DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 102

PROPERTIES OF PORTLAND CEMENT HAVING A HIGH MAGNESIA CONTENT

BY

P. H. BATES, Chemist

Bureau of Standards

ISSUED JANUARY 19, 1918

PRICE, 15 CENTS

Sold only by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1918

PROPERTIES OF PORTLAND CEMENT HAVING A HIGH MAGNESIA CONTENT

By P. H. Bates

CONTENTS

	Page
I. Introduction	3
II. Raw materials, their proportioning and burning	5
III. Petrography of the clinker	11
IV. Properties of the cement	14
1. Time of set	14
2. Constancy of volume	21
3. Strength of neat, mortar, and concrete test pieces	24
(*a*) Neat test pieces	26
(*b*) Mortar test pieces	31
(*c*) Concrete test pieces	32
V. Summary	40

I. INTRODUCTION

The question of the maximum amount of magnesia allowable in Portland cement is one of the most interesting encountered in the study of this complex material. There is as much diversity of opinion now as was shown by the committees of the German Portland Cement Manufacturers' Association appointed in 1891 and 1895 to investigate this subject. The committee of the latter year rendered majority and minority reports, the former considering magnesia in amounts not greater than 8 per cent harmless, whereas the minority considered amounts greater than 4 per cent injurious. The latter recommendation, strongly advocated by Dykerhoff, the chairman of the committee, was adopted. At present, however, 5 per cent magnesia is allowed by the German specifications.

Dykerhoff's recommendation having been so strongly opposed, further investigations were undertaken by the German association, but these were never finished; consequently no completed report was issued by this association covering its original program. The discussions continued, however, but excepting one of the last

investigations reported (Glasenapp, 1914 meeting) no very important data on this subject have been contributed.

All investigations to date have been at fault in that they did not take into consideration such important matters as the following: First, the history of the cements under investigation, particularly the kind and condition of the raw materials, the condition of firing, and the general characteristics of the clinker; second, the character and amounts of the constituents present in the clinker, especially as to how the constituents in clinker of low magnesia content have been changed in character and amounts by increasing magnesia content, and what new constituents, if any, have been produced; third, a sufficiently large number of cements with a gradual change in the magnesia content. The question has also been further involved by the use of magnesia added to ground cements in investigations which purported to be dealing with high-magnesia cements. Such, of course, can not be considered Portland cements.

Further investigations on this subject are needed because of the failures of mortars and concretes which have been attributed to such cements. The specifications under which cements are usually bought do not demand the making of test pieces of the material to be tested at late periods; but high-magnesia cements are generally conceded to be able to pass all the requirements demanded of the short-time tests. However, with the hydration of the compounds present in such cements it is claimed by some that there is a slow but gradual increase in volume, which is manifested at late periods by low results for the strength of test pieces and finally by complete disintegration of the material. While such cements may be satisfactory at early periods and pass the usual specifications, there is a strong belief in the minds of many that ultimately they will fail. As this phenomenon of the large increase in volume accompanying the slow hydration of the constituents in high-magnesia cements can be observed apparently only at late periods, it is essential to obtain some definite information in regard to this property, if it exists. It might be possible with this information to make definite predictions as to the ultimate behavior of such cements, even though short-time tests should show them to be satisfactory.

In the investigation herewith presented only those cements have been used which have been burned in the experimental rotary kiln of this Bureau (20 feet long by 2 feet in diameter) from raw

materials of which the character and fineness were known and at temperatures which were frequently determined during the burning and maintained constant within 25° C. The resulting clinker was carefully examined petrographically and the various constituents noted and their amounts quantitatively determined. Two series of burnings were made, the first consisting of the production of nine cements with a magnesia content ranging from 1.77 to 18.98 per cent, an average silica content of 22.31 per cent, and an average R_2O_3 (alumina plus ferric oxide) content of 10.32 per cent; and the second consisting also of nine cements with a lower average silica content (21.79 per cent) but higher average iron-alumina content (11.65 per cent) and a magnesia content ranging from 2.01 to 25.53 per cent.

Consequently, 18 different cements burned at as many different times were investigated. All of these were of normal composition except for the magnesia content. This procedure of having the high-magnesia clinker of approximately the same silica and R_2O_3 content as the low-magnesia clinker is open to some criticism, as, taking into consideration molecular proportions, the former should have had a higher silica or R_2O_3 content. Further burnings with this in mind are desirable, but the present investigation is confined to cements of usual composition.

It is not to be thought that this investigation was intended to show the desirability of increasing the amount of magnesia now allowed by the standard specifications. Its primary purpose was to determine what new constituents, if any, were produced in clinker by increasing the magnesia content, also how this latter increase affects the constituents already present, and, finally, to correlate the quantitative changes in the amounts of the various constituents with the changes which would be produced in the general physical properties of the cement.

II. RAW MATERIALS, THEIR PROPORTIONING AND BURNING

The analyses of the various materials used in preparing the "raw mixes" of the burns made are given in Table 1. These were proportioned in such a manner that, after burning and the addition of plaster of Paris and grinding, the cements have the composition shown in Table 2.

TABLE 1.—Analyses of the Raw Materials Used

	Clay	Lime-stone	Dolomite	Feldspar	Kaolin
	Per cent	Per cent	Per cent	Per cent	Per cent
SiO_2	60.07	0.08	0.17	70.83	45.86
Al_2O_3	20.37	.12	.11	16.60	37.56
Fe_2O_3	7.23		.10	.19	.52
CaO	.50	55.40	30.47	.44	.29
MgO	1.85	.79	21.43	.08	Trace.
Na_2O	.79	.....	.....	3.29	.37
K_2O	2.51	.....	.....	8.32	.63
Ignition loss	6.86	43.57	47.69	.63	14.79
	100.18	99.96	99.97	100.38	100.02

TABLE 2.—Analyses of the Various Burns

	Burn 16	Burn 25	Burn 26	Burn 27	Burn 28	Burn 29	Burn 30	Burn 31	Burn 32
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
SiO_2	21.49	21.81	22.08	22.08	22.09	22.61	22.71	23.12	22.84
Al_2O_3	6.77	7.08	7.60	7.51	7.11	7.93	7.07	7.67	7.78
Fe_2O_3	2.88	2.57	2.69	2.94	2.77	2.82	2.96	3.31	3.41
CaO	64.54	62.68	61.37	60.16	59.60	56.88	55.54	48.00	44.09
MgO	1.77	3.27	4.20	5.12	6.49	7.41	9.50	14.07	18.98
SO_3	1.62	1.43	1.54	1.65	1.10	1.60	1.63	1.58	1.61
Na_2O	.07	.10	.10	.12	.14	.09	.15	.18	.28
K_2O	.34	.57	.32	.26	.30	.34	.34	.41	.52
Ignition loss	.52	.71	.38	.36	.61	.64	.46	1.35	.60
Total	100.00	100.22	100.28	100.20	100.21	100.32	100.36	99.69	100.11

	Burn 33	Burn 34	Burn 35	Burn 36	Burn 37	Burn 38	Burn 39	Burn 40	Burn 41
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
SiO_2	22.35	22.33	22.11	21.76	21.53	21.39	21.38	21.22	21.60
Al_2O_3	8.95	8.32	8.79	8.50	8.32	7.85	8.36	8.46	8.15
Fe_2O_3	3.39	3.24	3.10	3.16	3.19	3.43	3.15	3.27	3.35
CaO	36.32	43.92	49.30	53.77	56.30	57.26	58.02	61.40	62.67
MgO	25.53	19.45	13.96	10.33	8.03	7.80	6.62	3.59	2.01
SO_3	1.43	1.73	1.83	1.61	1.62	1.67	1.62	1.56	1.63
Na_2O	.38	.00	.09	.13	.06	.09	.03	.00	.06
K_2O	.56	.16	.17	.27	.23	.38	.15	.16	.08
Ignition loss	1.01	.71	.68	.47	.59	.55	.61	.67	.42
Total	99.92	99.86	100.03	100.00	99.87	100.42	99.94	100.33	99.97

Burn 16 was made from a raw mix containing limestone, clay, and some feldspar (this latter was added to increase the silica somewhat without increasing the alumina to too great an extent, the ratio of silica to alumina in the feldspar being much greater than in the clay). In burns 25 to 32, inclusive, the raw materials were clay, limestone, and dolomite, but with the increasing serial number of the burns increasing amounts of the limestone were replaced with dolomite to give increasing amounts of magnesia. In burn 33 clay, dolomite, and kaolin were used (the latter to increase the alumina content over that obtainable with the clay alone). The same raw materials were used in burns 34 to 40, inclusive, but decreasing amounts of dolomite were replaced with limestone, until finally in burn 41, as in burn 16, limestone without any dolomite was used.

These raw materials, after having been crushed and passed through rolls until all passed a 10-mesh screen, were weighed out in the proper amounts and ground in a ball mill until 85 per cent passed a 200-mesh screen. They were then burned in a natural-gas-fired rotary kiln to such a temperature as produced a satisfactory clinker. In two cases (burns 25 and 26) an unfortunately low gas pressure did not allow of the production of the desired temperatures, with the result that there was obtained an underburned product. The average temperature of burning is given in Table 3. These temperatures were determined every 15 minutes by use of a Wanner pyrometer, which was sighted directly upon the clinker in the hot zone. As determined, they should be true to within ±15° C. The use of natural gas in a kiln of this size permits of fairly accurate temperature determination.

TABLE 3.—Average Temperatures at which the Various Cements Were Burned

Burn No.	Per cent MgO	Degrees centigrade	Burn No.	Per cent MgO	Degrees centigrade	Burn No.	Per cent MgO	Degrees centigrade
16	1.77	1520	30	9.50	1497	36	10.33	1437
25	3.27	1430	31	14.07	1521	37	8.03	1423
26	4.20	1486	32	18.98	1499	38	7.80	1434
27	5.12	1512	33	25.53	1413	39	6.62	1450
28	6.49	1505	34	19.45	1410	40	3.59	1447
29	7.41	1530	35	13.96	1420	41	2.01	1446

2533°—18——2

In making burnings the kiln was gradually heated up to a rather bright red with gas burners using admixed air at atmospheric pressure. The burners were then changed to a type using air at a pressure up to 40 pounds per square inch. When the temperature with these had reached about 1250° C, the air was increased to such an amount that the gas no longer burned at the end of the burners but on the hot clinker. There was, consequently, no envelope of partially burning gases interfering with the direct sighting of the pyrometer on the clinker, and it was, furthermore, possible to sight directly on the hottest clinker, the latter in the hot zone being also hotter than any part of the kiln.

