

## REACTION OF WATER ON CALCIUM ALUMINATES

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## ABSTRACT

The four calcium aluminates ( $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $3\text{CaO} \cdot 0.5\text{Al}_2\text{O}_3$ ,  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) have been made, and the mechanism of their reaction with water has been studied. The tricalcium aluminate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , reacted so rapidly with water that changes in the composition of the resulting solutions could not be followed. The other calcium aluminates, as well as a high alumina cement, reacted with water to form metastable and supersaturated monocalcium aluminate solutions in the early periods. The metastable solutions decomposed as the reaction proceeded with the precipitation of varying amounts of hydrated alumina and crystalline hydrated tricalcium aluminate, with attendant increases in both the pH and molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , in the resultant solutions. The constitution of the aluminate solutions has been discussed. Calculations based upon electrometric measurements and chemical analyses indicate that the aluminate in solution is the calcium salt of monobasic aluminic acid. A study of the subsequent changes in the aluminate solutions, attended by increasing concentrations of calcium hydroxide, indicates that a hydrated tetracalcium aluminate may be formed in solutions where the pH value is greater than 12.0. An electrometric titration study of aluminum chloride and calcium hydroxide and an investigation of the calcium chlor-aluminates are described.

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## I. INTRODUCTION

Investigations<sup>1</sup> of the ternary system, lime-alumina-silica, have established the constitution of all definite combinations of lime and alumina, lime and silica, alumina and silica, and lime, alumina, and silica. They have shown that lime can combine with alumina at high temperatures only in the following molecular proportions:  $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ ,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . Tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) appears to be the only aluminate in Portland cement of normal composition and normal properties. The other main constituents of such cements are tricalcium silicate ( $3\text{CaO} \cdot \text{SiO}_2$ ) and the beta form of dicalcium silicate ( $2\text{CaO} \cdot \text{SiO}_2$ ). The monocalcium aluminate ( $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) and the 3:5 calcium aluminate ( $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ ) occur in the cements characterized by a high alumina content. Such cements have the property of hardening in a short time and acquiring meanwhile very high strengths. The cementing qualities of the calcium aluminates have been reported by Bates;<sup>2</sup> the properties of the calcium silicates and calcium aluminates occurring in normal Portland cement, by Bates and Klein;<sup>3</sup> and the hydration and hydrolysis of the compounds which may occur in Portland cement, by Klein and Phillips,<sup>4</sup> and by Lerch and Bogue,<sup>5</sup> respectively.

These investigations have indicated that the setting of all calcium aluminates is accompanied by the formation of hydrated tricalcium aluminate with or without hydrated alumina. Recently some preliminary experiments, undertaken at the bureau, had indicated that the setting of the calcium aluminates and high alumina cements might be closely related to their reaction with water in the formation of metastable and supersaturated solutions of calcium aluminates. From these solutions the hydrated tricalcium aluminate and hydrated alumina precipitated. It was decided, therefore, to investigate this reaction and obtain more information as to its mechanism.

The first part of this paper concerns not only the chemical composition and pH values of these solutions as they are formed in the early period of setting, but also the changes which they undergo as the solutions pass from a metastable condition to one of equilibrium. Then, at this point, a further study was also made of subsequent changes in the aluminate solutions attended by increasing concentrations of calcium hydroxide, a product of the hydrolysis of the cal-

<sup>1</sup> Rankin and Wright, "The ternary system lime-alumina-silica," *Am. J. Sci.*, **39**, p. 1; 1915; Bowen and Greig, "The system  $\text{Al}_2\text{O}_3\text{-SiO}_2$ ," *J. Am. Cer. Soc.*, **7**, p. 238; 1924; Hansen, Dykerhoff, Ashton, and Bogue, "Studies of the system lime-alumina-silica. The composition  $8\text{CaO} + \text{Al}_2\text{O}_3 + 2\text{SiO}_2$ ," *J. Phys. Chem.*, **31**, pp. 607-615; 1927.

<sup>2</sup> Bates, Cementing Qualities of the Calcium Aluminates, B. S. Tech. Paper No. 197.

<sup>3</sup> Bates and Klein, Properties of the Calcium Silicates and Calcium Aluminate Occurring in Normal Portland Cement, B. S. Tech. Paper No. 78.

<sup>4</sup> Klein and Phillips, Hydration of Portland Cement, B. S. Tech. Paper No. 43.

<sup>5</sup> Lerch and Bogue, "Studies of the hydrolysis of compounds which may occur in Portland cement," *J. Phys. Chem.*, **31**, p. 1627; 1927.

cium silicates. The second part of the paper deals with an electro-metric titration study of aluminum chloride and calcium hydroxide and an investigation of the calcium chlor-aluminates.

## II. REACTION OF WATER ON THE CALCIUM ALUMINATES

### 1. PREPARATION OF COMPOUNDS

The following calcium aluminates were made by W. Lerch by the methods developed in this laboratory:<sup>6</sup>

3:5 calcium aluminate.....	3CaO.5Al <sub>2</sub> O <sub>3</sub>
Monocalcium aluminate.....	CaO.Al <sub>2</sub> O <sub>3</sub>
5:3 calcium aluminate.....	5CaO.3Al <sub>2</sub> O <sub>3</sub>
Tricalcium aluminate.....	3CaO.Al <sub>2</sub> O <sub>3</sub>

For the preparation of these binary compounds, chemically pure calcium carbonate and alumina were mixed in the proper proportions with a little water, molded into bars, and burned in an up-draft, gas-fired kiln for four hours at a temperature<sup>7</sup> of  $1,350 \pm 20^\circ$ . To obtain a homogeneous product the material was ground, remolded, and reburned at the same temperature. No free lime was found in any of these reburned aluminates either by the White's test<sup>8</sup> or by the method of titration with ammonium acetate.<sup>9</sup> Microscopic examinations<sup>10</sup> showed the resultant material to be homogeneous and of the desired constitution. The materials were then ground to a degree of fineness such that about 90 per cent passed a No. 200 sieve.

### 2. APPARATUS AND SOLUTIONS EMPLOYED

For the determination of the hydrogen-ion concentration of the aluminate solutions, the electrometric method was used. The potentiometric system consisted of a Leeds and Northrup type K potentiometer and type R galvanometer with properly shielded switchboard and wiring. The Weston cell values were certified by the electrical division of this bureau.

The saturated KCl-calomel electrode was used in the hydrogen ion set-up. Its use does not necessitate the protection from contamination by the saturated KCl used in making liquid junctions required in the use of normal and tenth-normal electrodes. A gooseneck siphon, constricted at the tip, connected the tightly stoppered bottle containing the saturated KCl of the liquid junction with the hydrogen electrode vessel of 100 ml capacity. By this arrangement the contamination of the solutions was reduced to a minimum, and any inherent error was probably very small and constant. The stem of a separa-

<sup>6</sup> B. S. Tech. Papers Nos. 43, 78, and 197; Lerch and Bogue, *J. Phys. Chem.*, **31**, p. 1627; 1927.

<sup>7</sup> All temperatures in this work are expressed in the centigrade scale.

<sup>8</sup> A. H. White, *J. Ind. Eng. Chem.*, **1**, p. 5; 1909.

<sup>9</sup> Lerch and Bogue, *Ind. Eng. Chem.*, **18**, p. 739; 1926.

<sup>10</sup> Made by F. W. Ashton, of this bureau.

tory funnel, filled with saturated KCl, led into the bottle containing the saturated KCl of the liquid junction. By opening the stopcock of this funnel the gooseneck siphon could be washed free of any contamination from the solution of the hydrogen electrode vessel.

A simple wire type of hydrogen electrode was used. By bubbling hydrogen through a small hole in the side of the glass tube containing the platinized wire, the solution of the electrode vessel was surged about the electrode. A small hole in the stopper of the electrode vessel served as an outlet for the hydrogen. By this arrangement air was conveniently expelled from the electrode vessel and excluded during the measurement. In fact, all operations were made with protective measures against contamination by atmospheric carbon dioxide. The hydrogen used was electrolytic hydrogen supplied in tanks. It was passed through a series of wash bottles containing solutions of alkaline potassium permanganate, alkaline pyrogallol, mercuric chloride, and a solution similar to that contained in the electrode vessel, respectively.

All materials were purified with great care, and the system was checked against standard buffered solutions and was found to conform to the standard as recommended by W. M. Clark.<sup>11</sup>

The cells and the solutions to be studied were kept in an air thermostat well insulated by an air space of 1 inch between double glass walls. There were also double glass doors through which, when opened, the apparatus could be reached. Heating of the air was effected by bare nichrome resistance wire strung on an open frame of asbestos board. A small electric blower, with well-insulated piping, mounted outside the thermostat provided for a rapid circulation of air. The heater was placed at the air exit of this blower. The thermostat maintained a temperature of  $30 \pm 0.05^\circ$  by means of a toluene-mercury regulator connected to an electric control similar to the device of D. J. and J. J. Beaver,<sup>12</sup> but modified for operation with a U. X. 201-A radio tube.

In accordance with custom, the hydrogen ion concentration is expressed in this paper in terms of Sørensen's pH, which is defined by the relation  $pH = \log \frac{1}{[H^+]}$ . As all electrometric measurements were made at  $30^\circ$ , the pH of the solutions was calculated from the formula

$$pH = \log \frac{1}{[H^+]} = \frac{E. M. F. (\text{observed}) - 0.2437}{0.06011}$$

where the *E. M. F.* is expressed in volts.

<sup>11</sup> W. M. Clark, Determination of Hydrogen Ions, Williams & Wilkins, Baltimore; 1922.

<sup>12</sup> D. J. and J. J. Beaver, J. Ind. Eng. Chem., 15, p. 359; 1923.

### 3. METHOD OF PROCEDURE

Preliminary experiments indicated that metastable calcium aluminate solutions were formed during the reaction of water with the anhydrous calcium aluminates or high alumina cement. It was, therefore, decided to study not only the chemical composition and pH of these solutions as they were formed in the early period of the setting processes, but also to follow the changes which they underwent as the solutions passed from a more or less metastable condition to one more nearly approaching equilibrium.

The procedure followed in this study was to shake the anhydrous calcium aluminate or high alumina cement with distilled water in the proportion of 50 g of solid to 1 liter of water for a given time and then filter the mixture rapidly through a Büchner funnel. Samples of these filtrates were taken at once for chemical analyses and for pH determinations. In the analyses the solutions were made slightly acid with hydrochloric acid and the aluminum was precipitated as the hydroxide and ignited to the oxide according to Blum's method.<sup>13</sup> In the analyses of the more concentrated aluminate solutions the aluminum hydroxide was dissolved and reprecipitated before ignition. The calcium was precipitated as the oxalate, ignited to constant weight in a platinum crucible, and weighed as the oxide.

After the samples had been taken the filtered solutions were set aside in well-stoppered flasks for further observations. On standing, part of the lime and alumina precipitated from the clear solutions in changing from a metastable condition to one more nearly approaching equilibrium. After two weeks the resulting mixtures were filtered. Samples of these filtrates were also taken for chemical analyses and for pH determinations. The precipitates were washed with alcohol and ether and dried in a desiccator containing anhydrous calcium chloride. The dried material was examined with the petrographic microscope<sup>14</sup> and analyzed chemically for lime, alumina, and water (loss on ignition). It was preferable to make the analyses for alumina and lime on samples other than those used for the determination of loss on ignition, since heat converted a portion of the alumina to a form difficultly soluble in acids.

### 4. REACTION OF WATER ON MONOCALCIUM ALUMINATE ( $\text{CaO} \cdot \text{Al}_2\text{O}_3$ )

Klein and Phillips<sup>15</sup> have shown, by petrographic methods, that monocalcium aluminate starts to hydrate almost immediately upon the addition of water. Bates<sup>16</sup> has pointed out that the high alumina cements, which contain this aluminate, develop most of their high

<sup>13</sup> W. Blum, Determination of Aluminum as Oxide, B. S. Sci. Paper No. 286.

<sup>14</sup> Examinations made by Dr. H. Insley, of this bureau.

<sup>15</sup> B. S. Tech. Paper No. 43.

<sup>16</sup> B. S. Tech. Paper No. 197.

strengths within 24 hours. It has also been observed that the reaction of water on the other calcium aluminates progresses rapidly. For these reasons the study herein described was particularly concerned with those reactions occurring within the first few hours.

