	1 mo.	.038	.691	3.12	Gibbsite; hexagonal plates. Gibbsite; 4CaO·Al ₂ O ₃ ·13H ₂ O; 3CaO·Al ₂ O ₃ ·CaCO ₃ ·11H ₂ O.
			11 mo.	.022	.629	3.61	

^a As used here, "trace" is equivalent to "barely sufficient to be detected on the X-ray diffraction pattern." ^b Gibbsite added to solution.

The calculated molar ratio of CaO to Al₂O₃ (C/A) in the precipitate in the early stages is indicated in each case.

Solution 1 was essentially unchanged after 1 day, but subsequently a very voluminous precipitate appeared. The X-ray diffraction pattern showed it to be chiefly CaO·Al₂O₃·10H₂O, with a detectable amount of 2CaO·Al₂O₃·8H₂O. Under the electron microscope the predominant phase was observed to consist of slender prismatic crystals, less than 0.1 μ in thickness. A few much larger hexagonal crystals, presumably of 2CaO·Al₂O₃·8H₂O, were noted. There

were also a few masses of felted fibers, finer than the prismatic crystals. It could not be determined whether these were of the same composition or whether they were a different phase, possibly amorphous hydrated alumina. Precipitation was essentially complete after 11 days, and no change in appearance was observed after 13 months.

In the other members of the series, precipitation was more rapid, increasingly so as the CaO/Al₂O₃ ratio increased. No. 2 yielded a precipitate consisting largely of CaO·Al₂O₃·10H₂O, appearing as rosettes of prismatic crystals much coarser than those

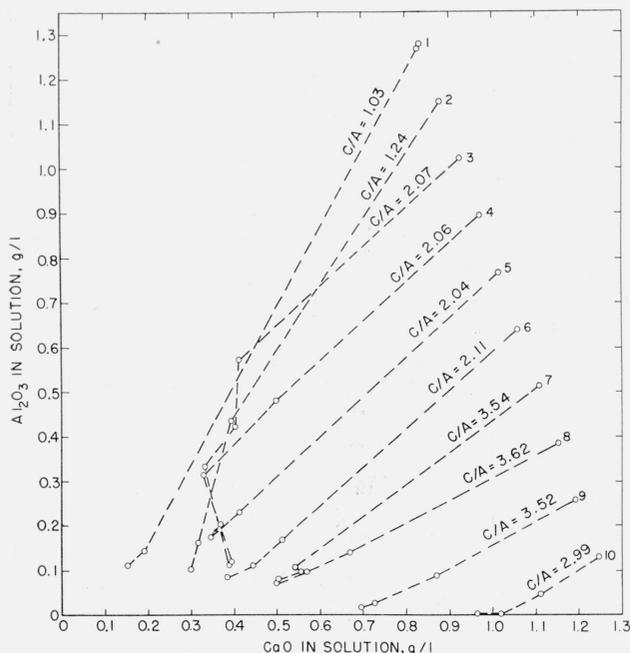


FIGURE 1. Change in concentration of calcium aluminate solutions resulting from precipitation at 1° C.

C/A = molar ratio, CaO/Al₂O₃. Numbers refer to experiments in table 1.

in No. 1. A detectable amount of the dicalcium compound was also present. After 75 days a steady state apparently had been reached, with no change except for the appearance of a detectable amount of the carboaluminate. At that time the precipitate was filtered off for use in further experiments.

The change in slope of the concentration curve for solution 2 suggested that the initial precipitate may have been richer in lime than was indicated by the analysis after 1 day. Another solution of comparable concentration therefore was prepared and examined at shorter intervals. This is designated No. 11 in table 2; it has been omitted from figure 1 to avoid confusion. The initial precipitate was observed to be 2CaO·Al₂O₃·8H₂O, and the ratio of CaO to Al₂O₃ after 3 hr was nearer 2 than 1. However, after 1 day, only CaO·Al₂O₃·10H₂O was observed. Thus the initially formed dicalcium compound must have redissolved, in agreement with the observed change in slope of the concentration curve.