An examination of Table 3 in connection with Table 2 shows the effect of the increase of the alumina-iron oxide content and the decrease in the silica content in lowering the temperature of clinkering. But it does not appear that the increased amounts of magnesia have produced the decrease in clinkering temperature that would be expected. But while the clinkering temperature was not reduced very appreciably, yet the indications are that the "softening point" was decidedly reduced. In cement-manufacturing practice the proper clinkering temperature is the lowest temperature at which the lime will combine with the clay (or other argillaceous material) to such an extent that the ground clinker will produce both a sound cement and one containing but a small amount of insoluble material.[1] Usually this temperature is decided entirely by the appearance of the clinker, and invariably this serves all purposes, though it may happen that a very vitreous clinker may contain so much free lime that the resulting cement may not be sound.[2] In the present case the high-magnesia raw mixes gave clinker that, when burned at the proper temperature as judged by the appearance, "dusted"[3] in a very short time (5 to 30 minutes, depending upon the rate of cooling). If the temperature was increased until a decidedly overburned or very hard clinker was obtained, "dusting" again resulted. At a temperature somewhat lower than the latter a clinker was obtained that showed minimum immediate "dusting," though it slowly changed to the powdered condition. Therefore, the temperatures as shown in Table 3, at which the higher-magnesia cements were burned, are

[1] U. S. Government Specifications for Portland Cement. Bureau of Standards Circular No. 33. Paragraphs 2 and 29 and "Insoluble Residue" under II.

[2] There is in the Pittsburgh branch of the Bureau a piece of very hard vitreous clinker that has been exposed to the air for three years without signs of slaking and yet contains so much free lime that the cement made from it is decidedly unsound.

[3] Change of the β orthosilicate of lime ($2\ CaO.SiO_2$) to the γ form, with accompanying increase in volume of almost 10 per cent.

the temperatures that are decidedly beyond those required to combine the basic and acidic components, but are the temperatures that gave the maximum amounts of satisfactory clinker. In Fig. 1 is shown the progressive "dusting" of burn 33 at the end of 30 minutes, and 24 hours after dropping from the kiln. This continued for a period of about a year, when equilibrium seemed to have been reached.

This slow "dusting" was not noted in any of the burns containing less magnesia than that shown by No. 30 (9.50 per cent); but to prevent this phenomenon in these cases a higher temperature was used than that actually required to bring about combination of the basic and acid components of the mix. It is well known that in such mixtures as used in making Portland cement an increase of magnesia lowers the softening point of the mixture. In usual cement-mill practice, where complete analyses of the raw mixes are not made frequently, and where the magnesia content may reach a fairly high amount, the latter condition is first noted in the kiln by a decided tendency of the clinker to "ball" or form "logs," due to the lowering of the softening point.[4]

The whole phenomenon of "dusting," or the changing of the beta form of the orthosilicate of lime to the gamma form, is worthy of attention and further investigation. Low-burned or very slowly cooled clinker may contain the latter form. Well-burned clinker of the proper composition or clinker which has been rapidly cooled through the inversion point of the beta to the gamma form (675° C) will not contain it. But, as noted above, the beta form in certain instances does gradually change to the gamma form very slowly and over long periods. As this change is accompanied by an increase in volume of 10 per cent, it can readily be seen what damage would be produced in a concrete if this change should take place after the clinker has been ground and made into a concrete. It would be well, therefore, when examining disintegrated concrete to look for the gamma form of orthosilicate.

With marked increase in magnesia content the difficulties of burning increased considerably. This was very marked when the percentage of magnesia was increased beyond 9.5 per cent. When the amount was less than this, the clinker was both approximately normal in appearance and normal in its behavior in the kiln, giving the usual black glistening cokelike material, which rolled about in the kiln without any tendency to form large balls or "logs" or

[4] "High Magnesia Cements." Discussion by Prof. Glasenapp, Mitt. der Central. zur Forder. der Deutch. Port. Cement Ind., 4, pp. 58–62.

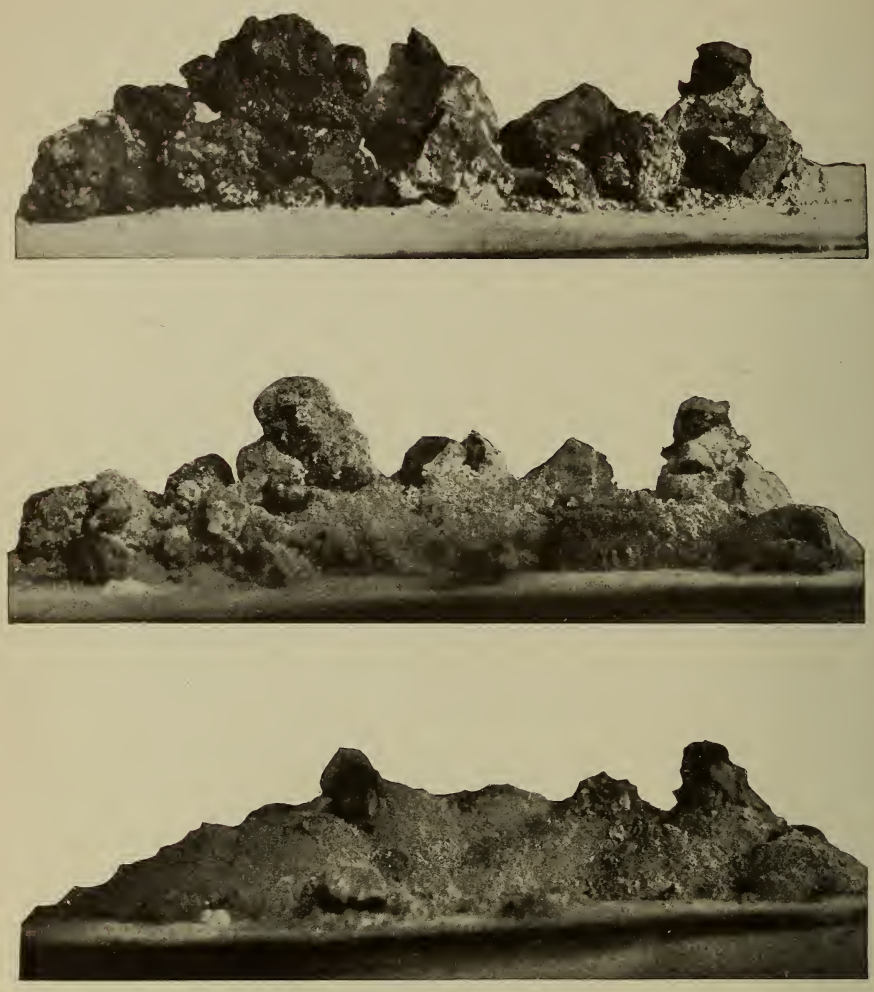


FIG. 1.—*Clinkers from burn 33*

Top, hot clinker; middle, same clinker at end of half hour; bottom, same clinker at end of 24 hours. This shows the inversion of the beta to the gamma orthosilicate, accompanied by a large increase in volume. This phenomenon is usually referred to as dusting of the clinker

to "ring up." When this amount was exceeded, the clinker was of a reddish-yellow appearance, which gave a considerable amount of an ochrelike dust and a yellow cement, the latter giving a yellow, muddy, plastic concrete. The formation of rings was also excessive.

III. PETROGRAPHY OF THE CLINKER

One of the main reasons for making this investigation was to determine the constitution of the clinker and to note in particular the changes produced in clinker of low magnesia content by the replacement of increasing amounts of lime by magnesia. Klein and Phillips [5] in this laboratory were among the first to make a study of this matter in the light of the present exact data of the Geophysical Laboratory.[6] According to the results of Klein and Phillips, magnesia could exist in Portland cement in amounts as great as 7.5 per cent before there would appear a new compound not present in ordinary clinker; that is, below this amount it would form homogeneous compounds with either the beta orthosilicate or the tricalcium aluminate. Some doubt has been thrown upon their results, however, by Rankin,[7] who found that in the compound $3CaO.Al_2O_3$, in which 10 per cent of the lime had been replaced by magnesia, the latter was present as free magnesia, whereas Klein and Phillips found a homogeneous compound with a lower refractive index than that which the tricalcium aluminate has. However, a reexamination of this preparation failed to show any free magnesia, but it does contain appreciable amounts of silica and possibly a few tenths of a per cent of iron oxide. In the preparation approaching the composition of Portland cement but with high magnesia content they could not detect any free magnesia.

In the present investigation the constituents noted were those present in cement of normal composition and proper burning, namely, tricalcium silicate ($3CaO.SiO_2$), three forms—β, β', and γ—of dicalcium silicate or orthosilicate of lime ($2CaO.SiO_2$), and tricalcium aluminate ($3CaO.Al_2O_3$). When the percentage of magnesia reached about 8 per cent, monticellite ($MgO.CaO.SiO_2$) was noted; with a slightly greater percentage, spinel ($MgO.Al_2O_3$) appeared; and, finally, in the two burns of highest magnesia content

[5] Klein and Phillips, "Magnesia in Portland Cement," 8th Int. Cong. Appl. Chemistry, 5, p. 73.

[6] Rankin, "The Ternary System, $CaO.Al_2O_3.SiO_2$," Amer. Jour. Science, 39, No. 229; Jan., 1915. Rankin and Merwin, "The Ternary System, $CaO-Al_2O_3-MgO$." Jour. Amer. Chem. Society, 38, No. 3, p. 568. Jesser, "Magnesia in Portland Cement," Tonind. Zeitung., Oct. 21, 1911.

[7] Rankin, "The Constituents of Portland Cement Clinker," Jour. Ind. & Eng. Chem., 7, No. 6, p. 466, June, 1915; "The Ternary System, $CaO-Al_2O_3-MgO$," Jour. Amer. Chem. Soc., 38, No. 3, p. 568.

some free magnesia was noted. The constituents which are characteristic of the high-magnesia cements are, therefore, monticellite, spinel, and, of much less importance, free magnesia.

An attempt was made to determine quantitatively the percentage of constituents present in each of the burns. This was done by preparing thin sections of characteristic clinker of each burn. To avoid possible action of water during the grinding of the sections, they were ground in a nonsaponifiable oil, and immediately after being reduced to a satisfactory thinness were covered with a cover glass and sealed with balsam from all possible action of atmospheric moisture. These were then examined in the petrographic microscope in the following manner: Instead of the ordinary Huyghenian ocular a positive Ramsden ocular was used. This was fitted to a holder containing a slot in which a double-coordinate plate was inserted. The objectives used were the 4 mm and the 8 mm, depending upon the fineness of the individual grains, the former being used for the finer grains. The amount of the various constituents in a field was estimated in terms of the smallest square divisions of the double-coordinate plate, which covered an area in actual size of 0.00178 ± 0.00006 mm square with the 4 mm objective and 0.00385 ± 0.00025 mm square with the 8 mm objective. At least 20 fields taken at random, but including all parts of the thin section, were so integrated. The sum total of the constituents in terms of their units of area was obtained by adding the respective values for the individual fields, and these results were calculated to 100 per cent. These are shown in Table 4.

Such a method, of necessity, is only approximately quantitative, and it is rendered more inaccurate by the impossibility of distinguishing, in thin sections, between tricalcium silicate or tricalcium aluminate or spinel. Consequently, in the foregoing table these three constituents appear together. It is possible, however, to form an idea of the relative amount of tricalcium silicate present by bearing in mind that all the alumina is combined either as the tricalcium aluminate or spinel and that the latter appears only in the burns containing 9.5 per cent or more magnesia, increasing therefrom very slightly with increasing magnesia percentages. The results show, however, how the amount of β orthosilicate decreases with increased amounts of magnesia. Apparently, therefore, the monticellite, which increases with increased amounts of magnesia, has been formed at the expense of the orthosilicate. It is also evident that the

amount of tricalcium silicate has not been materially reduced. The β' orthosilicate was noted in some cases in small amounts, usually only in the presence of the greater amounts of magnesia. (In other work by this laboratory its presence has been noted in high-alumina cements.)