Accordingly, mixtures of anhydrous monocalcium aluminate and distilled water in the proportion of 100 g of solid to 2 liters of water were shaken in flasks to prevent setting. After a definite interval of time one of these mixtures was filtered through a Büchner funnel, and later, when another definite period of time had elapsed, a second mixture was filtered. This process was continued until all had been filtered. In this way successive definite increments of time were represented by each filtration. Filtering required between 5 and 10 minutes. After the samples had been taken the clear filtrates were set aside in well-stoppered flasks for further observations. Since these clear metastable solutions were metastable in varying degrees, it was necessary to examine them immediately after filtering from the reaction mixture. Thus, the determination of the pH values of the samples of the filtered solutions were started at once, as it was observed that a precipitation of lime and alumina from the clear metastable filtrates began, in some cases, within two or three hours after filtering. Then, at the end of two or three weeks, the mixtures resulting from the decomposition of the metastable solutions were also studied.

The data obtained in these investigations are recorded in Tables 1 and 2. In Table 1 the figures in the first column refer to the number of the experiment, and the second column gives the time of contact of the monocalcium aluminate with water before filtration. The columns designated by A (columns 3, 5, 7, 9, 11, and 13) contain the data as determined and calculated with respect to the solutions obtained directly upon filtering from the reaction mixtures and are, therefore, descriptive of conditions of the clear filtrates prior to any subsequent decomposition after filtering. In the columns designated B (columns 4, 6, 8, 10, 12, and 14), there are recorded the results of the same measurements as described under A. However, in the case of B the measurements were made upon the solutions (numbered the same as those of A in column 1), but after an elapse of two or three weeks, whereas the results and calculations tabulated under A refer to the same original solutions at the time immediately following filtration as above described. A comparison of the data of each column A to those of its adjacent column B shows, therefore, the changes which have occurred in the filtered solutions in passing from a more or less metastable condition to one more nearly approaching equilibrium and with an attendant precipitation of some of the alumina and lime.

TABLE 1.—Composition and pH of aluminate solutions from monocalcium aluminate (CaO.Al<sub>2</sub>O<sub>3</sub>)

No.	Time of contact of CaO. Al <sub>2</sub> O <sub>3</sub> with water before filtering	Total alumina in solution, g Al <sub>2</sub> O <sub>3</sub> per l		Total lime in solution, g CaO per l		Molar ratio CaO/Al <sub>2</sub> O <sub>3</sub> in solution		Lime in solution in excess of CaO.Al <sub>2</sub> O <sub>3</sub> , g CaO per l		Observed E. M. F. of solutions at 30°		pH of solutions at 30°		Ratio of lime in solution in excess CaO-Al <sub>2</sub> O <sub>3</sub> $\frac{(CaO)_A}{(CaO)_B}$	Ratio of hydroxyl-ion concentration $\frac{[OH^-]_A}{[OH^-]_B}$
		A	B	A	B	A	B	A	B	A	B	A	B		
		Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	15 minutes	2.1850	0.2500	1.2930	0.4455	1.08	3.21	0.0912	0.3080	0.9165	0.9481	11.19	11.72	0.296	0.300
2	30 minutes	2.3555	.2550	1.3970	.4320	1.08	3.08	.0912	.2917	.9186	.9492	11.22	11.73	.312	.310
3	1 hour	2.3500	.2460	1.3730	.4135	1.07	3.05	.0805	.2782	.9179	.9484	11.21	11.72	.290	.311
4	2 hours	2.2000	.2415	1.2880	.4005	1.06	3.01	.0780	.2677	.9182	.9483	11.21	11.72	.291	.316
5	4 hours	2.2350	.2420	1.2910	.4155	1.05	3.08	.0617	.2824	.9157	.9466	11.18	11.69	.218	.306
6	5 hours	2.0910	.2530	1.1960	.4060	1.04	2.84	.0459	.2668	.9179	.9474	11.21	11.70	.172	.323
7	6 hours	.9445	.2445	.6085	.4320	1.17	3.21	.0891	.2975	.9246	.9494	11.32	11.74	.300	.387
8	1 day	.4500		.4165		1.68		.1690		.9389		11.56			
9	3 days	.3170		.4560		2.61		.2816		.9453		11.67			
10	7 days	.2680		.4620		3.13		.3148		.9487		11.73			
11	14 days	.2400		.5165		3.90		.3746		.9498		11.74			
12	28 days	.2550		.5050		3.21		.3648		.9510		11.76			
13	420 days	.1600		.4715		5.36		.3835		.9500		11.76			

Accordingly, columns 3 and 4 give the alumina in solutions, as grams  $\text{Al}_2\text{O}_3$  per liter, directly upon filtering and at equilibrium, respectively, as previously described, and columns 5 and 6 the lime in the corresponding solutions as grams  $\text{CaO}$  per liter. Column 7 shows the molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , in solution directly upon filtering as calculated from the data of columns 3 and 5, and column 8 gives this ratio in the resultant equilibrium solutions as calculated from the alumina and lime in columns 4 and 6. Column 9 gives the lime, as grams  $\text{CaO}$  per liter in excess of monocalcium aluminate, obtained by subtracting from the lime of column 5 the calculated quantity of lime which will combine with the alumina of column 3 as a calcium aluminate of the composition,  $\text{CaO}.\text{Al}_2\text{O}_3$ . Column 10 gives this excess of lime, computed in the same manner, from the data of columns 6 and 4. Column 11 gives the observed E. M. F., as determined with the hydrogen-ion set-up, of the solutions (A) containing the alumina of column 3 and the lime of column 5, and column 12 the observed E. M. F. of the corresponding solutions (B) at equilibrium which contain the dissolved alumina of column 4 and the dissolved lime of column 6. Columns 13 and 14 contain the pH values calculated from the observed E. M. F. determinations of columns 11 and 12, respectively. The data of the last two columns (15 and 16) will be discussed later. In the light of the above description the subsequent tables, which contain the results of the reaction of water on the other aluminates, will be self-explanatory.

In Figure 1 the quantities of alumina and lime (recorded in columns 3 and 5 and expressed as grams  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  per liter, respectively), dissolved in water, are plotted against the time (in hours) of contact of the aluminate with water. The pH values of the solutions, recorded in column 13, are also plotted against this time.

From the data of columns 3 and 5 of Table 1, as plotted in Figure 1, it is seen that the reaction of water on monocalcium aluminate progresses rapidly. The quantity of both alumina and lime dissolved by the water attained a maximum in 30 minutes and then gradually decreased until about five hours had elapsed. Further shaking resulted in a rapid decrease, which, in turn, became less as time progressed. An apparent state of equilibrium was reached only after several weeks had elapsed.

It is interesting to observe (column 7, Nos. 1 to 7, inclusive) that anhydrous monocalcium aluminate reacted with water in the early periods to form calcium aluminate solutions with a molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , of approximately 1. The pH of these solutions (columns 13, Nos. 1 to 7, inclusive) was very nearly 11.20. At the later periods (Nos. 8 to 13, inclusive), the molar ratio of  $\text{CaO}/\text{Al}_2\text{O}_3$  in solution had increased, with a simultaneous increase in the pH, until the point pH 11.75 was reached, even though the actual quantities of both

alumina and lime in solution decreased. It should be noted (columns 9 and 13) that the increase in pH is accompanied by a corresponding increase of the lime in solution in excess of that calculated to be in combination with the alumina in solution as monocalcium aluminate. A more detailed discussion of this relation will be presented later in this paper.

Turning now to a consideration of the determined and calculated data of columns B of Table 1 in comparison to those of columns A of the same table, it can be seen that changes identical to those described above also took place in the more or less metastable solutions

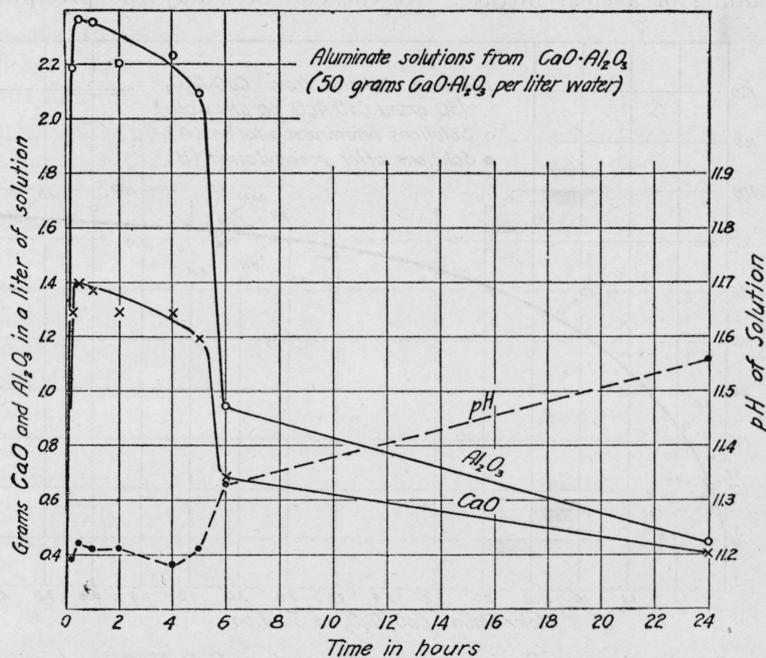


FIG. 1.—Showing the composition and pH of aluminate solutions from  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  as functions of the time of contact with water

which had been filtered from the reaction mixtures and subsequently had approached equilibrium on standing. A portion of the alumina and lime had precipitated from the clear metastable filtrates (Nos. 1 to 7, inclusive, of columns 3 and 5, respectively), leaving "equilibrium" solutions similar in composition (Nos. 1 to 7, inclusive, of columns 4 and 6, respectively) to those obtained when the anhydrous monocalcium aluminate had been left in contact with water for long periods (Nos. 10 to 13, inclusive, of columns 3 and 5, respectively). The molar ratio of lime to alumina increased as the metastable solutions approached equilibrium on standing, as can be noted from a comparison of the values of Nos. 1 to 7, inclusive, of column 7 to

those of column 8. This also was accompanied by an increase in pH (column 14) to about 11.75, the approximate value obtained for the solutions filtered from the reaction mixtures at the later periods (Nos. 10 to 13, inclusive, of column 13). In Figure 2 the pH values of all of the solutions are plotted against the molar ratio of lime to alumina,  $\text{CaO}/\text{Al}_2\text{O}_3$ , in these solutions.

Table 2 contains the chemical analyses of the material precipitated, at the end of two weeks, from the filtered metastable calcium aluminate solutions. Precipitation of this material started from the first six of these solutions within two or three hours after filtering and the obtaining of a clear filtrate. At the end of a day the precipitate

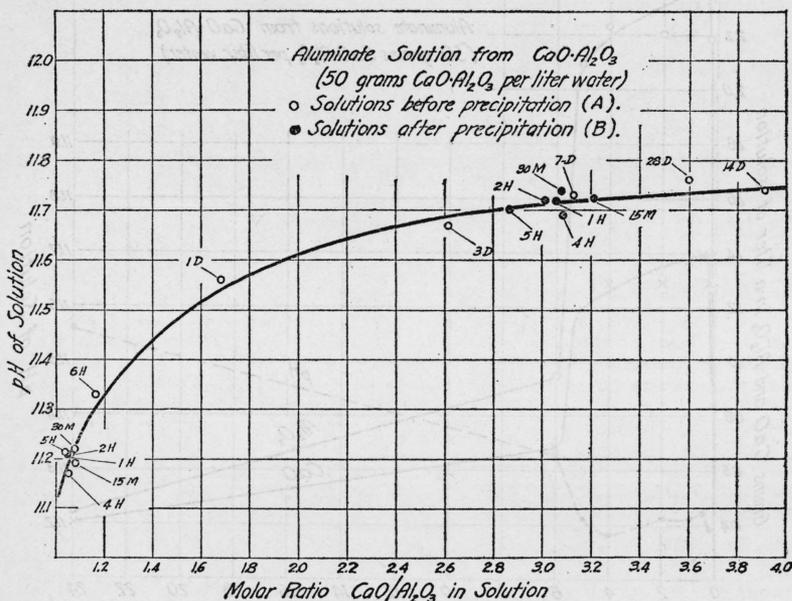


FIG. 2.—Showing the pH of aluminate solutions from  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  as a function of the molar ratio  $\text{CaO}/\text{Al}_2\text{O}_3$  in solution

covered the bottom of the flask to a depth of about 0.5 cm. Two or three days later small spherulites of crystals appeared on the walls of the flasks. These spherulites, in turn, were covered gradually by a thin film of amorphous material. Also, at the end of this two-week period, when the mixtures were filtered a portion of the material adhered so firmly to the walls of the flasks that it could not be loosened even by vigorous shaking. This loss of material in filtering probably accounts for the differences in the molar ratio of lime to alumina in the precipitate as calculated from the chemical analyses of the material recovered and that as computed from the analyses of the aluminate solutions in the metastable condition (A) and at "equilibrium" (B). In either case, however, the molar ratio of  $\text{CaO}/\text{Al}_2\text{O}_3$  in the precipi-

tate is less than 1.0. This indicates that the precipitate was composed either of a calcium aluminate hydrate with a molar ratio, lime to alumina, less than 1.0, or else was a mixture of hydrated alumina and a more basic calcium aluminate hydrate.