Solutions 3, 4, 5, and 6 all precipitated 2CaO·Al₂O₃·8H₂O as the primary phase. The calculated CaO/Al₂O₃ is consistently slightly higher than 2. Any attempted explanation would be speculative, but it is clear that the inclusion of a small amount of tetracalcium aluminate or carboaluminate would tend to raise the ratio. The precipitate in No. 3 underwent partial conversion to CaO·Al₂O₃·10H₂O within 7 days, as indicated by the change in CaO/Al₂O₃ ratio, later confirmed by X-ray diffraction. The same reaction occurred in No. 4, but in this case it did not start until after 1 month.

Experiment 12, table 2 (omitted from fig. 1) was intermediate between Nos. 4 and 5 in initial CaO/

Al₂O₃ ratio. It behaved like No. 4, except that the appearance of the monocalcium aluminate was still longer delayed. Nos. 5 and 6 showed none of the latter compound even after 9 months.

Solutions 7, 8, and 9 precipitated mixtures of 2CaO·Al₂O₃·8H₂O and 4CaO·Al₂O₃·13H₂O, with very little change after 11 days except for the appearance of small amounts of carboaluminate. The molar CaO/Al₂O₃ ratio in the precipitate was between 2 and 4. The initial ratio in the precipitate from solution 10 was calculated to be 2.99. This is suspected of being in error, as the low-alumina concentration in this region greatly magnifies the effect of small analytical errors. The X-ray patterns of the precipitate showed only 4CaO·Al₂O₃·13H₂O.

To recapitulate: No. 1 precipitated only CaO·Al₂O₃·10H₂O; Nos. 11, 2, 3, 4, and 12 gave 2CaO·Al₂O₃·8H₂O first, which was replaced by CaO·Al₂O₃·10H₂O, more slowly and less completely as the proportion of CaO in solution increased; Nos. 5 and 6 gave only 2CaO·Al₂O₃·8H₂O; Nos. 7, 8, and 9 yielded mixtures of the dicalcium and tetracalcium aluminate hydrates; and No. 10 precipitated only the tetracalcium compound.

Reaction mixtures 13 to 16 constitute a series in which the initial concentration of both Al₂O₃ and CaO was much lower than in the foregoing group. One gram of solid gibbsite was added in each case, in an attempt to induce precipitation of this stable phase instead of the metastable aluminates. As indicated by the results in table 2, this attempt was unsuccessful. Aside from supplying additional data, this group is of interest chiefly in that the crystalline phases formed very slowly, yielding crystals of adequate size for optical study.

2.4. Solution Experiments

It is evident from the foregoing that the approach to equilibrium from supersaturation at 1° C is a very slow process. Attempts were therefore made to approach it from the opposite direction, that is, by determining the solubilities of the various solid phases in different concentrations of calcium hydroxide. In each experiment the solid phase was added in moderate excess to pure water or to lime water of known concentration. The procedures for storage, analysis, and examination were the same as for the precipitation experiments.

a. Hydrates Formed by Precipitation

It will be convenient to consider first, as a group, the three ternary compounds found in the precipitation experiments; namely, CaO·Al₂O₃·10H₂O, 2CaO·Al₂O₃·8H₂O, and 4CaO·Al₂O₃·13H₂O. Data for this group are given in table 3, concerning which a few explanatory notes are in order. Final concentrations were determined by analysis, whereas initial concentrations were calculated. In certain cases the solids were introduced in the form of a suspension in the solution in which they were prepared. This accounts for the fact that not all the experiments started from zero Al₂O₃ concentration.

TABLE 3. Solubilities of $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$, $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$, and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ in calcium hydroxide solutions