TABLE 4.—Petrographic Analyses of the Various Burns

Burn No.	Percentage MgO	Percentage of the various constituents					
		Tricalcium silicate, tricalcium aluminate, spinel [a]	β Calcium orthosilicate	"Ferrite"	Monticellite	Spinel	Free lime
16	1.77	61.6	30.6	7.6	None	None	Trace
25	3.27	38.9	47.0	10.4	None	None	3.7
26	4.20	43.2	45.3	9.1	None	None	2.4
27	5.12	51.8	39.6	8.2	None	None	.5
28	6.49	47.9	41.6	9.0	None	None	1.5
29	7.41	49.8	40.3	9.9	None	None	Trace
30	9.50	54.1	35.7	10.2	[b] Present	None	None
31	14.07	56.0	[c] 32.4	8.3	2.2	Present	None
32	18.98	57.1	20.7	7.8	11.5	Present	None
33	25.53	52.0	[d] 13.5	11.3	23.2	Some	None
34	19.45	53.2	[e] 20.7	8.9	17.2	Some	None
35	13.96	46.8	[f] 26.9	11.4	14.9	Little	None
36	10.33	50.6	29.8	10.5	9.1	Very little	None
37	8.03	51.2	35.8	9.7	4.3	None	None
38	7.80	53.0	37.2	8.9	.9	None	None
39	6.62	54.3	36.6	9.1	None	None	None
40	3.59	55.7	35.8	8.5	None	None	None
41	2.01	56.2	33.5	9.9	None	None	Trace

[a] See text for the reason of this grouping.
[b] Present in such small quantities and so poorly developed as not to be distinguishable from the β orthosilicate in thin sections.
[c] β' orthosilicate present (about 1.1 per cent).
[d] β' orthosilicate present (about 3.7 per cent).
[e] β' orthosilicate present (about 2.1 per cent).
[f] β' orthosilicate present (about 1.7 per cent).

The appearance of the structure of the clinker of these cements is very characteristic, there being a remarkable tendency to the formation of large grains and crystals. The formation of the tricalcium silicate in the presence of large amounts of magnesia is very similar to its formation in the presence of large amounts of alumina. In both cases it tends to crystallize in large well-defined needles. This tendency is, however, not restricted to either of these classes of cements alone, as both burns 40 and 41 exhibited this characteristic and are neither high-magnesia nor high-alumina cements, but this tendency is more marked than

with cements of normal composition. As will be seen later, this formation of large grains plays an important part in the properties of these cements. In Figs. 2 to 6 are shown a number of photomicrographs of thin sections of the cements used in this investigation, examined both with and without crossed nicols. In these the distinct granularity of the major constituents may be particularly noted.

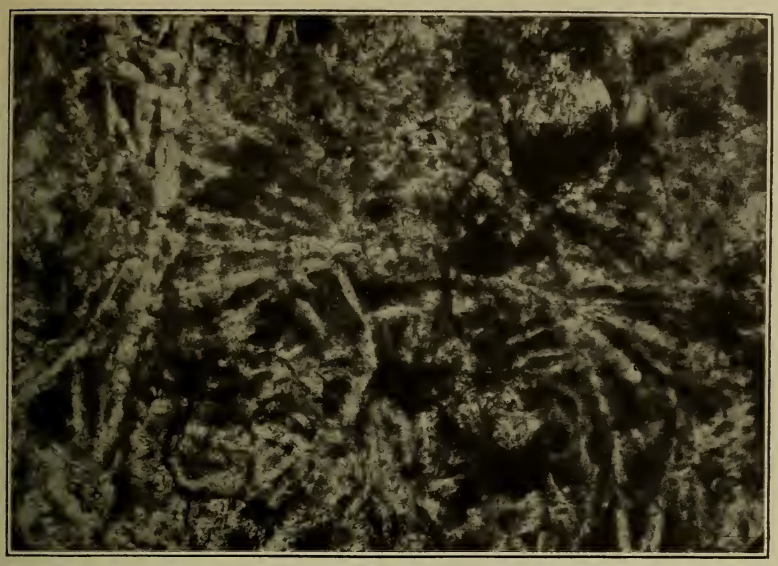
IV. PROPERTIES OF THE CEMENT

1. TIME OF SET

The clinker, without either quenching or storing, was crushed in jaw crushers, passed through rolls until all passed a 20-mesh screen, and after the addition of approximately 3 per cent of plaster was ground in a porcelain-lined ball mill to the fineness shown in Table 5. Without any storage or aeration, the ground cement was then tested for time of set, constancy of volume, and strength in the form of neat tension and 2-inch-cube compression briquettes, 1:3 Ottawa-sand tension and 2-inch-cube compression briquettes, and 6-inch 1:1½:4½ gravel-concrete cubes.

TABLE 5.—Fineness and Soundness of the Different Cements

Burn No.	Per cent passing sieve		Pats subjected to—			
	100-mesh	200-mesh	Boiling water	Steam	28 days in air	28 days in water
16	96.0	79.6	O. K.	O. K.	O. K.	O. K.
25	99.2	75.8	Disintegrated	Disintegrated	O. K.	O. K.
26	98.4	79.8	Disintegrated	Disintegrated	O. K.	O. K.
27	97.6	78.6	O. K.	O. K.	O. K.	O. K.
28	99.0	77.6	O. K.	O. K.	O. K.	O. K.
29	97.2	76.0	O. K.	O. K.	O. K.	O. K.
30	92.0	73.2	O. K.	O. K.	O. K.	O. K.
31	95.4	79.0	O. K.	O. K.	O. K.	O. K.
32	97.2	90.4	Soft and cracked	Soft and cracked	O. K.	O. K.
33	97.0	81.4	Soft	Soft	Warped	O. K.
34	94.4	76.0	O. K.	O. K.	O. K.	O. K.
35	94.9	79.2	O. K.	O. K.	O. K.	O. K.
36	96.4	78.8	O. K.	O. K.	O. K.	O. K.
37	95.6	78.4	O. K.	O. K.	O. K.	O. K.
38	97.4	79.0	O. K.	O. K.	O. K.	O. K.
39	97.8	80.1	O. K.	O. K.	O. K.	O. K.
40	97.0	78.0	O. K.	O. K.	O. K.	O. K.
41	96.6	78.6	O. K.	O. K.	O. K.	O. K.



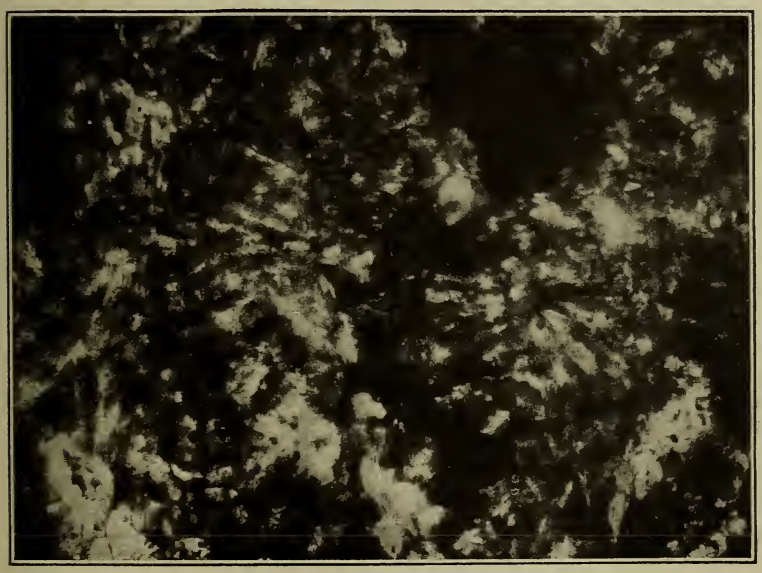


FIG. 2.—*Photomicrographs of a thin section of clinker of burn 40*

Shows the development of long crystals of the tricalcium silicate. Top examined in plane-polarized light; bottom examined with the nicols crossed. This development of the tricalcium silicate was very marked in the burns in this investigation, being more noticeable in those containing higher percentages of magnesia. It is characteristic of well-burned commercial clinkers containing considerable fluxing material. Magnified 275

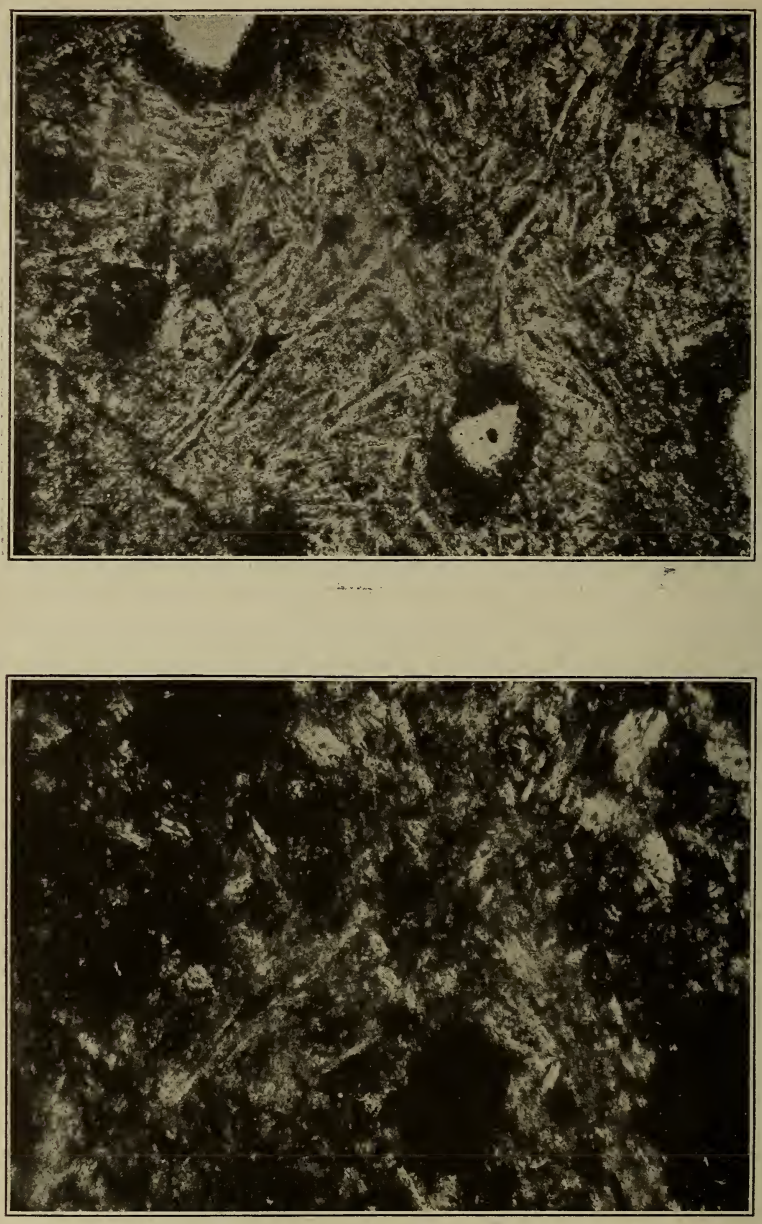
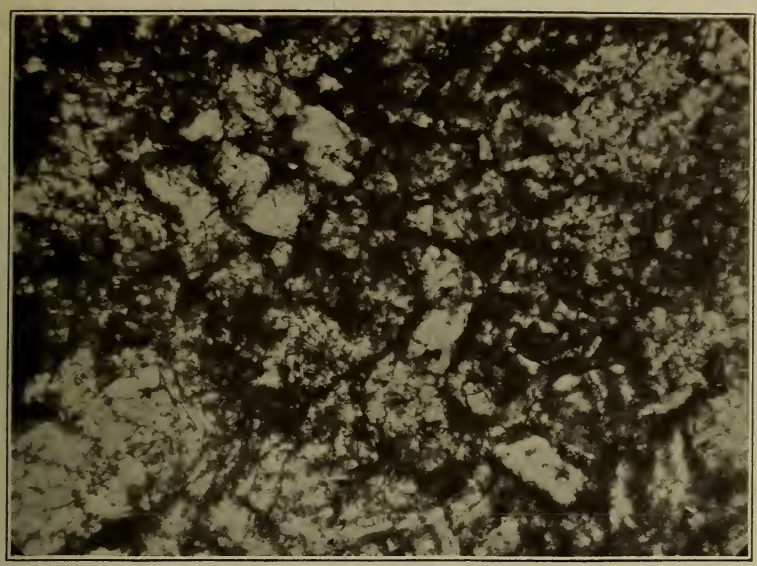