Microscopic examination showed that all samples were composed wholly of the following three phases:

A. A crystalline phase in flat, hexagonal plates with the refractive indices as follows:  $\omega = 1.535 \pm 0.004$ ,  $\epsilon = 1.515 \pm 0.005$ . The plates were uniaxial negative. The spherulites consisted of radiating aggregates of these crystals.

B. Amorphous material, apparently colloidal aggregates, often in spheroidal form in irregular clumps. Portions of these areas sometimes showed the uniaxial cross as in spherulites and in colloidal portions of fibers. The amorphous material sometimes occurred in thin flakes with polyhedral boundaries, as if broken away from the sides of the containing vessel. It was difficult to obtain the index of the amorphous material. The average index was about 1.48, but was a variable quantity.

C. Calcite. This occurred in aggregates of very minute crystals seldom exceeding  $5 \mu$  in greatest dimension. This appeared in very small amounts in all samples except No. 3.

TABLE 2.—Chemical analyses of the material precipitated from the clear metastable calcium aluminate solutions prepared by shaking anhydrous monocalcium aluminate with water in the proportion of 50 g  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  per liter of water

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Time of contact of aluminate with water before filtering.....	15 min.	30 min.	1 hr.	2 hrs.	4 hrs.	5 hrs.	6 hrs.
Analysis of precipitate:							
Per cent $\text{CaO}$ .....	17.48	19.28	18.90	17.09	17.52	17.16	(1)
Per cent $\text{Al}_2\text{O}_3$ .....	40.72	42.80	42.28	40.19	39.86	40.40	(1)
Per cent $\text{H}_2\text{O}$ .....	42.33	37.51	39.00	42.30	42.60	43.78	(1)
Total.....	100.53	99.59	100.18	99.58	99.98	101.34	-----
Molar ratio $\text{CaO}/\text{Al}_2\text{O}_3$ in the precipitate from above analyses.....	0.780	0.819	0.813	0.773	0.825	0.772	-----
Molar ratio $\text{CaO}/\text{Al}_2\text{O}_3$ in the precipitate computed from analyses of solutions (A and B) before and after precipitation.....	.743	.820	.822	.820	.749	.726	0.458

<sup>1</sup> Too small amount for analysis.

From the chemical analyses and the petrographic examination it is apparent that the material is composed of amorphous hydrated alumina, of varying refractive index, and a hydrated calcium aluminate occurring in hexagonal plates. The refractive indices of these plates are in fair agreement with those given by Klein and Phillips for tricalcium aluminate hydrate in their revised data presented in an unpublished note to P. H. Bates, of this laboratory. Their revised refractive indices are  $\omega = 1.520 \pm 0.003$  and  $\epsilon = 1.504 \pm 0.003$  and serve to correct their previous values, as given on page 8 of Bureau

of Standards Technologic Paper No. 48,  $\epsilon = 1.552 \pm 0.003$  and  $\omega = 1.535 \pm 0.003$ . They found further that the hexagonal plates were uniaxial negative rather than uniaxial positive. More recently Pulfrick and Link<sup>17</sup> have obtained a crystalline hydrated tricalcium aluminate of the composition  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$  as hexagonal plates which are uniaxial negative. The refractive indices which these authors give, for sodium light, are  $\omega = 1.538 \pm 0.0015$  and  $\epsilon = 1.523 \pm 0.0015$ .

Comparing the optical properties of the crystalline phase in the material as precipitated from the unstable solutions with the revised data of Klein and Phillips for tricalcium aluminate hydrate, it is seen that the crystals, in both cases, occur in flat hexagonal plates, are uniaxial negative, and within the limits of experimental error exhibit the same double refraction. The optical properties agree even better with those of Pulfrick and Link. The refractive indices of these different hydrated crystals, however, differ slightly. This is not surprising, since very thin crystals of this character have such large surfaces that the adsorbed water may be a source of error in the determination of the refractive indices. The data of Table 2 show the percentage of water, as determined as loss on ignition. Both the degree of hydration and adsorption of water may also account for the varying index of the amorphous hydrated alumina.

The small quantity of calcite found in the precipitated material undoubtedly resulted from slow carbonation after the equilibrium mixtures were filtered, since no carbonate was found directly upon filtering.

From this study it would appear, therefore, that, as the reaction of water with monocalcium aluminate progresses, there may be formed more or less metastable and supersaturated calcium aluminate solutions from which hydrated alumina and crystalline hydrated tricalcium aluminate precipitate as equilibrium subsequently is approached. The fact that the aluminate solutions apparently attain the same equilibrium, whether left in contact with the monocalcium aluminate for long periods or whether filtered from the reaction mixtures in the early periods and then allowed to approach equilibrium on standing, indicates that the two solid phases mentioned above may be formed during the "setting" of monocalcium aluminate. It does not permit any conclusions to be drawn as to the relative importance of the above reactions in the actual setting of monocalcium aluminate, nor does it exclude the possibility of the formation of other products in the unfiltered mixtures. This investigation, however, may help to explain the mechanism of the formation of hydrated alumina and hydrated tricalcium aluminate, as noted by Klein and Phillips in their study of the reaction of water with monocalcium aluminate.

<sup>17</sup> *Kolloid-Z.*, **34**, p. 117; 1924.

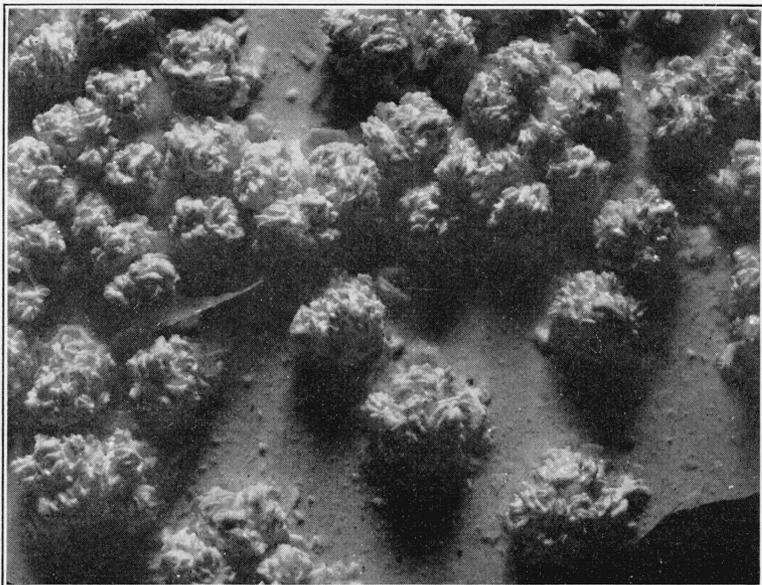


FIG. 3.—Clusters of hexagonal plates of tricalcium aluminate hydrate imbedded in and partially covered with a thin film of hydrated alumina. ( $\times 9$ .)

These two solid phases precipitated slowly from solution 7 of Table 1 in passing from a metastable condition to one more nearly approaching equilibrium

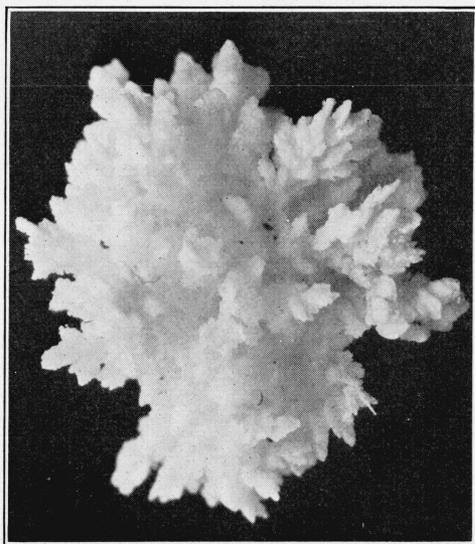


FIG. 4.—Large individual cluster of hexagonal plates of tricalcium aluminate hydrate removed from the walls of the flask and photographed with a black background. ( $\times 9$ .)

### 5. REACTION OF WATER ON THE 3:5 CALCIUM ALUMINATE ( $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$ )

The method of procedure used in the study of the 3:5 calcium aluminate was essentially the same as that already described in the investigation of the reactions of monocalcium aluminate.

In Table 3 there are tabulated the composition and pH of the more or less metastable aluminate solutions (columns A) obtained from the 3:5 calcium aluminate directly upon filtering from the reaction mixture and the data relative to these same solutions at the end of two weeks (columns B). In Figure 5 the quantities of alumina and lime in solution (recorded in columns 3 and 5 and expressed as grams  $\text{Al}_2\text{O}_3$  and

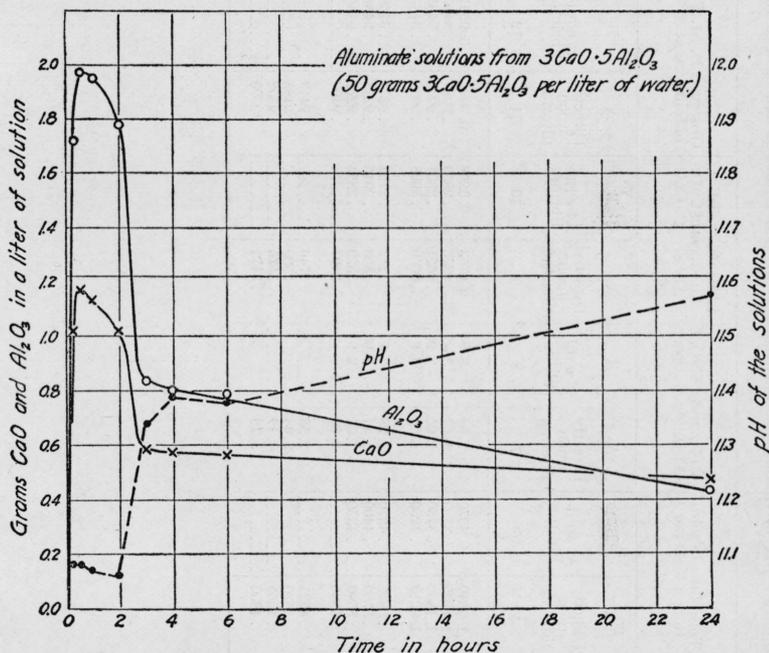


FIG. 5.—Showing the composition and pH of aluminate solutions from  $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$  as functions of the time of contact with water

$\text{CaO}$  per liter, respectively) are plotted against the time (in hours) of contact of the aluminate with water before filtering. The pH values of the solutions (column 13) are also plotted against this time.

From the data (columns 3 and 5 of Table 3, as plotted in Figure 5) it is apparent that the reaction of water on the 3:5 calcium aluminate progresses rapidly. The quantity of both lime and alumina dissolved by the water attained a maximum in 30 minutes and thereafter gradually decreased until two hours had elapsed. Between two and three hours there was a rapid decrease of alumina and lime in solution, and this rate of diminution, in turn, became less as time progressed. An apparent state of equilibrium was reached only after an elapse of several weeks.

TABLE 3.—Composition and pH of aluminate solutions from 3:5 calcium aluminate ( $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ )

No.	Time of contact of $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ with water before filtering	Total alumina in solution, g $\text{Al}_2\text{O}_3$ per 1		Total lime in solution, g $\text{CaO}$ per 1		Molar ratio $\text{CaO}/\text{Al}_2\text{O}_3$ in solution		Lime in solution in excess of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , g $\text{CaO}$ per 1		Observed E. M. F. of solutions at $30^\circ$		pH of solutions at $30^\circ$		Ratio of lime in solution in excess $\text{CaO} \cdot \text{Al}_2\text{O}_3$ $\frac{[\text{CaO}]_A}{[\text{CaO}]_B}$	Ratio of hydroxyl-ion concentration $\frac{[\text{OH}^-]_A}{[\text{OH}^-]_B}$
		A	B	A	B	A	B	A	B	A	B	A	B		
		Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	15 minutes.....	1.7230	0.2015	1.0240	0.4370	1.08	3.94	0.0763	0.3268	0.9097	0.9501	11.08	11.75	0.233	0.213
2	30 minutes.....	1.9725	.1875	1.1725	.3890	1.07	3.77	.0876	.2859	.9097	.9450	11.08	11.67	.306	.259
3	1 hour.....	1.9520	.1720	1.1360	.3750	1.05	3.90	.0624	.2804	.9093	.9493	11.07	11.74	.222	.216
4	2 hours.....	1.7710	.2095	1.0210	.4250	1.05	3.69	.0669	.3098	.9085	.9485	11.06	11.72	.216	.216
5	3 hours.....	.8350	.2865	.5855	.4370	1.28	2.77	.1252	.2794	.9254	.9458	11.34	11.68	.447	.457
6	4 hours.....	.8020	.2700	.5760	.4400	1.31	2.96	.1350	.2915	.9283	.9465	11.39	11.69	.463	.454
7	6 hours.....	.7875	.2720	.5690	.4350	1.31	2.91	.1359	.2854	.9277	.9465	11.38	11.69	.476	.487
8	1 day.....	.4360	.....	.4805	.....	2.00	.....	.2407	.....	.9400	.....	11.58	.....	.....	.....
9	3 days.....	.3245	.....	.4525	.....	2.53	.....	.2740	.....	.9419	.....	11.61	.....	.....	.....
10	7 days.....	.2475	.....	.4670	.....	3.44	.....	.3309	.....	.9485	.....	11.72	.....	.....	.....
11	14 days.....	.2030	.....	.4655	.....	4.17	.....	.3538	.....	.9502	.....	11.75	.....	.....	.....
12	407 days.....	.1505	.....	.4300	.....	5.19	.....	.3473	.....	.9500	.....	11.75	.....	.....	.....