Experiment	Solid phases initially present	Initial concentration		Duration of contact	Final concentration		Solid phases present at end of experiment
		Al_2O_3	CaO		Al_2O_3	CaO	
1	$\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$	<i>g/liter</i>	<i>g/liter</i>	<i>Months</i>	<i>g/liter</i>	<i>g/liter</i>	$\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$; calcite, gibbsite. $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$; carboaluminate. $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$; very little carboaluminate.
2		0.000	0.000	12	0.070	0.169	
3		.056	.211	2	.119	.222	
4	$\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O} + 2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$.000	.000	5	.130	.368	$\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$; $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$.
5	$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$.000	.000	5	.161	.339	$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$; carboaluminate.
6		.000	.12	6	.182	.324	
7	$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}^a$.001	.35	4	.081	.419	$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$; $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$. $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$. $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$; $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$.
8		.001	.52	4	.049	.537	
9		.001	.69	4	.024	.630	
10	$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O} + 4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$.005	.514	4	.040	.550	$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$; $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$.
11		.005	.743	4	.014	.693	
12		.005	.922	3	.008	.889	
13		.003	1.143	4	.001	1.098	
14	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}^b$.000	0.000	1	.020	0.314	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$.
15		.000	.000	1	.028	.396	
16		.000	.000	1	.026	.442	
17		.000	.000	1	.024	.489	
18		.000	.000	1	.026	.565	
19		.000	.000	1	.022	.610	
20				<i>Weeks</i>			
21		.000	6	.009	.758		
22		.000	6	.008	.868		
23		.000	6	.001	.971		
		.000	6	.002	1.103		

^a Contained a minor amount of $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$.

^b Contained $\text{Ca}(\text{OH})_2$. In experiments 14 to 19, concentration of $\text{Ca}(\text{OH})_2$ in solution was varied by using increasing amounts of the solid preparation.

Great difficulty was experienced in obtaining single-phase preparations for starting materials. Thus the dicalcium aluminate hydrate used in experiments 7 to 9 contained some monocalcium aluminate hydrate. This phase persisted in No. 7 but dissolved in the two more basic solutions. Tetracalcium aluminate hydrate usually was obtained as a mixture with the dicalcium compound. (Such a mixture was used in experiments 10 to 13.) In order to avoid the less basic aluminate it was found necessary to have free calcium hydroxide present. The latter contaminant dissolved completely during the solution experiments, and in experiments 14 to 19 the equilibrium concentration of $\text{Ca}(\text{OH})_2$ was varied merely by varying the amount of solid originally used.

In this group of experiments a steady state was attained in a week or two, no doubt because of the extreme fineness of the crystals. The final concentrations given in table 3 are represented in figure 2 by filled circles, and the tentative solubility curves

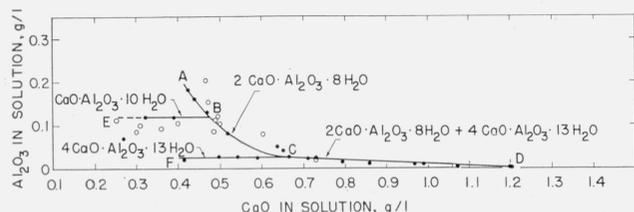


FIGURE 2. Solubilities of $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$, $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$, and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ in calcium hydroxide solutions at 1°C .

Curves are based on data from table 3 (filled circles). Data from table 2 (open circles) are included for comparison.

are drawn with reference to these points. The open circles represent the final data from the precipitation experiments (table 2), and are included here to facilitate comparison of the two sets of data.

Curve ABC, figure 2, represents approximately the solubility values for $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$. The corresponding concentration values from table 2 lie somewhat above the curve, but not far from it. Curve CD fits equally well the data for solubility of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ or for a mixture of the tetra- and dicalcium compounds, including the values from both table 2 and table 3. The horizontal line FC fits the data for $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ in the region below 0.6 g of CaO per liter. (There is, of course, no counterpart of this in table 2.) Line EB represents roughly the solubility of $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$. Here the values from table 2 (open circles) all fall below the curve, as does the value for experiment 1 in table 3.

There should be an invariant point (metastable) at the intersection (B) of the curves for the mono- and dicalcium aluminate hydrates. The precipitates obtained in experiments 4 and 7 in table 3, and 3 and 4 in table 2, ended essentially as mixtures of $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ and $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$. Three of these had compositions very close to B, probably within the limits of accuracy of the procedures, but the fourth was appreciably removed. This may reasonably be attributed to lack of attainment of equilibrium.