FIG. 3.—*Photomicrographs of a thin section of clinker of burn 37*

Also shows the development of long crystals of tricalcium silicate embedded in the orthosilicate. Top examined in plane-polarized light; bottom examined with the nicols crossed. (See remarks under Fig. 2.) Magnified 275



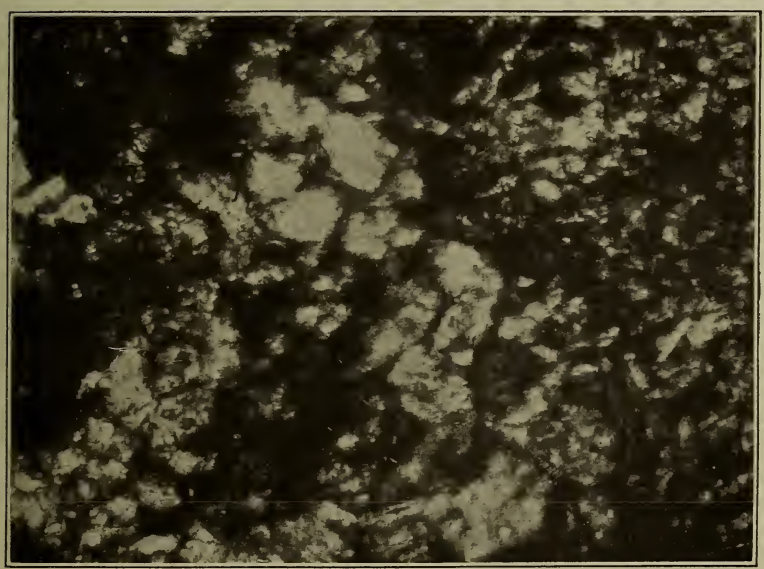


FIG. 4.—*Photomicrographs of a thin section of clinker of burn 33*

Some of the larger well-defined grains are monticellite embedded in the orthosilicate; others are tricalcium silicate. Top examined in plane-polarized light; bottom examined with crossed nicols. Monticellite is a characteristic constituent of clinker high in magnesia. Magnified 275

FIG. 5.—*Photomicrograph of burn 37*

Shows an area of very large elongated crystals of tricalcium silicate embedded in the orthosilicate. This shows how the constituents in a clinker are not uniformly distributed throughout the mass. This is characteristic also of commercial clinker. Magnified 275

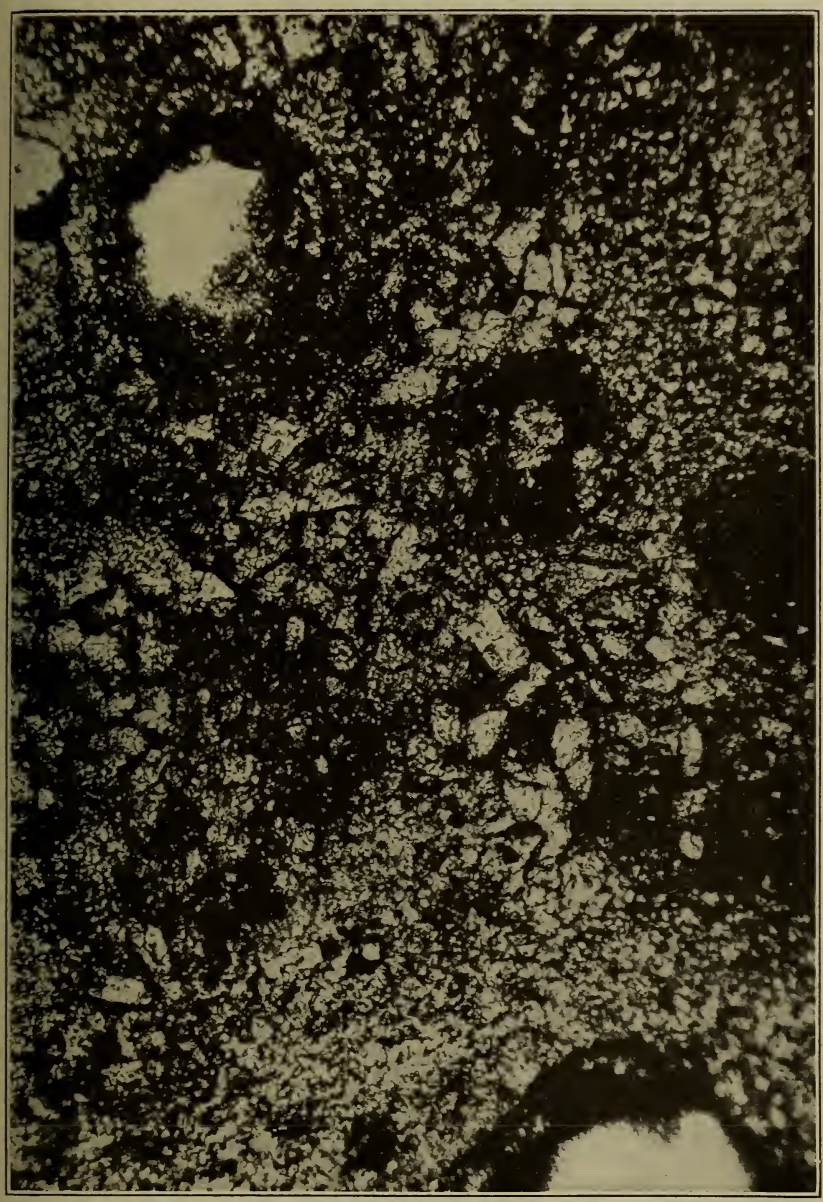


FIG. 6.—*Photomicrograph of burn 33*

The white grains are either monticellite or tricalcium silicate; the dark ground is largely the orthosilicate. There is also spinel present but it can not be distinguished from the monticellite or tricalcium silicate in the photomicrograph. Magnified 220

The normal consistency, time of set, and specific gravity of the finished cements are shown in Table 6. It can be seen from this table that there is no marked change in the time of set until the percentage of magnesia approaches 10 per cent. At this amount there is a tendency toward quick setting, especially in the development of a quick initial set and an apparently quick final set. The latter, however, can hardly be called a true final set, but is really a rapid drying out of the test piece due to the excessive heat evolved by the very early hydration. This evolution of heat was so marked that the test pieces gave off steam in the cases of burns 31, 32, 34, and 35. In the case of burn 33 the heat evolved was not so marked. The time of set shown for burn 32 was not the true time, since in order to obtain a test specimen an excessive amount of water was used, which undoubtedly masked a "flash" or an almost instantaneous set. Burn 33 also gave a "flash" set.

TABLE 6.—Time of Set, Consistency, and Specific Gravity of the Various Cements

Burn No.	Per cent MgO	Normal consistency	Time of set								Specific gravity
			Vicat				Gilmore				
			Initial		Final		Initial		Final		
			hrs.	min.	hrs.	min.	hrs.	min.	hrs.	min.	
16	1.77	20.0	0	55	6	40	3	00	8	05	3.192
25	3.27	21.0	2	15	6	10	3	05	8	30	3.157
26	4.20	20.5	2	15	7	30	3	45	9	15	3.200
27	5.12	19.0	2	40	6	15	4	00	8	30	3.234
28	6.49	21.0	1	35	5	10	2	35	6	30	3.216
29	7.41	20.5	1	20	6	30	4	25	9	00	3.259
30	9.50	19.0	1	00	9	30	3	20	13	00	3.243
31	14.07	18.0	[a] 1	05	[a] 1	25	[a] 0	06	[a] 2	05	3.225
32	18.98	31.0	[a] 1	00	[a] 30	00	[a] 5	00	[a] 48	00	3.178
33	25.53	18.5	[b] 0	30	[b] 25	00	[b] 4	00	[b] 48	00	3.275
34	19.45	24.0	[a] 0	05	[a] 0	15	[a] 0	10	[a] 1	30	3.225
35	13.96	24.5	[a] 0	05	[a] 0	12	[a] 0	08	[a] 1	25	3.110
36	10.33	18.5	1	30	3	30	2	00	4	00	3.240
37	8.03	19.0	2	10	5	00	3	15	5	50	3.230
38	7.80	19.0	2	20	4	10	3	05	5	00	3.224
39	6.62	19.5	1	55	4	15	3	35	5	25	3.200
40	3.59	19.5	1	35	4	00	2	10	4	45	3.193
41	2.01	19.5	1	35	5	00	2	05	5	40	3.205

[a] All test pieces became quite warm, especially the Vicat. [b] Flash set (?), see text.

Unless the relative amounts of the various constituents of the cement were known, and also their characteristic formation—distinctly granular and distinctly separated from one another—it

would be extremely difficult to explain the rôle of magnesia in making the cement quick-setting. An examination of Table 4 shows that the amount of the orthosilicate of lime has rapidly decreased when the magnesia was increased beyond 7.5 per cent; further, the amounts of tricalcium silicate, tricalcium aluminate, and spinel have remained approximately constant; and while the amount of spinel did increase with increased magnesia, yet it was very small at all times. Consequently the amount of the quickly hydrating compounds (tricalcium silicate and tricalcium aluminate) has increased considerably when compared with the amount of slowly hydrating material (orthosilicate of lime). As a consequence, the high-magnesia cement must of necessity develop a very quick set and one accompanied by the evolution of a large amount of heat.[8]

This quick hydration and setting takes place with this class of cements, notwithstanding the presence of the relatively large amount of monticellite. This latter material can be considered as not hydrating, at least within the course of several months. Furthermore, it is not present in the cement in the same manner as the orthosilicate. This latter does not occur in large well-defined grains like the former, but more like a fused mass surrounding the grains of the other constituents, and after crushing it may still in a measure cover these and prevent the water rapidly reaching them on account of its very slow hydration. It can readily be seen, therefore, how the structure and constitution of the high-magnesia cements should produce rapid setting.