The 3:5 calcium aluminate is less basic than the monocalcium aluminate,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . However, both of these anhydrous calcium aluminates reacted with water in the early periods to form calcium aluminate solutions with a molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , of approximately 1. This indicates that the lime and alumina are dissolved by the water as the calcium salt of monobasic aluminic acid. A more complete discussion of this relation will be presented later in this paper.

At the later periods (Table 3, Nos. 8 to 12, inclusive) the molar ratio of lime to alumina in solution (column 7) increased, with a simultaneous increase in the pH (column 13), until once more the point pH 11.75 was reached, as in the case of corresponding solutions from the anhydrous monocalcium aluminate. Changes identical to these also took place in the more or less metastable solutions when filtered from the reaction mixture of 3:5 calcium aluminate and water. A portion of the lime and alumina precipitated, leaving "equilibrium" solutions (Table 3, columns B) similar to those obtained when the anhydrous aluminate had been left in contact with the water for long periods (Table 3, columns A, Nos. 9 to 12, inclusive). Again the molar ratio of lime to alumina increased, as can be noted from a comparison of the values of Nos. 1 to 7, inclusive, of column 7 to those of column 8, Table 3. This was accompanied by an increase in pH (column 14) to about 11.75, the value obtained for the solutions filtered from the reaction mixtures of the water and 3:5 calcium aluminate at the later periods (Table 3, column 13, Nos. 9 to 12, inclusive), and also for the "equilibrium" solutions from the anhydrous monocalcium aluminate previously discussed.

In Figure 6 the pH values of all the solutions are plotted against the molar ratio of lime to alumina,  $\text{CaO}/\text{Al}_2\text{O}_3$ , in these solutions.

Table 4 contains the chemical analyses of the material precipitated at the end of two weeks from the clear metastable calcium aluminate solutions. (Table 3, columns A, Nos. 1 to 7, inclusive.) Precipitation of this material was initiated in the more concentrated solutions (Nos. 1 to 4, inclusive) within two or three hours after filtering. The small spherulites did not appear until two or three days later. On the other hand, the more dilute solutions (Nos. 5 to 7, inclusive) remained clear for a day or two, following which small spherulites were observed on the walls of the flasks. Later these crystals were covered with a thin film of amorphous material. Chemical analyses and petrographic examinations of the material precipitated from the metastable solutions indicated that hydrated alumina and hydrated tricalcium aluminate were precipitated as equilibrium was approached. Except for a small quantity of calcite in three of the samples, no other phases were observed. The refractive index of the amorphous material in sample No. 2 was approximately 1.55. The index,  $\omega$ , of

the hexagonal plates in samples Nos. 5, 6, and 7 varied between 1.522 and 1.532. These variations may be due to the degree of drying and presence of some water between the laminae of the crystals. It does not, however, prove the presence of a new compound.

TABLE 4.—Chemical analyses of the material precipitated from the clear metastable calcium aluminate solutions prepared by shaking anhydrous 3:5 calcium aluminate with water in the proportion of 50 g  $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$  per liter of water

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Time of contact of aluminate with water.....	15 min.	30 min.	1 hr.	2 hrs.	3 hrs.	4 hrs.	6 hrs.
Analysis of precipitate:							
Per cent $\text{CaO}$ .....	16.08	17.14	17.20	15.70	13.62	( <sup>1</sup> )	( <sup>1</sup> )
Per cent $\text{Al}_2\text{O}_3$ .....	44.50	41.68	41.70	45.44	50.02	( <sup>1</sup> )	( <sup>1</sup> )
Per cent $\text{H}_2\text{O}$ .....	39.72	41.17	42.17	38.23	36.98	( <sup>1</sup> )	( <sup>1</sup> )
Total.....	100.30	99.99	101.07	99.37	100.62	-----	-----
Molar ratio $\text{CaO}/\text{Al}_2\text{O}_3$ in the precipitate from above analyses.....	0.642	0.747	0.749	0.625	0.495	-----	-----
Molar ratio $\text{CaO}/\text{Al}_2\text{O}_3$ in the precipitate computed from analyses of solutions before and after precipitation.....	.700	.808	.777	.689	.483	0.465	0.452

<sup>1</sup> Too small amount for analysis.

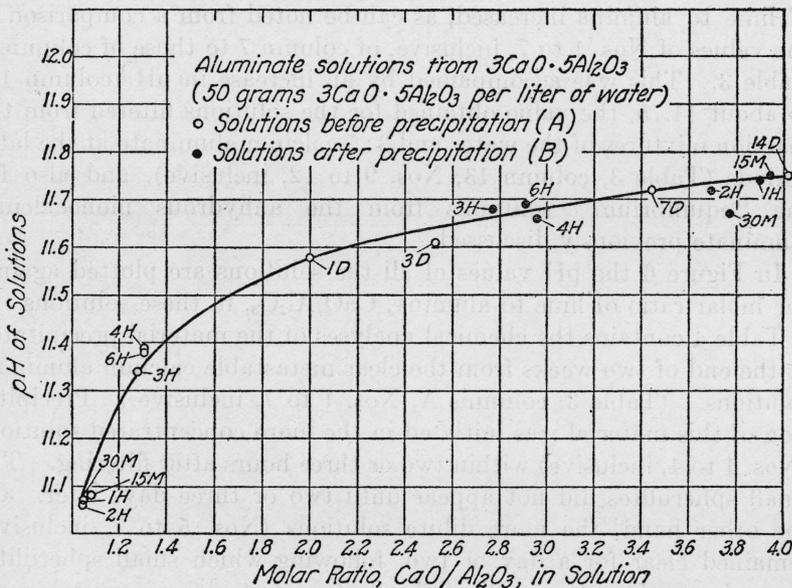


FIG. 6.—Showing the pH of aluminate solutions from  $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$  as a function of the molar ratio  $\text{CaO}/\text{Al}_2\text{O}_3$  in solution

It is seen, therefore, that the reaction of water with 3:5 calcium aluminate is analogous to its reaction with monocalcium aluminate

previously described in more detail. In the early periods of the reaction, metastable calcium aluminate solutions are formed which have a molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , approximately 1. After these solutions are filtered from the reaction mixtures they subsequently decompose on standing, with an attendant precipitation of a portion of the alumina and lime as hydrated alumina and hydrated tricalcium aluminate. The resulting solutions, which are in equilibrium with these two solid phases, attain the same composition as the solutions obtained by filtering the mixtures of water and either of the anhydrous aluminates after several weeks have elapsed. In all cases the pH values of the solutions at the later periods are higher than those of the corresponding metastable solutions obtained directly upon filtering from the reaction mixtures. The molar ratio of lime to alumina in the solutions obtained at the later periods is also higher.

#### 6. REACTION OF WATER ON THE 5:3 CALCIUM ALUMINATE ( $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ )

The procedure for the study of the reaction of water on the 5:3 calcium aluminate,  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ , was the same as that adopted in the investigation of the mono and 3:5 calcium aluminates. Although the reaction mixtures of the 5:3 calcium aluminate and water were shaken vigorously to prevent setting, nevertheless, a portion of the material soon agglomerated in small lumps as a result of the formation of hydrated material on the outside of the individual grains, which had a tendency to cohere and prevent the further penetration of water. The mixtures of this aluminate and water did not filter as readily as those of either the mono or 3:5 calcium aluminate.

The composition and pH of the resulting aluminate solutions are recorded in Table 5 and represented diagrammatically in Figure 7. It may be noted from columns 3 and 5 of Table 5, as plotted in Figure 7, that the total quantities of both alumina and lime dissolved by the water increased rapidly for 30 minutes, then more slowly, and finally reached a maximum at the end of two hours. This was followed by a rapid decrease, which, in turn, became less after six hours had elapsed. An apparent state of equilibrium was reached only after several weeks had elapsed. Also, the total quantities of alumina and lime dissolved by the water in the early periods were less than the corresponding quantities of these same materials taken into solution



in the case of the other two aluminates (1:1 and 3:5, each of higher alumina content) previously studied. Nevertheless, the aluminate solutions formed during these periods had a molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , of approximately 1, as can be seen from Table 5, column 7, Nos. 1 to 6, inclusive. This again indicates that initially the lime and alumina are dissolved as the calcium salt of monobasic aluminic acid. From these investigations it is apparent that, although monocalcium aluminate is dissolved as such, in each case, in the early

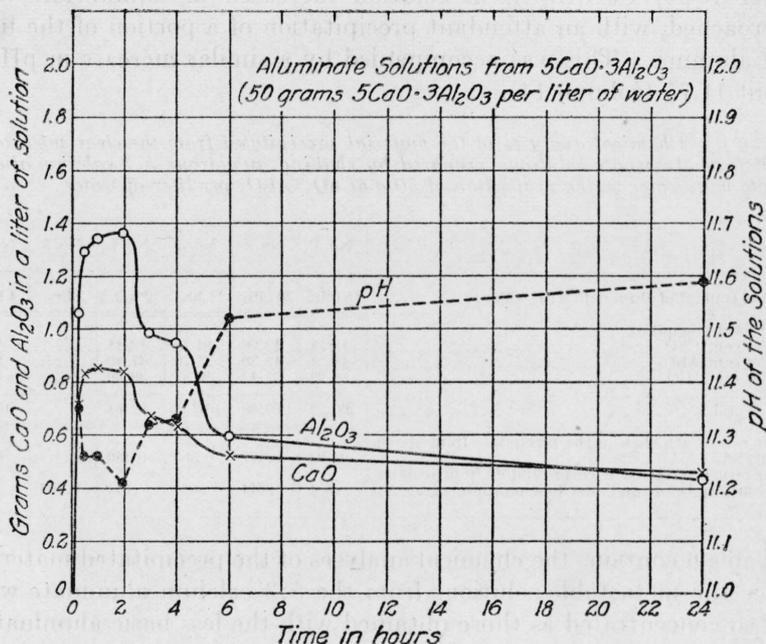


FIG. 7.—Showing the composition and pH of aluminate solutions from  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  as functions of the time of contact with water

periods of the reaction, yet its total concentration, in grams per liter, is related to the chemical composition of the anhydrous aluminate from which it is formed. In the further study of the subsequent changes in the aluminate solutions, attended by increasing concentrations of calcium hydroxide, a more detailed discussion of the lower concentration of monocalcium aluminate in solution from the 5:3 calcium aluminate will be presented in this paper.

It is noted that at the later periods the molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , in solution increased (Table 5, column 7), with a simultaneous increase

in the pH (Table 5, column 13), until the point pH 11.75 was reached. Lerch and Bogue<sup>18</sup> also have shown recently that the pH of equilibrium of 5:3 calcium aluminate and water is about 11.7, approximately this same value. *These values are also approximately those obtained when either the mono or the 3:5 calcium aluminate had been left in contact with water for long periods.*

Likewise, identical changes took place in the metastable solutions which were filtered from the reaction mixtures. On standing, the molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , in solution increased as equilibrium was approached, with an attendant precipitation of a portion of the lime and alumina. This was accompanied by a similar increase in pH to about 11.75 (column 14).