Point C does not represent an invariant point. The compound $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ appears to be in equilibrium all along the line FCD. The fact that $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ coexists, seemingly indefinitely, with $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ between C and D (and in

fact, beyond D to the limit of $\text{Ca}(\text{OH})_2$ solubility), points to extreme slowness of attainment of equilibrium in the area. If this view is correct, there should be two solubility curves between C and D, one for each hydrate, but they must be practically coincident.

b. $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$

From earlier investigations [5, 6, 7] it is known that the isometric $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ exists as a stable phase in the system $\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{H}_2\text{O}$ from 20° to about 200° C. The experiments summarized in table 4 comprise a series in which the solubility of this compound in water and in calcium hydroxide at 1° C was sought. The results were highly erratic. The most interesting fact, however, is that the original solid phase was largely replaced by $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ in experiments 3 and 4 and partially by $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ in Nos. 7, 9, and 11. Inasmuch as these hexagonal phases were known to be absent from the original solid, it must be concluded that $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ is not stable in these areas. The final concentrations here fall close to the solubility curves for the respective hexagonal phases.

The final concentration data in table 4 are plotted in figure 3, superimposed upon the solubility curves of the hexagonal aluminates, borrowed from figure 2. It is evident that the plotted points, taken as a single group, cannot be connected by any reasonable curve. The experiments may, however, be separated into two groups: (a) those in which the residue was partially transformed to di- and tetracalcium aluminate hydrates, and (b) those in which the $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ remained unchanged (except for minor formation of carboaluminate). Group (a) is represented in figure 3 by filled circles, which fall not far from curve ABCD, the solubility curve of the di- and tetracalcium aluminates. Group (b) is represented by open circles, which appear to be scattered at random appreciably below curve ABCD.

It is concluded that $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ is less stable than $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ at 1° C, but that it goes into solution extremely slowly. For some unexplained reason, certain experiments in group (b) failed to reach equilibrium concentrations even after as long as 16 months of storage. Others

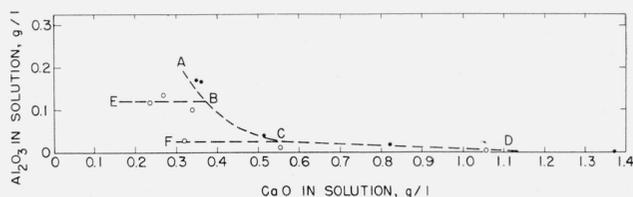


FIGURE 3. Solubility of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ in calcium hydroxide solutions at 1° C.

Open circles represent mixtures in which the solid phase was essentially unchanged; closed circles those in which phase transformations had occurred. Solubility curves, taken from figure 2, are included as a frame of reference.

in group (a) reached concentrations relatively quickly (within 1 month for experiments 3 and 4), at which time they were supersaturated with respect to the hexagonal phases, whereupon the latter precipitated out. Even here the reaction had not gone to completion after prolonged storage. It is conceivable that the small amount of carboaluminate appearing during the long storage period may have formed a protective film on the crystals.

c. $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$

Although the 4:3:3 ternary compound is stable only above approximately 200° C [7], it was considered of interest to study its behavior at 1° C. In water the compound dissolved slowly, without formation of a precipitate, and after 10 months had reached the surprisingly high concentration of 0.382 g of Al_2O_3 and 0.285 g of CaO per liter. By reference to figure 2 it appears that such a solution must be highly supersaturated with respect to $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$.

The solubility in calcium hydroxide was studied at only one concentration, 0.58 g of CaO per liter. The reaction proceeded slowly, and involved simultaneous dissolution of the 4:3:3 compound and precipitation of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$. The final concentration was 0.092 g of Al_2O_3 and 0.435 g of CaO per liter, which is close to curve BC, figure 2.

d. Gibbsite ($\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$)

An attempt was made to determine the solubility of gibbsite in a series of lime solutions ranging from 0.2 g of CaO per liter up to saturation, but the results were unsatisfactory. After 4 months at 1° C, the Al_2O_3 in solution was barely detectable. In an effort to speed up the process, the mixtures were allowed to

TABLE 4. Solubility of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ in calcium hydroxide solutions

Experiment	Initial concentration, CaO	Duration of contact	Final concentration		Solid phases present at end of experiment
			Al_2O_3	CaO	
	<i>g/liter</i>	<i>Months</i>	<i>g/liter</i>	<i>g/liter</i>	
1.....	0.000	16	0.117	0.235	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$.
2.....	.000	15	.134	.268	Do.
3.....	.000	9	.166	.360	$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$.
4.....	.000	9	.169	.349	Do.
5.....	.128	15	.100	.338	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$.
6.....	.257	16	.028	.319	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$.
7.....	.434	15	.040	.515	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$; very little $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$.
8.....	.535	14	.010	.554	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$.
9.....	.778	14	.018	.822	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 11\text{H}_2\text{O}$; $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$.
10.....	1.039	14	.003	1.055	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$.
11.....	^a 1.476	10	.001	1.371	$\text{Ca}(\text{OH})_2$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; very little $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$.