2. CONSTANCY OF VOLUME

The constancy of volume was determined by subjecting the pats of the usual form, 24 hours after making, to an atmosphere of steam for 4 hours at atmospheric pressure, to storage in air for 28 days, to storage in water for 28 days, and to storage in boiling water for 4 hours. The pats showed soundness except in the following cases: Burns 24 and 25 showed bad disintegration when subjected to steam and boiling water, burns 32 and 33 were soft when subjected to steam and boiling water, and burn 33 showed a slight warping when subjected to air storage for 28 days. As stated before, the first two burns mentioned above were, owing to low gas pressure, distinctly underburned. Burns 32 and 33, however,

[8] Klein and Phillips, "The Hydration of Portland Cement," Technologic Paper No. 43, Bureau of Standards. It has been found in the laboratory when large amounts of pure tricalcium aluminate (1 kilo) are mixed with water, in the proportion of two of the former to one of the latter, the heat evolved raises the mass beyond the boiling point of water.

were really not set when subjected to the boiling and steam treatment, and undoubtedly burn 33 showed warping of the pat stored in air for the same reason of slow set, having dried out and warped before it set.

Some of these cements were subjected to a more quantitative test for their constancy of volume. Duplicate bars of 1:1½:4½ gravel concrete (5 by 5 by 45 inches) were made of these cements, and at the end of 24 hours an initial measurement of a gauged length (approximately 39 inches) was made. They were then removed from the form and one bar allowed to remain indoors subjected to the air of the laboratory. The other bar was kept for one week under wet burlap, and then, having gained sufficient strength to permit of handling, was placed in water. Subsequent readings of changes in length were made at various periods. The results are shown in Table 7. It was not possible to secure bars of the very high-magnesia cements, all bars made having been broken in handling owing to their very low early strength.

The measurements at the various periods were made with an extensometer made of two parallel ¾ by ¾ by 42 inch oak rods, joined at the ends and at two equidistant points between with pieces of oak of the same cross section. Through one of the end cross rods there was securely fastened a steel set screw and on the other an Ames dial graduated to 0.001 mm. In making measurements the set screw was brought up against the outer side of one of the copper gauge points placed in the concrete, which projected about ½ inch above the concrete, and then the spindle of the Ames dial brought against the outer side of the other gauge point. The reading of the dial was then noted and could be checked to 0.003 mm. Immediately after making the reading the distance between the end of the spindle and the end of the set screw was determined with a microscopic comparator. All readings are corrected to 20° C, using 0.000009 and 0.0000108 as the temperature coefficients of expansion of concrete and steel, respectively.

This table (7) shows that the high-magnesia cements produce concrete showing a similar deportment, so far as expansion is concerned, to concrete made from cements of normal composition. They show usually contraction when stored in air and expansion when stored in water, but it does not appear that the magnitudes of these changes are consistently greater when the cement contains a large amount of magnesia. It should further be noted that this change is greater in the later burns in which the silica-

TABLE 7.—Expansion (in Per Cent of Original Length) of 1:1½ : 4½ Concrete Bars

[Unless otherwise noted, expansion in air is negative and in water positive. Reduced to 20° C]

Burn No.	Per cent MgO	Stored in—	1 week	2 weeks	1 month	2 months	3 months	4 months	6 months	9 months	12 months	15 months	19 months	23 months	29 months	35 months
16	1.77	Air	0.004	0.014	0.018	0.024	0.019	0.032	0.036	0.044	0.044	0.039	0.038	0.036	0.039	0.040
		H_2O	.007	.020	.026	.039	.067	.054	.058	.062	.064	.064	.065	.055	.051	.055
25	3.27	Air	.007	.013	.023	.019	.006	.....	.011	.015	.017	.016	.014	.009	.009	.010
		H_2O	.003	.046	.042	.086	.134	.195	.194	.195	.196	.197	.203	.199	.196	.188
26	4.20	Air	.019	.022	.033	.036	.048	.053	.052	.052	.063	.063	.067	.063	.054	.053
		H_2O	− .010	− .000	− .001	− .006	− .002	.....	− .007	− .005	− .028	− .018	− .012	+ .037	.066	.079
27	5.12	Air	.017	.032	.035	.043	.038	.044	.056	.063	.069	.060	.070	.....	.....	.....
		H_2O	.009	.012	.027	.029	.027	.038	.030	.038	.032	.042	.058	.053	.047	.047
28	6.49	Air	.008	.017	.019	.018	.045	.043	.045	.051	.054	.051	.054	.050	.044	.047
		H_2O	.003	.013	.022	.032	.033	.036	.034	.039	.047	.050	.048	.047	.044	.041
29	7.41	Air	.016	.035	.044	.038	.048	.047	.048	.051	.051	.053	.....	.055	.064	.064
		H_2O	− .001	.011	.010	.021	.007	.011	.017	.018	.028	.024	.019	.....	.071	.081
30	9.50	Air	.017	.033	.039	.057	.071	.071	.074	.078	.077	.079	.074	.070	.076	.075
		H_2O	− .005	.009	.003	.005	.012	.012	.017	.015	.025	.022	.033	.047	.077	.084
31	14.07	Air	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
		H_2O	− .027	− .061	− .038	− .032	− .008	− .002	− .013	.017	.010	.006	.004	.003	.007	[a] .005
36	10.33	Air	.058	.058	.059	.073	.082	.090	.084	.085	.092	.092	.087	.100	.089	.095
		H_2O	− .009	.000	.005	.008	.009	.010	.027	.033	.033	.053	.056	.073	([a])	([a])
37	8.03	Air	.028	.032	.043	.049	.055	.057	.057	.058	.064	.060	.064	.063	.062	.064
		H_2O	− .022	− .023	− .017	− .008	− .003	.008	.013	.022	.014	.035	.033	.041	.060	.074
38	7.80	Air	.015	.015	.014	.017	.022	.027	.023	.023	.035	.034	.029	.033	.033	.033
		H_2O	.007	.025	.044	.050	.051	.....	.056	.061	.061	.070	.078	.087	.092	.097
39	6.62	Air	.005	.031	.039	.048	.058	.068	.058	.059	.061	.061	.061	.062	.059	.065
		H_2O	.031	.045	.045	.042	.045	.034	.064	.090	.089	.104	.094	.096	.095	.100
40	3.59	Air	+ .021	+ .017	+ .012	+ .006	+ .002	− .001	.....	+ .006	+ .000	− .002	− .010	− .012	.012	.012
		H_2O	.045	.052	.057	.058	.057	.056	.061	.068	.076	.081	.....	.....	.....	.....
41	2.01	Air	.052	.056	.057	.061	.068	.067	.061	.068	.070	.075	.081	.086	.078	.077
		H_2O	− .008	.000	.002	.006	.004	.004	.....	.010	.007	.009	.....	.001	.006	.004

[a] These bars are expanding unequally on the top (exposed to damp atmosphere during the first 24 hours after making) and on the bottom (resting on the bottom of form in which it was cast during the first 24 hours). This causes a curving of the bar, which may result in the readings showing a contraction, since they are made on the side showing little or no expansion.

alumina ratio was a little lower than in those (burns 33–41) in which the ratio was greater. It would appear somewhat as if the alumina content affected the volume changes as much as the magnesia content. However, there were not a sufficient number of test pieces, neither are the readings sufficiently accurate, nor was it possible to control either the humidity of the specimen stored in air or the many other variables which naturally affect these measurements, to make the results much more than qualitative.

Attention should also be called to the measurements made on burns 25 and 26. These, as noted before, were unsound according to the boiling and steaming tests for constancy of volume. The concrete from burn 25 shows that it has contracted less in air and expanded more in water than the other cements, showing thereby that it is acting as an unsound cement usually does. However, as a concrete specimen, when examined macroscopically, it appears perfectly normal at the end of two and one-half years. Burn 26 shows a large contraction in air and a contraction also in water over a rather extended period, as shown in the table. After a year the contraction changed to an expansion, and the latter is now continuing very rapidly, as found by later measurements. All the results show the difference in concretes made from different cements, although it is undoubtedly premature to say that differences in the coefficient of expansion of various concretes are due to the use of a different cement. The cement is but one of the many variables in this very complex material, and it is possible to conceive that differences in consistency and amount of tamping would allow of very great differences in this coefficient, though in the present case these were kept as uniform as possible.[9]

3. STRENGTH OF NEAT, MORTAR, AND CONCRETE TEST PIECES

The different test pieces made for the determination of the strengths developed by the various cements were (*a*) neat-tension briquettes and 2-inch compression cubes; (*b*) tension briquettes and 2-inch compression cubes of 1:3 standard Ottawa-sand mortar; (*c*) 6-inch compression cubes of 1:1½:4½ gravel concrete.

For some unknown reason cements with a high-magnesia content have been considered readily susceptible to the action of sea water. For some time specifications for Portland cement

[9] See Taylor ("The Elasticity of Compound Bars with Special Reference to Reinforced Concrete Columns," Concrete and Construct. Eng. 9, No. 12, p. 722; 1914) for a striking presentation of the various values obtained for the coefficient of expansion of concrete.

used very widely limited the amount of magnesia to 3 per cent when the cement was to be used in contact with sea water, while allowing 4 per cent when used for all other purposes.

How this prejudice against high-magnesia cements arose is a question. The usual explanation given is that it was found that cements which had failed in sea water contained a large amount of magnesia. But it is never stated sufficiently definitely whether this magnesia was in the cement before it was placed in sea water or was found there after it had been in contact with the water. If the latter was actually the case, there is no reason to assume that the cement was originally high in magnesia, as the first effect of placing cement in sea water is the reaction between the lime freed from the cement by the water and the magnesia salts in solution, resulting in the solution of the lime and the deposition of the magnesia. The solution by sea water of the lime freed from Portland cement is an expected and normal action, and it must be accompanied by the deposition of magnesia from the sea water.