TABLE 6.—*Chemical analyses of the material precipitated from the clear metastable calcium aluminate solutions prepared by shaking anhydrous 5:3 calcium aluminate with water in the proportion of 50 g  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  per liter of water*

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Time of contact of aluminate with water .....	15 min.	30 min.	1 hr.	2 hrs.	3 hrs.	4 hrs.
Analysis of precipitate:						
Per cent $\text{CaO}$ .....	15.78	12.96	10.78	12.44	-----	13.58
Per cent $\text{Al}_2\text{O}_3$ .....	48.24	49.30	53.70	47.40	-----	48.90
Per cent $\text{H}_2\text{O}$ .....	36.29	37.42	36.87	39.80	-----	37.71
Total .....	100.29	99.68	101.35	99.64	-----	100.19
Molar ratio $\text{CaO}/\text{Al}_2\text{O}_3$ in the precipitate from above analyses .....	0.593	0.477	0.365	0.480	-----	0.505
Molar ratio $\text{CaO}/\text{Al}_2\text{O}_3$ in the precipitate from analysis of solutions before and after precipitation .....	.694	.614	.625	.614	0.603	.460

Table 6 contains the chemical analyses of the precipitated material. Since the metastable solutions from the 5:3 calcium aluminate were not so concentrated as those obtained with the less basic aluminates, the precipitation was delayed. Accordingly, in growing more slowly the spherulites of tricalcium aluminate adhere more firmly to the walls of the flasks. Consequently, the resultant loss of this portion of the crystals firmly attached to the walls of the container might account for the lower molar ratio of lime to alumina in the precipitate, as calculated from the chemical analyses of the material recovered, in comparison to that computed from the analyses of the solutions before and after precipitation. Chemical analyses and petrographic examination of the material precipitated from the metastable solutions indicated that hydrated alumina and hydrated tricalcium aluminate were precipitated as equilibrium was approached. No calcite was found in any of the samples. The hexagonal plates, with

<sup>18</sup> J. Phys. Chem., **31**, p. 1627; 1927.

optical properties similar to those noted in previous aluminate precipitates, were present in all samples. The refractive index,  $\omega$ , of these plates varied between 1.525 and 1.535. In samples Nos. 1, 4, and 6 the index of refraction of the amorphous isotropic material was approximately 1.48. In samples Nos. 2 and 3 it was nearly 1.55. Also, in samples Nos. 2, 3, and 4 a new phase in small amounts was noted. This consists of isotropic, isometric crystals with an index of refraction very close to 1.605. Incidentally, this index of refraction is about that of the isotropic crystals of the anhydrous 5:3 calcium aluminate. However, the crystals in the precipitated material appear as well-formed icositetrahedrons or rhombic dodecahedrons, and in this respect are unlike the irregular isotropic grains characteristic of the finely ground anhydrous 5:3 calcium aluminate. It is planned to investigate further this new phase, with the hope that its identity may be established.

It would appear, therefore, that during the reaction between water and anhydrous 5:3 calcium aluminate there are formed metastable and supersaturated monocalcium aluminate solutions from which hydrated alumina and hydrated tricalcium aluminate subsequently precipitate as equilibrium is approached. In these respects the reactions are analogous to those previously described in case of the mono and 3:5 calcium aluminate. Furthermore, at the later periods the solutions resulting from the reaction of water with these various anhydrous aluminates apparently approach the same equilibrium. A new phase, the identity of which has not yet been established, has been observed as a decomposition product of several of the metastable solutions obtained by filtering mixtures of the 5:3 aluminate and water. To what extent this phase, as well as the other two phases (hydrated alumina and hydrated tricalcium aluminate), may be present in the unfiltered mixture of the 5:3, 1:1, or 3:5 aluminates and water has not been determined.

## 7. REACTION OF WATER ON TRICALCIUM ALUMINATE ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ )

From his experiments on the time of set of the calcium aluminates, Bates<sup>19</sup> concludes that the mono and 3:5 calcium aluminates react with water much more slowly than the others high in lime. He found that by the use of about 10 per cent more water, in terms of cement, than is used in gauging Portland cement it is possible to knead thoroughly the 5:3 calcium aluminate without the appearance of any flash set. Initial set occurs in from 3 to 5 minutes after molding, and final set occurs in from 15 to 30 minutes, the latter

<sup>19</sup> B. S. Tech. Paper No. 197.

being accompanied by a marked evolution of heat. On the other hand, the addition of water to the tricalcium aluminate produces a very vigorous reaction, manifesting itself almost immediately by a rapid rise in temperature, until the mass steams vigorously and assumes a "flash set."

Notwithstanding, it was hoped that it would be possible to follow the changes in the composition of the solutions resulting from the reaction of water on the tricalcium aluminate in a manner similar to that used in the case of the other aluminates. However, the attempt was soon abandoned. When the finely powdered tricalcium aluminate was added to the water it quickly agglomerated into balls which hydrated on the exterior to hard masses which prevented the penetration of water to the interior; consequently, large masses of unhydrated material were present. Furthermore, the resulting mixture filtered very slowly, evidently due to the precipitation of material within the pores of the filter paper, since the clear filtrates, which were first obtained, became cloudy very quickly on standing. Thus, since the addition of water to freshly prepared tricalcium aluminate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , produces such a very vigorous reaction, the changes in the composition of the resulting solutions could not be followed. Previous investigations<sup>20</sup> have indicated that its setting is due to the formation of hydrated tricalcium aluminate without the formation of hydrated alumina. This hydrated material may result entirely or in part from the direct hydration of the anhydrous aluminate, or, by analogy to the reactions of the other aluminates, from the reaction of the excess of lime on a calcium aluminate formed in the very early period of setting.

### 8. REACTION OF WATER ON A HIGH ALUMINA CEMENT

Having studied the mechanism of the reaction of water on the calcium aluminates, a commercial brand of high alumina cement was investigated.

The chemical analysis<sup>21</sup> of this cement was:

	Per cent		Per cent
$\text{SiO}_2$ .....	5.09	$\text{CaO}$ .....	40.83
$\text{Fe}_2\text{O}_3$ .....	10.92	$\text{MgO}$ .....	0.81
$\text{Al}_2\text{O}_3$ .....	38.98	Insoluble.....	2.83
$\text{TiO}_2$ .....	1.90	Loss on ignition.....	1.51

The monocalcium aluminate ( $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) and the 3:5 calcium aluminate ( $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ ) are the chief constituents of high alumina cements of this composition, and the dicalcium silicate ( $2\text{CaO} \cdot \text{SiO}_2$ ) and iron compounds are the minor constituents.

In the study of the reaction of water on this cement the procedure was that followed in the investigation of the calcium aluminates.

<sup>20</sup> Klein and Phillips, B. S. Tech. Paper No. 43.

<sup>21</sup> Analysis by H. C. Stecker, of this bureau.

The aluminate solutions were obtained by shaking 250 g of cement with 5 liters of distilled water. The composition and pH of the solutions are recorded in Table 7 and represented diagrammatically in Figure 8 from the data of columns 3, 5, and 13 of the table. The total quantities of both lime and alumina dissolved by the water increased for four hours, remained approximately constant for two more hours, and then decreased rapidly until about eight hours had elapsed, after which the decrease became less as time progressed. It was evident that a rapid precipitation of alumina and lime from solution occurred shortly after six hours, since the solutions above the cement became cloudy at this time. As in the reaction of the calcium aluminates, an apparent state of equilibrium was reached only after several weeks had elapsed. In general, the mechanism of the reaction of water on the high alumina cement was the same as with the mono, 3:5, and 5:3 calcium aluminates studied previously; that is, the formation of metastable solutions with lime and alumina in a molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , of approximately 1, in the early periods of the reaction, followed by the precipitation of a portion of this lime and alumina as equilibrium is approached. In the same way the molar ratio of lime to alumina increased after this precipitation and was attended by an increase in the pH to about 11.70.

The chemical analyses of the materials precipitated, at the end of two weeks, from the clear metastable calcium aluminate solutions are recorded in Table 8. Precipitation of this material started from the more concentrated of these solutions (Table 7, columns A, Nos. 1 to 6, inclusive) within two or three hours after filtering. It was not until a day or two later that any precipitation was apparent in the more dilute solutions, Nos. 7 and 8, with the appearance of spherulites on the walls of the flasks. A day or two later these crystals were, in turn, covered with a thin film of amorphous material. Microscopic examination revealed no phases other than those heretofore described. No calcite was found in any of the samples. The hexagonal plates, with optical properties similar to those noted previously, were observed in all samples. The isotropic and probably amorphous hydrated alumina had no perceptible birefringence, and a refractive index of about  $1.570 \pm 0.003$ . Although Gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) is rather strongly birefringent and is undoubtedly crystalline, its mean refractive index, 1.573, agrees fairly well with the refractive index  $1.570 \pm 0.003$  of the hydrated alumina. Also, in several of the samples, the isometric crystals with an index about 1.60 were found. These crystals appeared to be either icositrahedrons or rhombic dodecahedrons and were similar to those observed previously in several samples from the 5:3 calcium aluminate. None of the samples showed any reaction with White's solution (used for the detection of free lime) after one hour of contact with this reagent.

TABLE 7.—Composition and pH of aluminate solutions from high alumina cement

No.	Time of contact of the cement with water before filtering	Total alumina in solution, g Al <sub>2</sub> O <sub>3</sub> per l		Total lime in solution, g CaO per l		Molar ratio CaO/Al <sub>2</sub> O <sub>3</sub> in solution		Lime in solution in excess of CaO·Al <sub>2</sub> O <sub>3</sub> g CaO per l		Observed E. M. F. of solutions at 30°		pH of solutions at 30°		Ratio of lime in solution in excess CaO·Al <sub>2</sub> O <sub>3</sub> $\frac{(\text{CaO})_A}{(\text{CaO})_B}$	Ratio of hydroxyl-ion concentration $\frac{[\text{OH}^-]_A}{[\text{OH}^-]_B}$
		A	B	A	B	A	B	A	B	A	B	A	B		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	15 minutes	1.5400	0.2415	0.9720	0.4715	1.12	3.55	0.1250	0.3387	0.9193	0.9452	11.24	11.67	0.369	0.371
2	30 minutes	1.5210	.2325	.9790	.4675	1.17	3.66	.1424	.3396	.9188	.9447	11.23	11.66	.419	.371
3	1 hour	1.6785	.2255	1.0535	.4960	1.14	4.00	.1303	.3720	.9164	.9465	11.19	11.69	.350	.316
4	2 hours	1.8930	.2050	1.1500	.4360	1.10	3.87	.1089	.3200	.9166	.9448	11.19	11.66	.340	.339
5	4 hours	2.0175	.1940	1.2080	.3860	1.09	3.62	.0990	.2793	.9152	.9473	11.17	11.70	.354	.291
6	6 hours	2.0200	.2085	1.2040	.4255	1.08	3.70	.0930	.3108	.9138	.9477	11.15	11.71	.299	.271
7	8 hours	.9880	.2555	.6610	.4195	1.22	2.98	.1176	.2790	.9217	.9430	11.28	11.62	.421	.442
8	10 hours	.9015	.2810	.6115	.4100	1.23	2.65	.1158	.2554	.9225	.9399	11.29	11.58	.453	.512
9	1 day	.4410	-----	.4375	-----	1.80	-----	.1950	-----	.9338	-----	11.48	-----	-----	-----
10	3 days	.2315	-----	.3880	-----	3.03	-----	.2607	-----	.9446	-----	11.66	-----	-----	-----
11	7 days	.1585	-----	.3055	-----	3.55	-----	.2183	-----	.9437	-----	11.64	-----	-----	-----
12	14 days	.1900	-----	.3660	-----	3.50	-----	.2615	-----	.9453	-----	11.67	-----	-----	-----

TABLE 8.—Chemical analyses of the material precipitated from the clear metastable calcium aluminate solutions prepared by shaking a high alumina cement with water, in the proportion of 50 g per liter of water

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Time of contact of cement with water.	15 min.	30 min.	1 hr.	2 hrs.	4 hrs.	6 hrs.	8 hrs.	10 hrs.
Analysis of precipitate:								
Per cent CaO .....	13.96	13.32	13.77	14.66	13.00	16.00	-----	-----
Per cent Al <sub>2</sub> O <sub>3</sub> .....	46.40	50.52	49.36	44.44	48.80	44.88	-----	-----
Per cent H <sub>2</sub> O .....	39.39	36.61	38.54	41.15	37.95	39.40	-----	-----
Total .....	99.95	100.45	101.67	100.25	99.75	100.28	-----	-----
Molar ratio CaO/Al <sub>2</sub> O <sub>3</sub> in the precipitate from the above analyses.....	0.547	0.463	0.507	0.600	0.484	0.632	-----	-----
Molar ratio CaO/Al <sub>2</sub> O <sub>3</sub> in the precipitate computed from analyses of solutions before and after precipitation.....	.700	.722	.700	.768	.819	.781	0.694	0.590

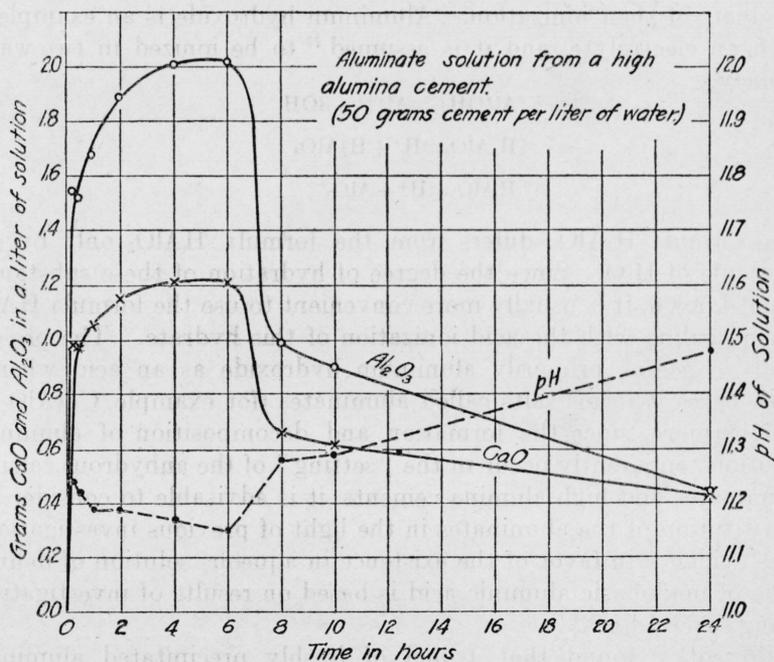


FIG. 8.—Showing the composition and pH of aluminate solutions from a high alumina cement as functions of the time of contact with water

A microscopic examination of the fractured surfaces of some briquettes of high alumina cement which had been stored in water for a year revealed in some small cavities hexagonal plates with optical properties similar to those noted previously. Several of these crystals are seen in Figures 9 to 12, inclusive.