^a Contained excess $\text{Ca}(\text{OH})_2$ in suspension.

stand 6 months at room temperature, after which they were again stored at 1° for 10 months. In the first solution (0.2 g of CaO per liter), the Al_2O_3 concentration rose from 0.002 to 0.012 g per liter during the storage at room temperature, and failed to change on subsequent storage at 1° C. This figure approximates the solubility in lime solution of the same concentration at 21° C [5] and the true value at 1° would be expected to be lower.

In all the more basic solutions (0.4 g of CaO per liter and higher) there was precipitation of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$, indicating that the gibbsite had dissolved sufficiently to exceed the solubility of this aluminate. Final concentrations fell close to curve FCD, figure 2.

Because of the long time involved, further work on the solubility of gibbsite in lime solutions at 1° C was abandoned. The only conclusions to be drawn from the present data are: (1) That gibbsite appears stable in lime solutions up to 0.2 g of CaO per liter; (2) that the equilibrium concentration of Al_2O_3 at this point is between 0.002 and 0.012 g per liter; and (3) that at some higher lime concentration, the solubility curve of gibbsite intersects that of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$.

2.5. Phase Equilibrium Diagram

From the foregoing data it is possible to construct at least a partial diagram of stable and metastable phase equilibria in the system $\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{H}_2\text{O}$ at 1° C. Such a diagram is presented in figure 4. Certain assumptions and qualifications are necessary.

One assumption is that the carbon dioxide in solution and the carboaluminate precipitated were without effect. While this cannot be strictly true, it is evidently not far from correct. Carbon dioxide in very small concentration is known to react with lime solutions, forming calcite. In the present work the carboaluminate formed in preference to calcite in nearly every case, hence the CO_2 remaining in solution must have been even less. Also, the precipitated carboaluminate probably is the least soluble of the phases present (possibly excepting gibbsite), and it would therefore not alter the equilibrium concentration.

The position of the solubility curve of gibbsite, GF, is merely an estimate. The position of D, the solubility of calcium hydroxide, is based on values in the literature [11]. Curve CD, of course, cannot meet the horizontal axis at D; rather there must be an invariant point nearby, with an Al_2O_3 concentration about 0.001 g per liter. Two curves are assumed to exist between this invariant point and C; the lower one the stable curve for $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$, the upper a metastable curve for $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$.

Curve ABC is essentially a compromise between data obtained respectively from precipitation and from solution experiments. The upper end (near A) takes into account the inflection points of certain lines (3 and 4) in figure 1. Curve EB is somewhat uncertain as to position, as there is considerable scatter among the points on which it is based.

With these qualifications and assumptions in

mind, the diagram may now be summarized. The stable phases are gibbsite, tetracalcium aluminate hydrate, and calcium hydroxide. The position of point F, the invariant between gibbsite and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$, is not known. The invariant between $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$, at D, is estimated to be at 0.001 g of Al_2O_3 and 1.30 g of CaO per liter, and the solubility of $\text{Ca}(\text{OH})_2$ (from the literature [11]) is likewise placed at 1.30 g of CaO per liter. The compound $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ is in metastable equilibrium with solution along curve ABCD, the section CD being practically coincident with the curve for $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$. Nothing is known as to its extent above A. Curve EB represents the equilibrium of $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ and solution; its leftward extent is unknown. The point B is a metastable invariant between $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$, $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$, and solution.

Metastable solutions to the right of AB tend to precipitate $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ until the concentration reaches AB, whereupon $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ is formed, and the concentration shifts toward B (see table 2, experiments 3, 4, 11). Solutions richer in lime (for example, No. 7 in table 2) precipitate both di- and tetracalcium aluminate hydrates until the concentration reaches BC. At this point, presumably, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ continues to precipitate out, but as long as there is any $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ left, the latter will continue to control the concentration of the solution, which thus will still lie on BC. In time the dicalcium compound should be used up, and the concentration fall to curve FC, but this stage was not reached in any of the precipitation experiments described above.