In view of this prejudice against high-magnesia cements, it was decided to determine the effects of salts in solution on concrete made from the cements used in this investigation. Sea water, however, was not used on account of its inaccessibility and also because previous work of this laboratory[10] had shown that certain of the salts present in sea water had a greater destructive force on concrete when present in a different concentration than in sea water. Also, it had been found that alternate wetting and drying of the concrete produced the maximum destruction in the least time. Consequently, one set of the test pieces was stored for various alternate periods in air and in a 2 per cent solution of equal parts of crystallized sodium chloride, sodium sulphate, magnesium chloride, and magnesium sulphate. The cubes tested at the end of 28 days had been stored alternately in the solution and in air for four periods of one week each. Those tested at 90 days had the same storage as those tested at 28 days and in addition three periods of one week each in the solution with intermediate drying in air for one-week periods. The 26-week test pieces had the same treatment as the 90-day ones, plus an additional storage in the solution of two three-week and one four-week periods with intermediate dryings between each of these periods of one week in air. All remaining test pieces were given the same

[10] Bates, Phillips, and Wig, "The Action of the Salts in Alkali Water and Sea Water on Concrete," Bureau of Standards Technologic Paper No. 12.

treatment as the 26-week ones, but were further stored in the solution for periods of four weeks each with intermediate dryings of two weeks each until the end of one year, when all were removed and stored in air.

Another set of the concrete cubes was stored in tap water for the same periods of wetting and placed in air for the same periods of drying as the test pieces stored in the solution. This second set served as a standard with which to compare those stored in the solution. Concrete cubes were also made of some of the cements which, after 24 hours in a damp atmosphere, were stored constantly in the air of the laboratory. All neat and mortar test pieces were stored continuously in water after the first 24 hours in the damp closet.

(*a*) *Neat Test Pieces.*—The strengths developed by the neat specimens are shown in Table 8, these being the average for three test pieces. It is clearly seen from these that an amount of magnesia of approximately 7 per cent can be reached before there is a noticeable falling off in the strength of this kind of a specimen; with those cements containing the lower amounts of alumina and higher silica the magnesia content can be a little higher than this amount. With amounts greater than 10 per cent the early strengths are low, and while they do seem to increase with time at a greater rate than those of normal cements, yet the low early strengths are decidedly against them.

The various test pieces of the high magnesia cements have been carefully examined at all periods at which they were broken for evidence of approaching disintegration. All neat specimens were in good condition at the end of one year excepting those made from burns 32 and 33. In Figs. 7 and 8 are shown the condition of the neat specimens of burn 32 at the end of one year. Particular attention is called to Fig. 8, which shows two of the briquettes placed so as to show the warping produced in the disintegration. The face of the briquettes badly disintegrated and warped to the greatest extent is the face which was next to the glass plate during the storage of the test pieces in the molds in the damp closet. The face showing least warping was the one exposed to the air. This manner of disintegration and warping, relative to the face exposed during the first 24 hours to the air or glass plate, is characteristic. It has also been encountered in the laboratory repeatedly with unsound cements.

FIG. 7.—*Neat briquettes of burn 32 at end of one year*

The faces of the briquettes shown above are those on which the briquettes rested on the glass plate during storage in the damp closet. The faces exposed to the atmosphere during storage in the damp closet are not cracked.

TABLE 8.—Tensile and Compressive Strengths of Neat Test Pieces

[Pounds per square inch.]

Burn No.	Per cent MgO	Method	Tested at end of—						
			24 hours	7 days	4 weeks	13 weeks	26 weeks	1 year	3 years
16	1.77	Tension	275	925	965	951	893	951	799
		Compression	2528	11 343	13 469	14 238	14 849	15 793	16 292
25	3.27	Tension	329	645	623	608	704	693	673
		Compression	2955	5233	6840	7610	9162	9502	8925
26	4.20	Tension	305	609	756	764	688	844	815
		Compression	3102	5818	9851	10 855	11 710	13 507	14 404
27	5.12	Tension	329	657	911	957	1015	928	998
		Compression	3015	7614	10 812	11 821	15 388	13 583	16 412
28	6.49	Tension	292	627	821	827	812	795	920
		Compression	2833	5560	7206	10 363	13 181	11 372	12 090
29	7.41	Tension	258	445	591	774	723	1062	1004
		Compression	2268	4184	6787	9438	10 923	10 321	12 820
30	9.50	Tension	209	300	464	543	647	800	738
		Compression	1318	3078	4794	8112	9089	9730	12 262
31	14.07	Tension	170	196	359	311	377	652	652
		Compression [a]	.....	.....	.....	.....	.....	.....	.....
32	18.98	Tension	27	30	38	77	73	([b])	([b])
		Compression	292	330	322	564	972	([b])	([b])
33	25.53	Tension	25	24	99	79	124	54	([b])
		Compression	127	311	453	719	2163	949	([b])
34	19.45	Tension	59	165	190	279	258	207	([b])
		Compression	892	1366	2486	5017	4833	7025	([b])
35	13.96	Tension	147	210	142	210	244	277	([b])
		Compression	1414	1695	1910	3471	4696	5128	([b])
36	10.33	Tension	230	242	431	644	625	687	[c] 778
		Compression	1770	2904	4305	5893	6371	8224	[c] 6613
37	8.03	Tension	236	381	586	713	712	728	[c] 859
		Compression	2142	4979	6969	8232	9897	12 308	[c] 10 481
38	7.80	Tension	345	382	598	647	793	856	933
		Compression	2170	4571	7679	8536	10 183	11 748	7548
39	6.62	Tension	359	495	630	733	719	837	897
		Compression	2746	4554	7582	8378	9504	10 707	7878
40	3.59	Tension	312	642	743	811	850	946	893
		Compression	3058	6717	9178	10 997	11 750	14 022	9610
41	2.01	Tension	354	674	860	736	823	850	865
		Compression	3517	8096	9104	10 760	12 400	15 240	9968

[a] No test pieces made.
[b] Disintegrated.
[c] Specimens are unusually full of crystals, but no enlargement or checking noticed.

Burns 32 to 35, inclusive, during the period between one and three years began to show increasing amounts of disintegration. At the end of this period all of the small specimens of these burns had enlarged to such an extent that they were not tested. It was impossible to place the tension specimens in the testing machine on account of their increased size and the amount of

warping. The compression specimens were also warped and cracked.

An examination of the specimens which have disintegrated shows that the cracks and cavities are filled with crystals of lime hydrate ($Ca(OH)_2$), magnesium hydrate ($Mg(OH)_2$), and sometimes calcium sulphoaluminate ($3CaSO_4 \cdot 3CaO \cdot Al_2O_3 + H_2O$). The first two compounds crystallize very similarly in hexagonal needles or plates, as shown in Fig. 9. The sulphoaluminate crystallizes in very fine needles, which, owing to their slenderness and intermingling, appear in some cavities like a mass of white powder. Such a mass is shown in Fig. 10.

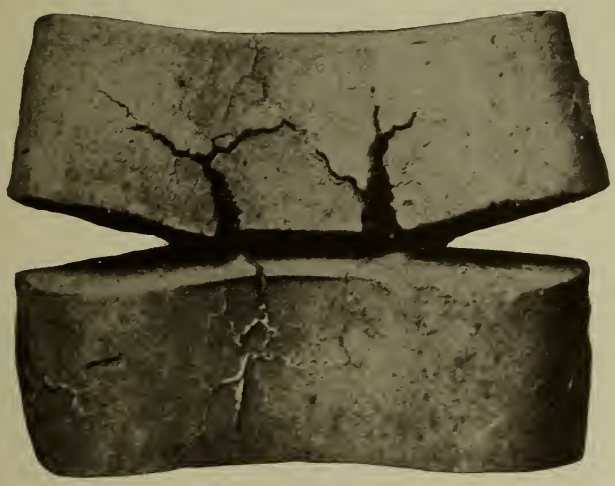


FIG. 8.—*Two of the briquettes of Fig. 7 placed so as to show the warping*

The cracked and most expanded surface was that next to the glass plate while the specimens were in the damp closet

The formation of the sulphoaluminate crystals occurs in larger amounts than has been noted before in this laboratory, but at the same time such pronounced disintegration has not been noted before. The indications, furthermore, would point to the fact that the sulphoaluminate has not produced the cracking, but has leached out into the cracks and voids and crystallized there. Fig. 10 shows this in particular. Here is a crack entirely free of crystals, yet immediately above and spanning it was a cavity well filled with them.

The presence of the magnesium-hydrate crystals can only be explained by the hydration of some of the compounds containing magnesia, which hydration was accompanied by the liberation of magnesia, followed by its hydration and accompanied by a very

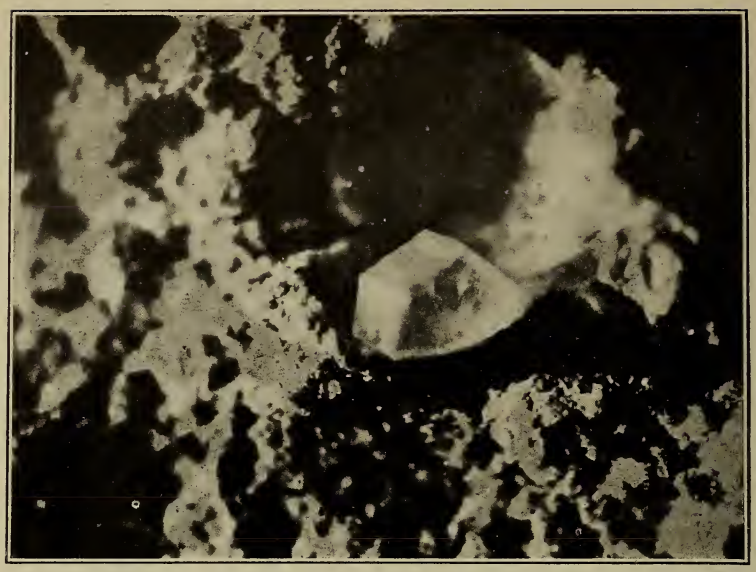


FIG. 9.—*A crystal of hydrated lime in a cavity of a neat specimen*

Frequently the cavity is almost completely filled with a network of crystals of this material. Two of such cavities are shown in Technologic Paper 78 of this Bureau. Magnified 16

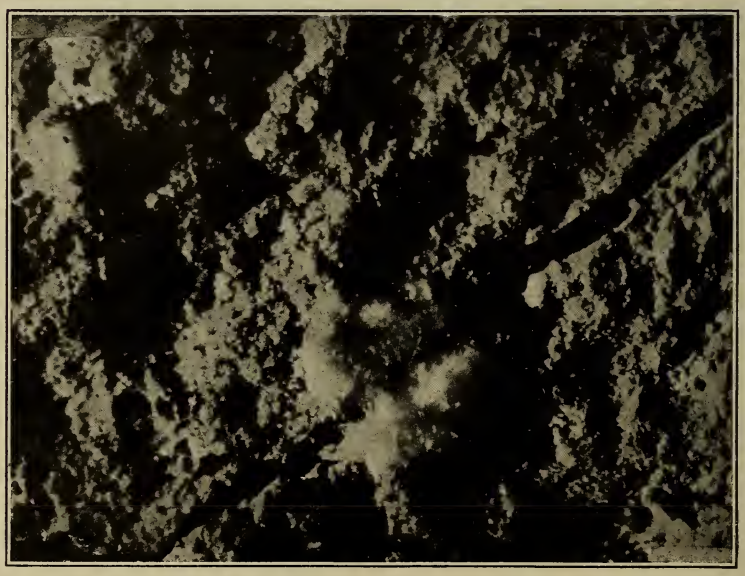


FIG. 10.—*A mass of very fine crystals of tricalcium sulphoaluminate* ($3CaSO_4.3CaO.Al_2O_3+H_2O$) *spanning a crack in a briquette made from burn 32 which had been stored in water*

The crystals are so fine that they appear as an amorphous mass except directly over the crack where there is a slight indication of their ocicular character. Magnified 16

much larger increase in volume than that which accompanied the hydration of lime. The magnesia occurs in these cements, when present in amounts less than 7.5 per cent, combined as a homogeneous compound either with the orthosilicate or the tricalcium aluminate; with greater amounts it is present as monticellite or spinel. So far as the hydration of these compounds is known, it is doubtful if magnesium hydrate would result from the tricalcium aluminate, as when pure it hydrates without splitting off any new compound. A microscopic examination of specimens shows that the spinel has not hydrated. A similar examination shows that the monticellite has hydrated, but the resulting compounds are not known. Recent work in this laboratory has shown that the orthosilicate of lime, in the presence of small amounts of water such as are usually used in making cement test pieces, does split off and allow the formation of calcium hydrate. Hence it would appear that the magnesium hydrate has resulted from the hydration of either the orthosilicate or the monticellite. That its formation would be more destructive than the formation of calcium hydrate is apparent from its relatively greater volume. It should be borne in mind that so far disintegration has been noted only in specimens containing very large amounts of magnesia. These consequently contain considerable amounts of monticellite and also, apparently, have the orthosilicate saturated with magnesia.