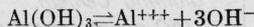
The reaction of the iron in the cement has not been determined. The constituents containing iron and silica apparently influence the

rate of the setting of the aluminates. However, no iron was detected in any of the aluminate solutions.

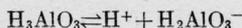
From these experiments it would appear that the reactions between water and the high alumina cement, as well as the monocalcium aluminate, the 3:5 calcium aluminate, and the 5:3 calcium aluminate, were in part related to the precipitation of hydrated alumina and crystalline hydrated tricalcium aluminate from metastable and supersaturated monocalcium aluminate solutions. It is hoped that the following consideration of the constitution of the aluminate solutions will throw further light upon the formation and decomposition of the metastable monocalcium aluminate solutions.

### 9. CONSTITUTION OF THE ALUMINATE SOLUTIONS

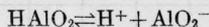
Amphoteric electrolytes give both hydrogen and hydroxyl ions as products of their ionization. Aluminum hydroxide is an example of such an electrolyte, and it is assumed<sup>22</sup> to be ionized in two ways, namely,



and



or



The formula  $\text{H}_3\text{AlO}_3$  differs from the formula  $\text{HAlO}_2$  only by one molecule of  $\text{H}_2\text{O}$ . Since the degree of hydration of these substances is not known, it is usually more convenient to use the formula  $\text{HAlO}_2$  when dealing with the acid ionization of this hydrate. The present study concerns primarily aluminum hydroxide as an acid wherein with bases it forms salts called aluminates (for example,  $\text{Ca(AlO}_2)_2$ ). Furthermore, since the formation and decomposition of aluminate solutions apparently occur in the "setting" of the anhydrous calcium aluminates and high alumina cements, it is advisable to consider the constitution of the aluminates in the light of previous investigations. The evidence in favor of the existence in aqueous solution of definite salts of monobasic aluminic acid is based on results of investigations along several lines.

Prescott<sup>23</sup> found that 1 mol of freshly precipitated aluminum hydroxide dissolves in exactly 1 mol of sodium or potassium hydroxide and maintained, therefore, that the solution must contain the monoaluminate (for example, the meta-aluminate). The same formula for the alkali aluminate was set forth by Cavazzi,<sup>24</sup> who found, by the addition of metallic aluminum to the alkalis, that 1 mol Al went into solution for each mol of NaOH or KOH. The same combination (1 alkali for 1 Al) was also found by Bogussky

<sup>22</sup> E. W. Washburn, Principles of Physical Chemistry, p. 362; 1921; McGraw-Hill Book Co., New York.

<sup>23</sup> J. Am. Chem. Soc., 2, p. 27; 1880; Chem. News, 42, p. 29; 1880.

<sup>24</sup> Gazz. chim. ital., 15, p. 205; 1885.

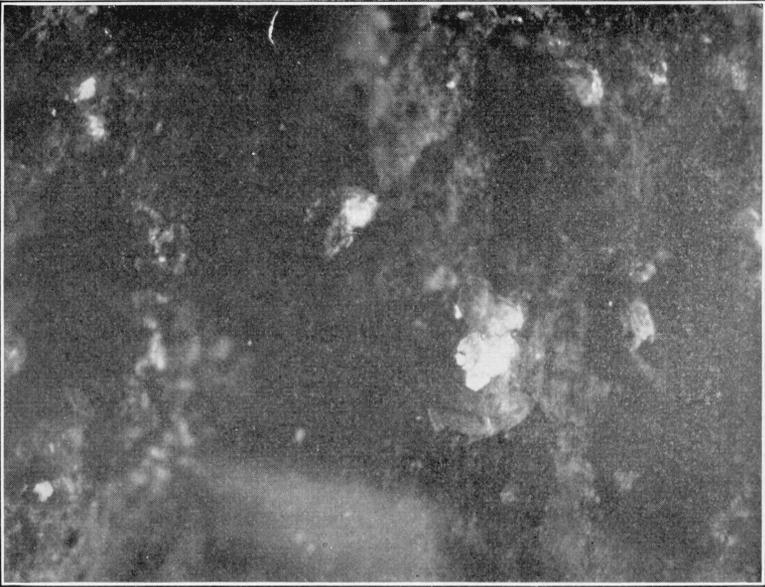


FIG. 9.—*Fractured surface of neat briquette of high alumina cement stored in water for one year, showing cavities containing hexagonal plates of colorless hydrated tricalcium aluminate. (X40.)*

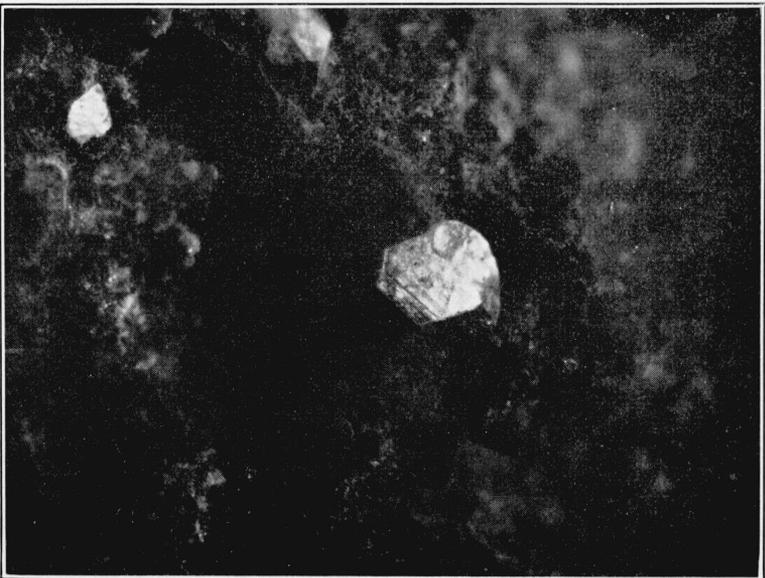


FIG. 10.—*A flat hexagonal plate of hydrated tricalcium aluminate removed from a cavity for photographing. (X40.)*



FIG. 11.—Fractured surface of neat briquette of high alumina cement stored in water for one year, showing cavities containing hexagonal plates of hydrated tricalcium aluminate. ( $\times 50$ .)

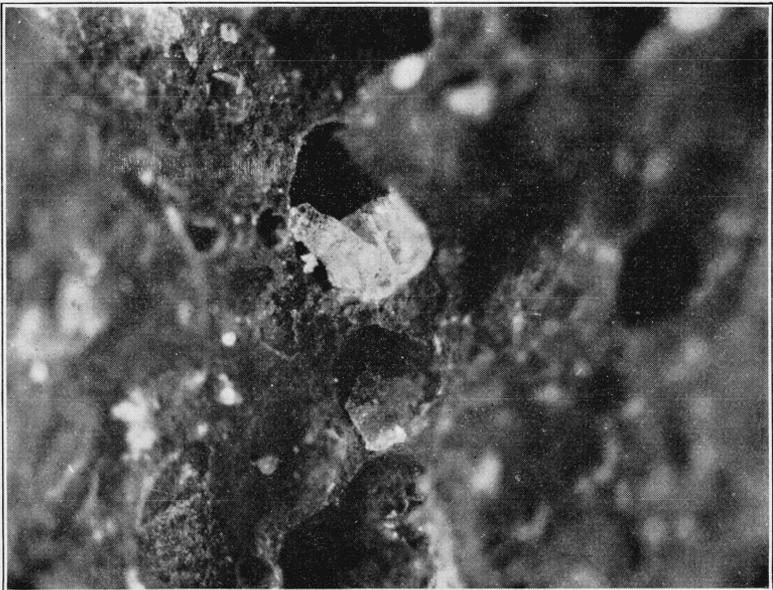


FIG. 12.—Same as Figure 11, but oriented. ( $\times 40$ .)

and Zaljesky,<sup>25</sup> as well as by Lyte.<sup>26</sup> Observations<sup>27</sup> on this subject were also made by H. St. C. Deville, A. Ditte, F. Russ, and A. Glässner. Numerous investigators have shown that gelatinous aluminum hydroxide, on standing, changes over to a new form which is often referred to as a crystalline variety and which is difficultly soluble, even in an excess of alkali. This change is known as the "aging" process. Therefore, the solubility ratio is only applicable for deducing a formula for the salt in solution when the freshly precipitated hydroxide is used. Herz<sup>28</sup> found that although freshly precipitated aluminum hydroxide dissolves in alkali to form the meta-aluminate,  $\text{NaAlO}_2$ , yet, if alumina is dried, an ortho-aluminate of the composition,  $\text{Na}_3\text{AlO}_3$ , is apparently formed. However, there seems to be no evidence for assuming that the latter solution contains the ortho-aluminate, as Slade<sup>29</sup> found that the ratio of alkali to alumina in the solubility determinations may range from 2 to 1 to 10 to 1, according to the condition of precipitation and the duration and mode of drying of the alumina. Wood's<sup>30</sup> solubility determinations of aluminum and of aluminum hydroxide in solutions of sodium hydroxide, after allowing for a slight excess of alkali over the amount required to form monosodium aluminate owing to partial hydrolysis of the salt, agree with the assumption that sodium meta-aluminate,  $\text{NaAlO}_2$ , is formed, but not the ortho-salt,  $\text{Na}_3\text{AlO}_3$ . Carrara and Vespignani<sup>31</sup> conclude that, even in presence of a large excess of potassium hydroxide, aluminum hydroxide forms only potassium monoaluminate.

The constitution of aluminate solutions has also been investigated by the freezing-point method. Noyes and Whitney<sup>32</sup> dissolved aluminum sheet metal in both sodium and potassium alkali solutions (ranging from about 0.2 to 0.5 *N*) and found no difference between the freezing point of these solutions and those free from aluminum and so concluded that the formula of meta-aluminate was  $\text{XAlO}_2$  ( $\text{X} = \text{alkali}$ ). Slade<sup>33</sup> also concluded from freezing-point determinations that sodium aluminate in solution is the salt of monobasic aluminic acid. His observations were confirmed by Heyrovsky for sodium, ammonium,<sup>34</sup> and also for alkaline earth aluminates.<sup>35</sup>

<sup>25</sup> Chem. Zt., **14**, p. 148; 1890.

<sup>26</sup> Chem. News, **51**, pp. 109, 201; 1885.

<sup>27</sup> Deville, Ann. chim. phys., **61**, p. 333; 1861; Ditte, Compt. rend., **116**, pp. 183, 386; 1893; Russ, Z. anorg. Chem., **41**, p. 216; 1904; Glässner, Chem. Ind., **25**, p. 186; 1902.

<sup>28</sup> Z. anorg. Chem., **25**, p. 155; 1900.

<sup>29</sup> Z. Elektrochem., **17**, p. 261; 1911; cf. W. Herz, Z. Elektrochem., **17**, p. 403; 1911

<sup>30</sup> J. Chem. Soc. (London), **93**, p. 417; 1908.

<sup>31</sup> Gazz. chim. ital., **30**, pp. ii, 35; 1900.