The area under GFCD represents stable solutions. Solutions above GF are supersaturated with respect to gibbsite, but the rate of precipitation is extremely slow. Solutions in the general area ABE can precipitate $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$.

3. Discussion

3.1. Relation to Earlier Data

After reviewing the literature on the system $\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{H}_2\text{O}$, one is impressed by the wide variance, not so much in the actual data as in the interpretation of the data. Some of the results obtained in the present study may help to explain some of the contradictory conclusions.

Several investigators of the calcium aluminates have stressed the necessity for rigid exclusion of carbon dioxide; yet it is probable that complete absence of CO_2 has seldom, if ever, been attained. Even freshly boiled distilled water retains some CO_2 , and the rubber stoppers commonly used for closures of the reaction flasks are by no means impermeable to atmospheric CO_2 . Formation of calcite has, in fact, been reported in some cases [10]. This phase, if present, is conspicuous under the microscope by reason of its high birefringence and distinctive crystal shape. It is only natural that the absence of calcite might lead the investigator to assume the absence of CO_2 from his reaction vessel. On the

other hand, if any of the carboaluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$, were present, it might readily be mistaken for $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$. This might help to explain the discrepancies in reported refractive indices (as has been suggested by Bessey [4]), as well as the presumed multiplicity of forms of tetracalcium aluminate hydrate. By reference to tables 2 and 3 it may be noted that the carboaluminate was present in mixtures including almost the entire range of lime concentration. It may be significant that D'Ans and Eick [6] showed a similar range for the solubility of their β -tetracalcium aluminate hydrate, whereas the α -form was confined to the more basic region approximating that indicated by Wells, Clarke, and McMurdie [5] for the tetracalcium compound.

Another possible source of confusion is the apparent instability of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ on drying. As was brought out above, this compound by itself underwent a dehydration to $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$, on drying over CaCl_2 , and the product gave an X-ray diffraction pattern that might conceivably have been mistaken for that of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$. This reaction was reversible. A different phenomenon was observed with precipitates consisting of mixtures of di- and tetracalcium aluminate hydrates. After drying over CaCl_2 , such precipitates often gave patterns showing the lines of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ only. Presumably the dicalcium compound had undergone decomposition to the tetracalcium compound and alumina.² This effect was not reversible. For precipitates of this type it was found necessary to obtain the X-ray pattern while the material was moist. Obviously this change on drying could lead to a false conclusion as to the solid phases present in contact with the solution.

3.2. Relation to the System at 21° C

If the equilibrium diagram (fig. 4) is studied in comparison with the diagram published by Wells, Clarke, and McMurdie [5] for the same system at 21° C, certain marked differences are noted, as well as some similarities. Curve ABCD in figure 4 has its counterpart in the 21° C diagram, and the same area of confusion between di- and tetracalcium aluminates exists in the approximate range CD. However, the 21° C diagram does not show a stable solubility curve for $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ comparable to FC. It should be noted in this connection that D'Ans and Eick [6] show a metastable solubility curve for the β form of this hydrate in the general area of FC. The absence from the 1° diagram of a stability field for the isometric $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ is also a difference of major importance. The existence of a metastable solubility curve for monocalcium aluminate hydrate at 1°, of course, was not unexpected. The other differences between the diagrams for 1° and 21° are more

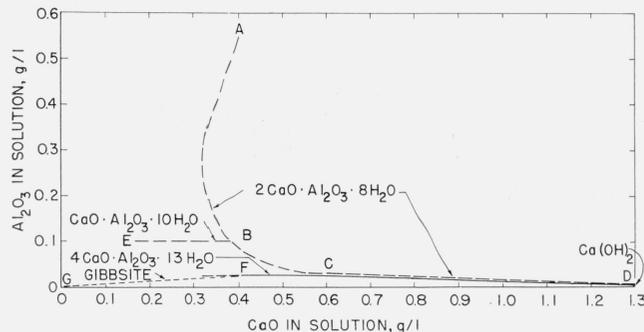


FIGURE 4. Portion of the system $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ at 1° C.