(*b*) *Mortar Test Pieces.*—In Table 9 are shown the results from the mortar test pieces. In general these bear out the statements made in regard to this class of cements when tested as neat test pieces. The increase of strength with age of the high magnesia cements in mortars is even more striking than as neat test pieces. This is to be expected, as a mortar usually allows more ready and complete hydration than the neat cement, so that the mortar would show a greater gain. The fact that a cement containing as much as 10.33 per cent magnesia (burn 36) at the end of one year has as a 1:3 mortar a tensile strength of 398 pounds per square inch and a compressive strength of 2802 pounds per square inch is certainly worthy of special mention.

When the three-year results with high magnesia are examined, as well as the three-year results of burn 30 (containing 9.5 per cent of magnesia), the lack of durability of such cements is clearly seen. It should be remembered, however, that in the expected life of a structure three years is a comparatively short time. The need of long-time tests for the other specimens is very clearly shown.

Burn 32 was the first of the cements to disintegrate as a mortar. This was noted at the end of one year. Some of the specimens of burn 33 next showed cracking. At the end of three years the specimens of burns 32 to 35, inclusive, were all enlarged and cracked. As noted above, the enlargement and cracking was least on the sides that were exposed to the atmosphere of the damp closet during the first 24 hours after molding. Fig. 11 shows the

FIG. 11.—*Two-year 1:3 standard sand mortar briquettes of burn 33 (on top) and burn 32 (below)*

This disintegration is characteristic of the very high magnesia cements

condition of some of the cubes of mortar made from burns 32 and 33 at the end of two years.

(*c*) *Concrete Test Pieces.*—The results from the concrete test pieces are shown in Table 10 and Fig. 15. These are the test pieces from which the behavior of high-magnesia cements can best be judged, yet it is readily seen from graphical representation of the results that their behavior was very similar to the small test pieces. It is necessary to increase the magnesia to almost 8 per

cent (the appearance of monticellite in the clinker) before there is any very marked change produced in the physical properties of the cement as a bonding material for making concrete.

TABLE 9.—Tensile and Compressive Strengths of 1:3 Standard Mortars

[Pounds per square inch.]

Burn No.	Per cent MgO	Method	Tested at end of—						
			24 hours	7 days	4 weeks	13 weeks	26 weeks	1 year	3 years
16	1.77	Tension	72	291	322	410	365	414	376
		Compression	398	2030	3516	4522	4199	4666	4329
25	3.27	Tension	156	193	281	363	362	347	203
		Compression	712	1284	1999	2156	3204	3374	2800
26	4.20	Tension	128	291	336	403	445	421	342
		Compression	555	1461	2725	3353	3761	4088	4200
27	5.12	Tension	108	275	445	443	480	459	408
		Compression	515	1326	3042	3379	4754	3896	4363
28	6.49	Tension	99	212	339	381	321	336	242
		Compression	640	1380	2504	3548	3715	3603	3882
29	7.41	Tension	91	149	341	427	430	376	274
		Compression	395	879	1708	2618	3368	3688	3963
30	9.50	Tension	58	110	217	378	367	355	141
		Compression	227	454	1324	1809	2977	2707	2633
31	14.07	Tension	29	52	79	160	186	224	224
		Compression [a]	.....	.....	.....	.....	.....	.....	.....
32	18.98	Tension	24	26	27	68	102	(b)	(b)
		Compression	117	133	140	288	612	442	(b)
33	25.53	Tension	Soft	Soft	38	87	73	116	(b)
		Compression	27	43	110	148	434	479	(b)
34	19.45	Tension	33	42	41	93	130	145	(b)
		Compression	147	137	545	896	1666	2374	(b)
35	13.96	Tension	69	65	55	134	150	82	(b)
		Compression	494	396	621	873	1628	1018	(b)
36	10.33	Tension	127	115	234	328	440	398	c 107
		Compression	318	455	1394	2216	2563	2802	c 1154
37	8.03	Tension	90	160	305	448	400	375	c 168
		Compression	386	844	2332	3550	3425	3193	c 3070
38	7.80	Tension	112	168	252	366	418	319	282
		Compression	489	911	1838	2018	2567	2986	2046
39	6.62	Tension	155	212	345	472	461	500	355
		Compression	653	928	2227	1939	2792	4508	2207
40	3.59	Tension	136	274	368	428	431	407	.....
		Compression	568	1585	2631	2697	3896	4100	2738
41	2.01	Tension	133	289	406	449	470	422	420
		Compression	673	1857	2696	3320	2758	4383	3315

[a] No test piece made.
[b] Disintegrated.
[c] Specimens are unusually full of crystals, but no enlargement or checking noticed.

As previously noted, the cements with the increasing amounts of magnesia show a very low strength at early periods; but with age the strengths become more nearly uniform, the high-magnesia

cements showing greater gains in strength. As the strengths are compressive strengths it might be argued that this is due to the late hydration of the magnesia compounds and consequent increased denseness of the test pieces, and that this hydration may continue and at very late periods cause disintegration. This may actually be the case, and only tests made after long periods will prove or disprove this statement. At the last period at which the concrete was tested (one and one-half years) there was a very satisfactory gain.

FIG. 12.—*Neat briquettes of the same cement broken: At upper right, 1 day; upper left, 7 days; lower left, 4 weeks; lower right, 1 year*

Note the difference of the fracture of the briquettes at the different periods. Magnified 3

It is well known that the denseness of the test pieces of cements of normal composition increases very markedly as they hydrate. This is seen in Fig. 12, which shows neat briquettes of the same cement broken at the end of 1, 7, and 28 days and 1 year. The continuous decrease in the sandy appearance is so marked as to require no comment, but it can be readily seen that if much further change takes place, especially if the mass hydrates to a different degree in different parts, a very great strain must result. In concrete where the cement is very unevenly distributed very uneven strains might be developed.

TABLE 10.—Compressive Strength of 1:1½:4½ Gravel-Concrete Cubes

[Pounds per square inch.]

Burn No.	Per cent MgO	Stored in—	Tested at end of—			
			4 weeks	13 weeks	26 weeks	1.5 years
16	1.77	Water	3491	4067	4081	6133
		Solution	3388	3829	3435	6245
25	3.27	Water	2910	3625	3765	5084
		Solution	2932	3756	3951	4996
26	4.20	Water	3275	3776	4379	6238
		Solution	3351	4261	4564	6558
27	5.12	Water	3410	4228	4605	6528
		Solution	3427	4194	4318	6276
28	6.49	Water	2489	3493	4185	5843
		Solution	2466	3173	3771	5875
29	7.41	Water	2059	3171	3431	5742
		Solution	1675	2813	3119	4650
30	9.50	Water	1616	2254	2589	4610
		Solution	1305	2343	2563	4068
31	14.07	Water	483	1040	1248	2608
		Solution	533	1342	1488	2989
34	19.45	Damp closet	133	476	787	1589
		Air	63	105	77	100
35	13.96	Water	408	768	1044	2062
		Solution	[a] 308	833	1127	2112
		Air	320	378	512	532
36	10.33	Water	1174	1868	2263	3903
		Solution	1003	1731	1917	3138
		Air	1271	1957	2002	2552
37	8.03	Water	1660	2580	2714	4454
		Solution	2008	2611	2744	3832
		Air	964	1262	1307	1657
38	7.80	Water	1836	2587	3232	4878
		Solution	1794	2624	3192	4697
		Air	1094	1404	1473	1604
39	6.62	Water	2261	3406	3142	4735
		Solution	1972	3330	3381	4186
		Air	1260	1362	1454	1562
40	3.59	Water	2286	2859	3037	4363
		Solution	2364	3032	3440	4522
		Air	1478	1612	1524	1838
41	2.01	Water	2416	2887	3206	4561
		Solution	2045	2729	3180	4348
		Air	1651	1800	1899	1882

[a] Wet when tested.

After the concrete specimens had been in the water or solution for the various alternate periods mentioned above for one year, they were stored continuously in the air of a building the temperature and humidity of which were those usually present in a laboratory. The result of this drying out was a very marked increase in strength at the end of one and one-half years over that noted at the end of a half year. Whether there will be a still greater

increase with time can only be ascertained when the specimens are broken, which will not be before five years. It is rather doubtful if this will be the case, as not only are the strengths abnormally high, but it can be seen from the results on the concrete stored only in air how slowly the hydration proceeded under such conditions.

When the specimens were removed from the solution at the end of one year, they were not different in appearance from those

FIG. 13.—*Pitting on a concrete cube of burn 36 at the end of 2.5 years*

This pitting occurs only over pieces of aggregate very close to the surface. It seems to be due to a more thorough hydration of the cement with a consequent increase in volume. This volume change tends to push the thin layers of cement away from the aggregate

removed from the water, excepting the white appearance due to the deposition of some hydrated magnesia. However, very slowly there appeared a pitting on some of the specimens, and at the end of one and one-half years it was quite marked on the specimens made from burns 36 and 37. At the end of two years it had also appeared on the specimens made from burns 38 and 39, though on the latter it was only seen after very close examination. At the end of two and one-half years the condition of the concrete

cubes of burn 36 is shown in Fig. 13. The character and amount of pitting are clearly shown, though it is not so readily noticeable that at the bottom of each pit is a piece of aggregate. (See Fig. 14.) These pits are not more than ⅛ inch deep. Apparently this has been caused by the solution penetrating through this ⅛-inch layer and, when subjected to the alternate wetting and drying, setting up stresses due to the more complete hydration. These stresses are sufficient to push the material out from the aggregate; but when there was no aggregate immediately present the stresses were distributed over the greater mass. Moreover, a microscopical examination shows complete hydration of both the

FIG. 14.—*Pitting on a concrete cube of burn 37 at the end of 2.5 years*

At the bottom of each pit is a piece of large aggregate. This is an enlargement of pitting similar to that shown in Fig. 13. Magnified 3

orthosilicate and the monticellite, also a relatively marked absence of crystalline products of hydration (the only pronounced one being calcium carbonate), but a very marked amount of isotropic material. Consequently the blistering has not likely been produced by a mechanical stress set up by the force of crystallization but rather by the uneven strain produced by the complete hydration of this thin layer restrained on one side by the aggregate.