<sup>32</sup> Z. physik. Chem., **15**, p. 694; 1894; Tech. Quart., **7**, p. 1; 1894.

<sup>33</sup> Z. Elektrochem., **17**, p. 261; 1911.

<sup>34</sup> J. Chem. Soc. (London), **117**, p. 1013; 1920.

<sup>35</sup> Chem. News, **125**, p. 198; 1922.

Conductance methods have also been used to determine the constitution of aluminate solutions. Carrara and Vespignani<sup>36</sup> found an appreciable decrease in the conductivity of potassium aluminate solutions as compared with the corresponding solutions of potassium hydroxide. Hantzsch<sup>37</sup> likewise found that solutions containing 1 Na for 1 Al, in the pure state, had a conductance lower than that of the corresponding solutions of sodium hydroxide. Upon the further addition of NaOH to a freshly prepared sodium aluminate solution, he discovered that the conductivity was additive, showing thereby that the additional alkali does not combine with the aluminate. This is further proof of the monobasic nature of the aluminic acid. He observed, also, that the monocalcium aluminate solutions were unstable and that aluminum hydroxide precipitated on standing. It will be recalled that aluminum hydroxide (hydrated alumina) was found to be one of the decomposition products of the metastable calcium aluminate solutions. Hantzsch considers the decomposition of the aluminate as resulting from its hydrolysis, proceeding in the following manner:



this being indicated by an increase in the conductivity. He found, however, that no visible deposition of hydrated alumina took place until the conductivity had increased considerably. Hantzsch believed this indicated that the aluminum hydroxide became colloidal prior to such deposition. Further conductivity measurements on dilute sodium aluminate solutions were made by Slade and Polack.<sup>38</sup> The solutions were obtained by saturation of sodium hydroxide with metallic aluminum, being guided by the volume of H<sub>2</sub> evolved in securing an atomic ratio of Na:Al in the solution as nearly 1:1 as possible. From their experiments they conclude that there is no evidence of the existence of colloidal aluminum hydroxide in the sodium aluminate solutions, as was supposed by Hantzsch, and that whenever hydrolysis takes place crystalline aluminum hydroxide is deposited. They also conclude that their examination of sodium aluminate solutions in the ultramicroscope gave no definite evidence of the existence or nonexistence of colloidal particles. Heyrovsky<sup>39</sup> also made a study of the conductance of aluminate solutions, prepared by adding metallic aluminum to dilute solutions of sodium hydroxide. He showed that the conductance falls regularly with increasing concentration of the aluminate. The slope of the equivalent conductance curve remains constant when the ratio of the gram-atoms Na:Al is either 3:1 or 2:1, indicating that no formation of a salt of tri or di basic

<sup>36</sup> Gazz. chim. ital., **30**, pp. ii, 35; 1900.

<sup>37</sup> Z. anorg. Chem., **30**, p. 280; 1902.

<sup>38</sup> Trans. Faraday Soc., **10**, p. 150; 1914.

<sup>39</sup> J. Chem. Soc. (London), **117**, p. 1013; 1920.

aluminic acid takes place. When, however, the ratio becomes 1:1, spontaneous decomposition of the solution occurs, during which crystalline aluminum hydroxide separates out, and the conductance resultantly increases in the manner described by Slade and Polack. Heyrovsky<sup>40</sup> also showed that the decrease in conductivity of barium hydroxide upon the addition of metallic aluminum is quite regular and linear until the atomic ratio Ba:Al in solution becomes 1:2. These experiments indicate that no ions other than monovalent anions substitute for the hydroxyl ions in neutralization.

Electromotive force measurements have also been employed in establishing the constitution of the aluminate solutions. Thus, Hildebrand<sup>41</sup> and Blum<sup>42</sup> have measured the change in hydrogen-ion concentration as sodium hydroxide or potassium hydroxide is progressively added to a solution of aluminum chloride until the aluminum hydroxide is precipitated and subsequently dissolved. The points of inflection in the precipitation curves, as obtained by Blum, confirm the observations of Prescott that 1 mol of freshly precipitated aluminum hydroxide dissolves in exactly 1 mol of an aqueous solution of sodium and potassium hydroxide and indicates, therefore, the existence of definite aluminates of the formulas  $\text{NaAlO}_2$  and  $\text{KAlO}_2$ , or multiples thereof. Blum found the points of inflection when the aluminum hydroxide was dissolved by sodium and potassium hydroxide to be at pH values of approximately 10.5 and 11.0, respectively. Britton<sup>43</sup> has investigated the constitution of the soluble aluminates of calcium, barium, and strontium. In each of his titrations the precipitated aluminum hydroxide redissolved completely when approximately another equivalent of alkaline earth hydroxide was added, the redissolving being indicated by the characteristic inflections of the titration curves. The points of inflection in the titration of aluminum chloride with barium and strontium hydroxides were at pH values of 10.43 and 10.60, respectively, and in the titration of aluminum sulphate with calcium hydroxide at pH, 10.17.

Hence, the bulk of the evidence (as based on the solubility ratio, the freezing point, conductivity, and electromotive force measurements) indicates that the alkali and alkaline earth aluminates exist in aqueous solution as salts of monobasic aluminic acid.

Nevertheless, Mahin and his coworkers<sup>44</sup> have concluded from their observations of the aluminate solutions that the aluminates do not exist in solution as definite salts, but that the solubility of aluminum hydroxide in bases is due principally to its colloidal properties. Their conclusions have been severely criticized by Blum and

<sup>40</sup> Chem. News, **125**, p. 198; 1922.

<sup>41</sup> J. Am. Chem. Soc., **35**, p. 864; 1913.

<sup>42</sup> J. Am. Chem. Soc., **35**, p. 1499; 1913.

<sup>43</sup> J. Chem. Soc., (London), p. 422; 1927.

<sup>44</sup> J. Am. Chem. Soc., **35**, p. 36; 1913.

by Slade and Polack. For details, one must consult the original articles.<sup>45</sup> Chatterji and Dhar<sup>46</sup> observed no appreciable changes in the conductivity of solutions of sodium hydroxide to which alumina was added and, hence, conclude that such solutions are instances of peptization and not of chemical combination. Weiser<sup>47</sup> has pointed out that the observations of Chatterji and Dhar merely indicate the failure of their experimental method to detect any change in conductivity in the highly alkaline solutions, rather than the absence of a change.

Therefore, it may be said that the constitution of the aluminates in aqueous solution is apparently well established. The work described in this paper adds to the evidence in favor of the existence in solution of a salt of monobasic aluminic acid. It has been shown that a high alumina cement and the anhydrous calcium aluminates, differing so widely in chemical composition, reacted with the water in the early periods of setting to form calcium aluminate solutions with a molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , in each case close to 1.

It has been shown by previous investigators that the aluminate solutions are metastable and that, on standing, hydrated alumina precipitates. Also, from the present study it is apparent that the instability of the calcium aluminate solutions is closely related to the reaction of both anhydrous calcium aluminates and high alumina cements due to the precipitation not only of hydrated alumina but also of hydrated tricalcium aluminate. The precipitation of alumina from the aluminate solutions is accompanied by an increase in pH. Johnston<sup>48</sup> accounts for the abnormal alkalinity of the alkali aluminates by the progressive hydrolysis which takes place owing to the slight solubility of the aluminic acid, which first separates in the gelatinous or colloidal and later in the less soluble crystalloidal form. Bayer<sup>49</sup> and Ditte<sup>50</sup> have likewise assumed that two forms of hydrated alumina (aluminic acid) are involved—the gelatinous and the crystalline. A solution which is saturated with the gelatinous aluminic acid must, therefore, be supersaturated with respect to the crystalline form, which is less soluble. Fricke<sup>51</sup> has made an extensive study of the hydrolysis of the alkali aluminates and has found that the intensity of "aging" is directly proportional to the hydroxyl-ion concentration. He<sup>52</sup> and other investigators,<sup>53</sup> by means of X-ray diffraction patterns, have shown that this aged alumina is crystalline. A saturated mono-

<sup>45</sup> Blum, *J. Am. Chem. Soc.*, **36**, p. 2383; 1914; cf. **35**, p. 1499; 1913; Slade and Polack, *Trans. Faraday Soc.*, **10**, p. 150; 1914; Mahin, *J. Am. Chem. Soc.*, **36**, p. 2381; 1914; cf. **35**, p. 36; 1913.

<sup>46</sup> *Chem. News*, **121**, p. 253; 1920.

<sup>47</sup> H. B. Weiser, *Hydrous Oxides*, p. 117; 1926; McGraw-Hill Book Co., New York.

<sup>48</sup> Private communication to Blum; *J. Am. Chem. Soc.*, **35**, p. 1503; 1913.

<sup>49</sup> Bayer, *Chem. Ztg.*, **12**, p. 1209; 1889.

<sup>50</sup> Ditte, *Compt. rend.*, **116**, pp. 183, 386, 509; 1893.

<sup>51</sup> *Z. Elektrochem.*, **26**, p. 129; 1920.

<sup>52</sup> Fricke and Weaver, *Z. anorg. allgem. Chem.*, **136**, p. 321; 1924.

<sup>53</sup> Böhm and Niclassen, *Z. anorg. Chem.*, **133**, p. 1; 1924.

calcium aluminate solution is, therefore, even more unstable, since it is also supersaturated with respect to the tricalcium aluminate hydrate which crystallizes from solution together with the hydrated alumina. This indicates that there must be some ortho-aluminic acid in solution. However, it is very probable that the ionization constant of tribasic aluminic acid is so small in comparison with that of the monobasic aluminic acid that the aluminate solutions behave as the salt of the latter.

The experimental work of others supports the theory that aluminic acid in dilute solutions behaves primarily as a monobasic acid. In this investigation the relation of the pH of the calcium aluminate solutions to their chemical composition is in good agreement with this theory, as is evident from the following consideration:

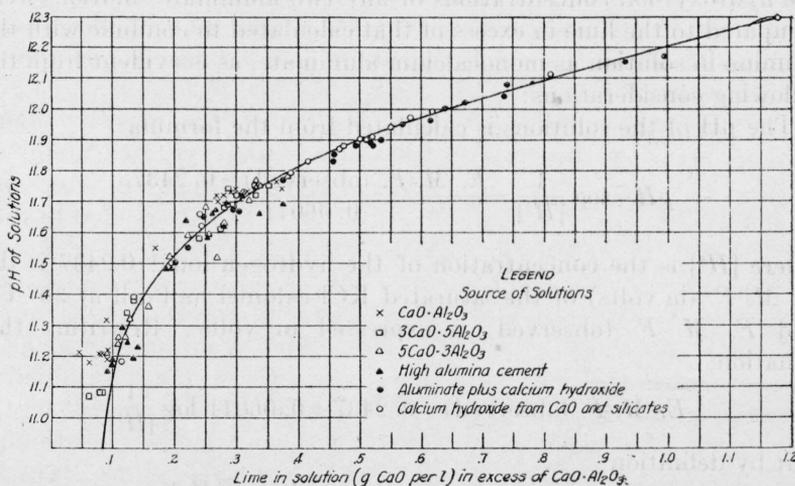


FIG. 13.—Showing the pH of solutions as a function of the lime in solution (g CaO per liter) in excess of that calculated to combine with the alumina as  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ .

In this consideration the tacit assumption has been made that all the alumina in solution is combined with the lime as a monocalcium aluminate, and that any additional lime exists in solution as calcium hydroxide. It is also further assumed that the conclusions of Slade, Blum, and Heyrovsky that aluminic acid behaves as a fairly strong monobasic acid are correct. The question of the strength of this acid will be discussed later. On the basis of these assumptions, the pH values of all the aluminate solutions are plotted (fig. 13) against the lime (expressed as grams CaO per liter) in excess of that calculated to combine with the alumina as  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . The data for these values are recorded in columns 9 and 10 of Tables 1, 3, 5, and 7. For comparison, some pH values of several pure calcium hydroxide solutions (also expressed as grams CaO per liter) are likewise plotted in

Figure 13. It can be seen from this figure that, in general, the two sets of values fall upon the same curve. The greatest deviations from the curve are those values representing the aluminate solutions which contain the higher concentration of monocalcium aluminate with the corresponding smaller concentration of "free" calcium hydroxide. In such solutions the hydrolysis of the monocalcium aluminate is a more important factor in establishing the resulting pH than it is in those solutions containing less monocalcium aluminate and relatively more of "free" calcium hydroxide.