ABCD, metastable equilibrium curve for $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$; EB, metastable solubility curve for $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$; GF, (assumed) stable equilibrium curve for gibbsite; FCD, stable equilibrium curve for $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$.

surprising, and it appears that further studies at one or more intermediate temperatures may be needed to define all the stability and metastability areas.

3.3. Application to Cement Hydration

The system $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ is not directly applicable to portland cement, which is predominantly a calcium silicate cement, with enough calcium sulfate added to combine with most of the alumina in the early stages. On the other hand, it has been shown [10] that the hydration of aluminous cements, at least to a first approximation, can be explained in terms of reactions in the system $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$. Aluminous cements are known to react with water to form highly supersaturated calcium aluminate solutions slightly more basic than monocalcium aluminate. The crystalline phase that precipitates first may be $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ or $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$, or a mixture of these, depending on temperature, basicity, and probably other factors. From the data in table 2 it may be concluded that, at 1° C, $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ either would precipitate first or would form rapidly after an initial precipitation of the dicalcium compound. Earlier work [10] indicates that, at room temperature, $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ forms initially and persists for long periods. However, it is clear from other data in the same report that the reactions of cement in paste form are not necessarily identical with those in the presence of a large excess of water. Thus $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$, rather than $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$, was shown by X-ray diffraction to be the predominant phase in pastes of aluminous cements after hydration at room temperature (24° C). From the data in the present report, coupled with that given in an earlier paper [13], it is concluded that monocalcium aluminate hydrate is also the chief crystalline product of hydration of aluminous cements at 1° C.

In connection with the hydration of cements, the carboaluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$, should also be mentioned. From tables 2 and 3 it is apparent that this phase was encountered throughout the range of lime concentrations studied, despite efforts to exclude CO_2 . Most other investigators likewise

² While this paper was in process of publication, two other papers bearing in part on this phenomenon appeared in the literature. The authors, Roberts [18] and Schippa and Turriziani [19], report similar observations, but offer a different explanation. According to their views, the X-ray lines here attributed to dicalcium aluminate hydrate may actually represent a different form of tetracalcium aluminate hydrate (with 19 H_2O , according to Roberts).

have sought to eliminate the extra component. In practice, however, cement is always mixed and placed in the presence of atmospheric CO_2 , hence the carboaluminate may form freely. Evidence of it has been found in the X-ray patterns of hardened pastes of aluminous cements. In one of the studies previously referred to [10] it was reported as "phase x"; the position of the diffraction lines now permits its identification as the carboaluminate.

Some of the recent investigations of Farran [17] into the nature of the contact film between hardened cement and aggregate are also of interest in this connection. Farran found that aluminous cement appeared to react superficially with calcite aggregate. The X-ray pattern of the reaction product included a series of lines that agree well with the pattern obtained in the present study for the carboaluminate. Farran was of the opinion that the pattern indicated the presence of a solid solution between $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ and a carboaluminate. Such a composition previously had been suggested by Bessey [4] for the mineral hydrocalumite. In the present work, however, and solely on the basis of the X-ray patterns, the carboaluminate and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ appear to exist side by side, with no evidence of solid solution between the two.

These questions cannot be resolved without further data. There can be little doubt, however, that carbon dioxide may play a significant role during, and subsequent to, the hardening of aluminous cements, and probably of other hydraulic cements as well.

4. Summary

A study of the system $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ at 1°C has been made. The stable phases appear to be gibbsite ($\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$), $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$, and $\text{Ca}(\text{OH})_2$. Metastable equilibrium curves were determined for $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$. A metastable invariant point for the latter two hydrates and solution exists at about 0.10 g of Al_2O_3 and 0.38 g of CaO per liter. The compounds $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ crystallize together over a wide range of concentration, but the former is presumed to be metastable throughout the range. The isometric $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ appears to be metastable at 1°C , being transformed very slowly to one or more of the hexagonal hydrates.