If this explanation is true, then it must also be granted that the salts in the solution have aided this hydration, since the specimens subjected to water do not show the blistering. This is quite likely the case, as in a previous paper from this Bureau

the accelerating influence of a chloride in the solution of cement was shown very clearly quantitatively.[11]

Another feature of this blistering is worthy of note. The cubes were molded in cast-iron molds, which, of course, allowed the

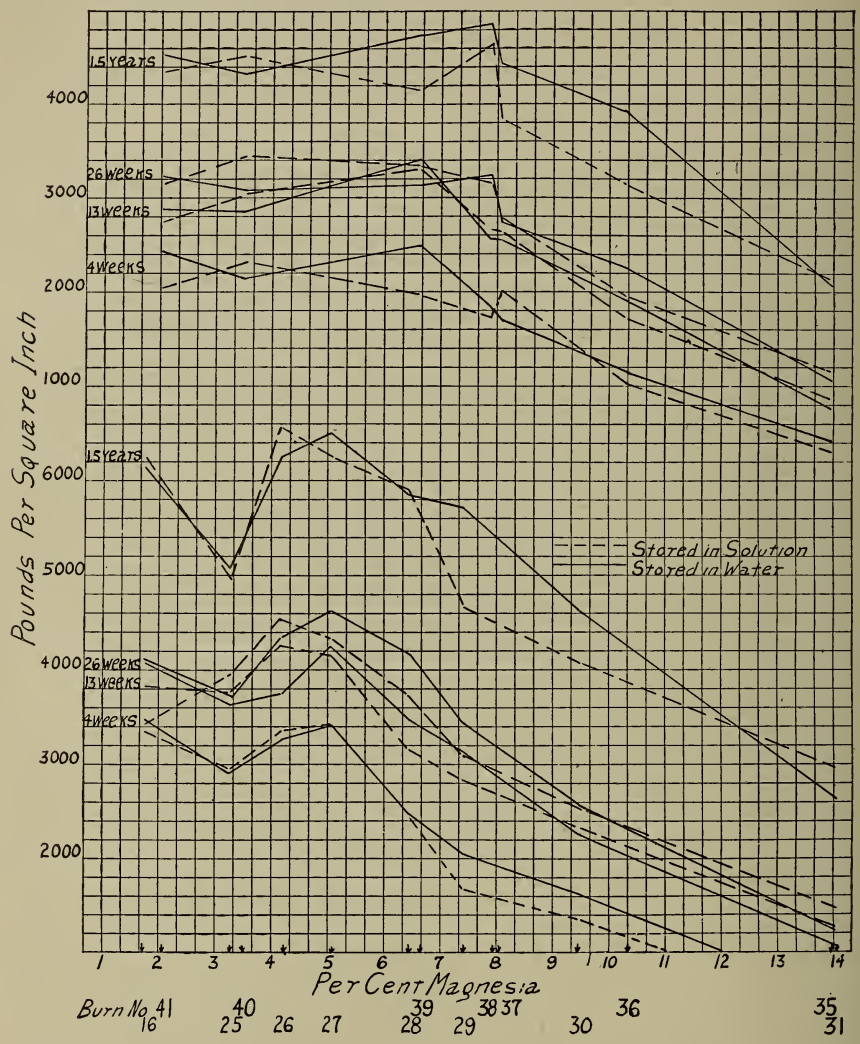


FIG. 15.—*Compressive strength 1:1.5:4.5 concrete*

upper side of the cube to be exposed to atmospheric influence immediately from the time of troweling off the surface. The surface was, therefore, exposed to the action of the carbon dioxide of the atmosphere, while it was still wet, for the first 24 hours

[11] Bates, Phillips, and Wig, "Action of the Salts in Alkali Water and Sea Water on Concrete," Bureau of Standards Technologic Paper No. 12.

after molding and before placing in the solution. This surface does not show any blistering. Apparently the comparatively short period of carbonation was sufficient to bring about a decided protective influence. Attention previously was called to the effect of the atmosphere on the exposed surface of neat briquettes during the first 24 hours after molding, when they are stored in the damp closet. It was shown that this surface warps and disintegrates to a very much less degree than the lower surface, which is protected from the atmosphere by the glass plate upon which it rests.

The concrete cubes of burn 31, which had been stored in water with the alternate dryings, show a number of very fine cracks filled with crystals. The nature and cause of these cracks is a matter of conjecture. They do not appear like disintegration cracks, which are usually very narrow at the center of the face and become larger as they extend toward the edge, but are of uniform thickness throughout their entire length. They appear more like shrinkage cracks, particularly on account of their uniform thickness and their somewhat irregular course on the surface. In view of the fact that these cubes were not placed in the water until the end of a week after making, on account of their very slow hardening, it is quite likely that they are shrinkage cracks, although they were covered with wet burlap during the first week of hardening, and no cracks were noticed when they were first immersed. The cubes of this burn, which had been stored in the solution, do not show these cracks, but this may be on account of the deposition of hydrated magnesia on their surface; the cracks may actually be present.

Another somewhat strange feature of this blistering of the cubes is the fact that it appears upon certain burns while upon other burns of very similar magnesia content it is not noticeable at all. Thus if it were a matter of magnesia alone, why have not the cubes of burns 28, 29, and 30, which have a magnesia content within the same limits as burns 36 to 39, shown the same results? While generally the former burns were of a lower alumina and higher silica content than the latter, this amount appears too small to cause such a difference. But at the same time their higher silica and lower alumina contents give strengths about 25 per cent higher throughout the entire test series. Consequently had the alternate wetting and drying continued, it might have followed that at a later period the cubes of burns 28

to 30 would also have shown the blistered disintegration, they being stronger than the cubes of burns 36 to 39, and consequently requiring a greater force to disrupt the thin film of mortar over the aggregate. In the case of the latter burns the treatment was sufficiently long to bring about the result, but did not extend to a longer period, for this blistering is never more than ⅛ inch deep and seldom that. Furthermore, it had not progressed to such an extent as to actually break the blisters; they were only raised slightly on the surface. The pittings shown in the photograph were produced by breaking the blister by rubbing. The thin exterior film of set neat cement was in almost perfect condition.

V. SUMMARY

1. Portland cement with a magnesia content of about 9.50 per cent may be burned in a rotary kiln without producing a clinker materially different from one containing less than 4 per cent. The clinkering temperature will be reduced somewhat, however. With greater amounts of magnesia present the resulting clinker is very vitreous and dusts more or less slowly, the rapidity and amount of dusting increasing with the magnesia content. High-magnesia clinker is of a light-brown color, in strong contrast to the usual dark, glistening, normal clinker. The resulting ground cement is of a light-brown color, which makes a concrete decidedly different in color from concrete made from normal cement.

2. No new constituents are present in the high magnesia cements until the magnesia has reached about 8 per cent. A very small amount of the mineral monticellite ($CaO.MgO.SiO_2$) is then noted. The amount of this constituent increases rather rapidly with the increase of the amount of magnesia. Further, when the latter has reached about 10 per cent, the mineral spinel ($MgO.Al_2O_3$) is noted; this also increases in amount as the magnesia increases. There was about 23 per cent of monticellite present in the clinker made from dolomite only (25.5 per cent MgO). The amount of spinel was not determined in this case, but it was not more than a minor constituent.

3. With the largely increased amounts of magnesia the amount of orthocilicate of lime was very decidedly decreased. The amount of tricalcium silicate was not affected materially. As the amount of spinel was very small in any case, the amounts of tricalcium aluminate were only slightly decreased in the case of the higher magnesia clinker.

4. The structure of the very high-magnesia clinkers was decidedly different from those of normal composition. The former were much more crystalline in character, the crystals having developed to a comparatively large size and with well-defined outline. In normal clinker the crystals are not only small but usually lack outline, being fused into and surrounded by the invariably poorly crystallized orthosilicate.

5. When the magnesia content did not exceed 9.5 per cent, there was no marked change noted in the time of set, though there was apparently a slight tendency toward slower final set. When the magnesia exceeded this amount, the initial set became quite rapid, accompanied by a marked evolution of heat. In some cases this produced a drying out, which caused the appearance of a quick, false, final set. In other cases the evolution of heat was not so marked, and there resulted a slow final set. This quick initial set could be predicted from the changes noted, by the microscopic examination, in the structure and the character of the constituents of the clinker. In this class of cements the constituents are well defined and not surrounded so uniformly by the slow-hardening orthosilicate. Furthermore, the amount of this latter constituent is materially reduced in the high-magnesia cements, while the quickly setting aluminate and tricalcium silicate are but slightly changed in amount.

6. With the exception of two of the very high-magnesia cements the other high magnesia cement pats showed these cements were sound either when stored in water for 28 days or in air for 28 days or subjected to boiling water or steam at the end of 24 hours. These two unsound cements developed a very slow final set, and when subjected to the boiling and steaming tests had not attained their final set; consequently, after the test they were soft and somewhat enlarged. (Burns 25 and 26, of low magnesia content, were also unsound, due to inability to secure sufficient gas for proper burning.)

7. The strengths developed, either by the neat cement or 1:3 sand mortar or 1:1½:4½ gravel concrete, show that cements containing as much as 7.5 per cent of magnesia are satisfactory. It would be impossible to predict from the strength tests at the end of one and one-half years which were the cements containing low magnesia or magnesia up to 7.5 per cent. With higher amounts the strengths developed decreased with increased magnesia, but even with the high-magnesia cements there is a notable increase of strength with age.

8. The strength of the concretes subjected to the action of the solution of salts was not materially different from that of those subjected to the action of water. While some of the specimens did show a slight disintegration, it was not sufficient to affect their strength at the last period at which they were tested, and, furthermore, it appeared in the case of concrete made from cements of moderate magnesia content and was not noted in those of high magnesia content.

9. The high-magnesia cements contain a large amount of "insoluble residue."[12] This residue is the monticellite and spinel, both of which are very largely insoluble in dilute acids.

10. Measurements to determine changes in the volume of the concrete with the progress of hydration, show in some cases a slightly greater change produced by the high-magnesia cements than by the low-magnesia ones.

11. Strength specimens to be tested at still later periods than those reported in this paper are on hand. It may be that at very late periods some of the conclusions which appear justified from the present results may require revision.

Attention should again be called to the fact that the work presented in this paper was not undertaken to show the advisability of allowing a greater magnesia content in cement, but only to determine how greater amounts of magnesia affect the constitution and properties of cement of normal composition.

Acknowledgments are due to A. A. Klein for the petrographic examinations and to E. R. Gates for superintending the molding and breaking of all test pieces.

WASHINGTON, MAY 1, 1917.

[12] Bureau of Standards Circular No. 33; United States Government Specifications for Portland Cement.