No evidence was found of the existence of a hexagonal tricalcium aluminate hydrate. Only one form of the tetracalcium aluminate hydrate was observed. A similar phase, which was observed in minor amounts in most of the solid residues in contact with solutions, especially after prolonged storage, was identified as a carboaluminate, probably $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot \text{CaCO}_3\cdot 11\text{H}_2\text{O}$. The hydrate $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$, on being dried over CaCl_2 , was found to lose 2 molecules of water reversibly. The lower hydrate has a characteristic X-ray pattern. Coprecipitated mixtures of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$, after drying over CaCl_2 , showed lines only of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ on the X-ray patterns. The dicalcium compound presumably was decomposed to the tetra-

calcium and amorphous alumina. This reaction was not reversible.

Owing to the extreme slowness of dissolution at 1°C , the solubility curve of gibbsite was not established.

During the earlier stages of this study the author was ably assisted by G. J. Halley. The X-ray diffraction patterns were prepared by H. E. Swanson and coworkers of the Microstructure Section. Their assistance is hereby gratefully acknowledged.

5. References

- [1] H. H. Steinour, Aqueous cementitious systems containing lime and alumina, Research and Develop. Lab. Portland Cement Assoc., Research Dept. Bul. 34 (Feb. 1951).
- [2] R. H. Bogue, The chemistry of portland cement, 2d ed. (Reinhold Publ. Corp., New York, N. Y., 1955).
- [3] F. M. Lea, The chemistry of cement and concrete, 2d ed. (St. Martin's Press, Inc., New York, N. Y., 1956).
- [4] G. E. Bessey, The calcium aluminate and silicate hydrates, Proc. of the Symposium on the Chem. of Cements, Stockholm, 1938. Ingeniörs Vetenskaps Akad., p. 178, Stockholm (1939).
- [5] L. S. Wells, W. F. Clarke, and H. F. McMurdie, Study of the system $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ at temperatures of 21° and 90°C , J. Research NBS **30**, 367 (1943) RP1539.
- [6] J. D'Ans and H. Eick, The system $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ at 20°C and the hardening of aluminous cements. Zement-Kalk-Gips **6**, 197 (1953).
- [7] R. P. Peppler and L. S. Wells, The system of lime, alumina, and water from 50° to 250°C , J. Research NBS **52**, 75 (1954) RP2476.
- [8] A. J. Majumdar and R. Roy, The system $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$, J. Am. Ceram. Soc. [12] **39**, 434 (1956).
- [9] G. Assarsson, The conditions of formation of the hydrated compounds in the system $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ (liquid) and the hydration of the anhydrous calcium aluminates, Sveriges Geol. Undersökn [C] **30**, No. 399, p. 202 (1936).
- [10] L. S. Wells and E. T. Carlson, Hydration of aluminous cements and its relation to the phase equilibria in the system lime-alumina-water, J. Research NBS **57**, 335 (1956) RP2723.
- [11] H. Bassett, Notes on the system lime-water, and on the determination of calcium, J. Chem. Soc., part II, 1270 (1934).
- [12] R. Hedin, Saturation concentration of calcium hydroxide, Svenska Forskningsinst. för Cement Betong vid Kgl. Tek. Högskol. Stockholm, Handl. No. 27, p. 14 (1955).
- [13] E. T. Carlson, Some observations on hydrated monocalcium aluminate and monostrontium aluminate, J. Research NBS **59**, 107 (1957) RP2777.
- [14] R. Salmoni, The dicalcium aluminate hydrates, Gazz. chim. ital. **64**, 719 (1934).
- [15] R. Turriziani and G. Schippa, On the existence of hydrated calcium monocarboaluminate, Ricerca sci. **26**, 2792 (1956).
- [16] A. W. Myers, C. E. Rogers, V. Stannett, and M. Szwarc, Permeability of polyethylene to gases and vapors, Modern Plastics **34**, No. 9, 157 (1957).
- [17] J. Farran, Mineralogical contribution to the study of the adherence between the hydrated constituents of cements and the embedded materials, Rev. matériaux construct. et trav. publ., C. No. 490, 155; No. 492, 191 (1956).
- [18] M. H. Roberts, New calcium aluminate hydrates. J. Appl. Chem. **7**, 543 (1957).
- [19] G. Schippa and R. Turriziani, The Hydrated calcium aluminates. Ricerca sci. **27**, 3654 (1957).

WASHINGTON, December 27, 1957.