However, the increase in pH is always attended by an increase of the lime in solution that is in excess of the amount calculated to be in combination with the alumina in solution as monocalcium aluminate. This very close relationship was brought out more clearly when the hydroxyl-ion concentrations of any two aluminate solutions were compared to the lime in excess of that calculated to combine with the alumina in solution as monocalcium aluminate, as is evident from the following considerations:

The pH of the solutions is calculated from the formula:

$$pH = \log \frac{1}{[H^+]} = \frac{E. M. F. \text{ (observed)} - 0.2437}{0.06011} \quad (1)$$

where  $[H^+]$  is the concentration of the hydrogen ions; 0.2437 is the *E. M. F.* (in volts) of the saturated KCl-calomel half cell at 30° C.; and *E. M. F.* (observed) is expressed in volts. Rewriting this equation,

$$E. M. F. \text{ (observed)} = 0.2437 + 0.06011 \log \frac{1}{[H^+]} \quad (2)$$

But by definition

$$Kw = [H^+][OH^-] = 10^{-14} \text{ or } \frac{1}{[H^+]} = \frac{[OH^-]}{10^{-14}} \quad (3)$$

Combining equations (2) and (3),

$$E. M. F. \text{ (observed)} = 0.2437 + 0.06011 \log \frac{[OH^-]}{10^{-14}} \quad (4)$$

or

$$E. M. F. \text{ (observed)} = 0.2437 + 0.06011 \log [OH^-] + 0.8415 \quad (5)$$

which may be finally written as,

$$0.06011 \log [OH^-] = E. M. F. \text{ (observed)} - 1.0852 \quad (6)$$

Equation (6) may, therefore, be used to calculate the ratio of the hydroxyl-ion concentrations of any two solutions. The numerical values of this ratio have been found to be, in general, in very good agreement with the ratio of the lime, in the same aluminate solutions, in excess of that calculated to combine with the alumina as a monocalcium aluminate of the formula,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ .

As an example of such calculations the following is presented: Two aluminate solutions are hereby designated as solutions A and B, and the necessary data concerning these solutions are to be found in Table 1, as solutions No. 1, under columns A and B. For convenience, the data are repeated in the following table, which also contains the calculated values of the third column:

SOLUTION A

Total alumina in solution as g $\text{Al}_2\text{O}_3$ per l	Total lime in solution as g CaO per l	Lime as g CaO per l calculated to form $\text{CaO} \cdot \text{Al}_2\text{O}_3$	Lime in solution in excess of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (g CaO per l)	E. M. F. (observed) at 30° C.	pH at 30° C.
2.1850	1.2930	1.2018	0.0912	0.9165	11.19

SOLUTION B

0.2500	0.4455	0.1375	0.3080	0.9481	11.72
--------	--------	--------	--------	--------	-------

The ratio of the lime in excess of that calculated as combined with alumina as monocalcium aluminate in solution A to the same kind of lime in solution B is

$$\frac{(\text{CaO})_A}{(\text{CaO})_B} = \frac{0.0912}{0.3080} = 0.296$$

The ratio of the hydroxyl-ion concentrations of solutions A and B can be calculated from equation (6), as follows:

$$\text{Solution A. } 0.06011 \log [\text{OH}^-]_A = 0.9165 - 1.0852$$

$$\text{Solution B. } 0.06011 \log [\text{OH}^-]_B = 0.9481 - 1.0852$$

Subtracting,

$$0.06011 \log \frac{[\text{OH}^-]_A}{[\text{OH}^-]_B} = -0.0316 \text{ or } \log \frac{[\text{OH}^-]_A}{[\text{OH}^-]_B} = -0.5240$$

From which it follows that the ratio,

$$\frac{[\text{OH}^-]_A}{[\text{OH}^-]_B} = 0.300$$

In the same manner the ratio of lime in the aluminate solutions in excess of monocalcium aluminate, as given in columns 9 and 10 of Tables 1, 3, 5, and 7, is calculated and recorded in column 15 of these tables. Column 16 of the same tables contains the calculated ratio of the hydroxyl-ion concentrations of the corresponding solutions. These ratios indicate, in general, that the difference in pH of two aluminate solutions is closely related to the difference in the quantity of the lime in these solutions that is in excess of the amount calculated

as that combined with the alumina in the same solutions as a calcium salt of monobasic aluminic acid. It is realized that this is not an exact relation, as the hydrolysis of the monocalcium aluminate is a factor of moment. However, the above relation would not hold as well as it does unless meta-aluminic acid were a fairly strong monobasic acid. This work, therefore, is in agreement with the conclusions of Slade, Blum, and Heyrovsky that aluminic acid is a relatively strong monobasic acid. This, then, again presents the question as to the actual strength of this acid.

Slade<sup>54</sup> has concluded that monobasic aluminic acid has an ionization constant of at least  $10^{-10}$ , which is about the same order of magnitude as that of boric acid. Assuming a saturated solution of crystalline aluminum hydroxide as containing 1 mg per liter, he calculated the concentration of the undissociated aluminic acid ( $\text{HAlO}_2$ ), in neutral or alkaline solutions, as approximately  $10^{-5}$ . The ionization constant,  $K_A$ , was then calculated from the equation

$$K_A [\text{HAlO}_2] = [\text{H}^+] [\text{AlO}_2^-] = 10^{-15}$$

giving the value

$$K_A = \frac{10^{-15}}{10^{-5}} = 10^{-10}$$

On the other hand, Blum<sup>55</sup> found an ionization constant,  $K_A = [\text{H}^+] [\text{AlO}_2^-] / [\text{HAlO}_2]$ , to be  $10^{-8.3}$ . The fact that this value is greater than that calculated by Slade is to be expected, since values of Slade were derived from solutions in equilibrium with the crystalline form of aluminum hydroxide, while those of Blum were obtained from solutions which were in equilibrium with the more soluble form of aluminum hydroxide. Even though these values might not be exact ones, they do show that aluminic acid is not a very weak monobasic acid. According to Heyrovsky,<sup>56</sup> aluminum hydroxide does not neutralize a base as does an acid, by furnishing hydrogen ions, but does so rather by the removal of hydroxyl ions to form complex anions,  $\text{Al}(\text{OH})_3 + \text{OH}^- = \text{Al}(\text{OH})_4^-$ . This is analogous to the behavior of compounds dissolved in an excess of reagents, for example,  $\text{Ag}(\text{CN})_2^-$ ,  $\text{HgI}_4^{2-}$ , etc. Heyrovsky shows, however, that in dilute solutions only monovalent ions exist, and that aluminic acid is for all practical purposes considered to be monobasic. He concludes that the acidity of aluminum hydroxide is greater than may be apparent from ordinary analytical data, and that the alkaline solutions show the highest degree of neutralization in which aluminum hydroxide reacts in the "nascent state." The solutions of aluminate result, which, in the absence of carbon dioxide, at room temperature and decinormal dilution are not more than 1.5 per cent hydrolyzed.

<sup>54</sup> Z. anorg. Chem., **77**, p. 457; 1912.

<sup>55</sup> J. Am. Chem. Soc., **35**, p. 1499; 1913.

<sup>56</sup> J. Chem. Soc. (London), **117**, p. 1013; 1920; Chem. News, **125**, p. 198; 1922.

The difficulty of obtaining an exact value for the ionization constant of aluminic acid is obvious a priori, from merely a consideration of the properties of this acid. However, the value,  $K_A = 1 \times 10^{-9}$ , has been assumed as being approximately correct for the purpose of calculating the degree of hydrolysis,  $h$ , which is defined as that fraction of the total monocalcium aluminate in solution which has immediately undergone hydrolysis. The following calculations have been made to determine the approximate degree of hydrolysis and the resulting pH of a monocalcium aluminate solution (as solution A in the above table) which contained 2.1850 and 1.2930 g  $Al_2O_3$  and CaO per liter, respectively, and with no free lime in excess of this amount. The degree of hydrolysis,  $h$ , can be calculated from the following approximation:<sup>57</sup>

$$\frac{h^2 C_S}{1-h} = \frac{K_W}{K_A} = K_H$$

$C_S$  is the total concentration, in mols per liter, of the dissolved  $CaO \cdot Al_2O_3$ ;  $K_W$  is the ionization constant of water,  $1 \times 10^{-14}$ ; and  $K_H$  is the hydrolysis constant of the aluminic acid. This equation is approximate, since there is involved the assumption that the degree of ionization of the strong base,  $Ca(OH)_2$ , in solution is numerically the same as the degree of ionization of the unhydrolyzed salt,  $CaO \cdot Al_2O_3$ , in solution.

Substituting the above data and the calculated value for  $C_S$

$$\frac{h^2(0.02143)}{1-h} = \frac{1 \times 10^{-14}}{1 \times 10^{-9}} = 0.00001$$

Hence,  $h = 0.0108$ , or, the per cent hydrolysis = 1.1, approximately, which is in good agreement with the value, < 1.5, determined by Heyrovsky. This means that  $0.02143 \times 0.011 = 0.000236$  mols, or 0.000472, equivalent of  $Ca(OH)_2$ , results from the initial hydrolysis of the monocalcium aluminate. To express this quantity of  $Ca(OH)_2$  in terms of pH it is necessary to know its degree of ionization into  $Ca^{++}$  and  $OH^-$  in the presence of the ions of the unhydrolyzed monocalcium aluminate. While the degree of ionization is not known yet, some other calculations, based on the pH measurements, have indicated that the calcium hydroxide behaves as though it were about 60 per cent ionized in the presence of the above quantity of monocalcium aluminate. Accordingly, with an assumed ionization of 60 per cent, the pH of the hydrolyzed calcium aluminate solution has been calculated as follows:

$$\begin{aligned} pH &= \log \frac{1}{[H^+]} = \log \frac{[OH^-]}{1 \times 10^{-14}} = \\ &= \log (0.000472 \times 0.6) + \log 10^{14} = \\ &= \log (0.0002832) + 14 = -3.55 + 14 = 10.45 \end{aligned}$$

<sup>57</sup> E. W. Washburn, Principles of Physical Chemistry, p. 369; 1921; McGraw-Hill Book Co., New York, N. Y.

Referring again to the electrometric titration curves obtained previously by Blum and by Britton, this value,  $\text{pH} = 10.45$ , is of the same order of magnitude as their  $\text{pH}$  values at the points of inflection in their curves wherein aluminum salts were titrated with alkali and alkaline earth hydroxides. These inflections mark the points at which aluminum hydroxide is completely redissolved with the formation of the monoaluminates.

It should be emphasized that the calculations submitted in this report give only approximate values. However, the values are approximately the same as those obtained by others and in this respect are in agreement with the assumptions that definite salts of monobasic aluminic acid exist in aqueous solution and that aluminic acid behaves as a relatively strong monobasic acid.

### III. REACTION OF CALCIUM HYDROXIDE AND CALCIUM SILICATES ON CALCIUM ALUMINATE SOLUTIONS

#### 1. REACTION OF CALCIUM HYDROXIDE ON CALCIUM ALUMINATE SOLUTIONS

From the experiments previously described in this paper, it would appear that metastable and supersaturated calcium aluminate solutions are formed in the early periods of the reaction of water with the high alumina cement and the 1:1, 3:5, and 5:3 calcium aluminates. Hydrated alumina and hydrated tricalcium aluminate subsequently precipitate from these solutions. The decomposition of the metastable monocalcium aluminate solutions was attended by an increase in  $\text{pH}$  in each case to about 11.75, even though the actual quantities of both lime and alumina in solution decreased as equilibrium was approached. The resulting solutions contained from 0.35 to 0.50 g of  $\text{CaO}$  and from 0.15 to 0.30 g of  $\text{Al}_2\text{O}_3$  per liter. Although the total quantity of lime in solution decreased with the precipitation of hydrated tricalcium aluminate and hydrated alumina, yet the uncombined calcium hydroxide, or the lime in excess of that calculated to be in combination with the alumina in solution as monocalcium aluminate, increased. It was shown that the increase of this kind of lime resulted in the increase in  $\text{pH}$  to about 11.75. Therefore, as calcium hydroxide is a product of the hydrolysis of the calcium silicates occurring in Portland cement, it was decided to conduct a study of the subsequent changes in the aluminate solutions attended by further increasing concentrations of calcium hydroxide.

In order to study the effect of increasing concentrations of calcium hydroxide on an aluminate solution, a series of reaction mixtures containing, in each case, a liter of solution was prepared. The volume of the aluminate solution (containing 0.3075 and 0.3925 g  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  per liter, respectively) was decreased in incre-

ments of 100 ml from one member of this series to another, with a proportionate increase in the volume of saturated calcium hydroxide (containing 1.176 g CaO per liter). The series of reaction mixtures was extended to that of a saturated calcium hydroxide solution, as this is the concentration of this base which is ultimately attained in the setting of Portland cement. The mixtures consisting of the calcium aluminate and calcium hydroxide solutions were set aside, for further observations, in tightly stoppered flasks in the air thermostat maintained at 30°. Since precipitation of very minute crystals started almost immediately upon the addition of the saturated calcium hydroxide solution to the aluminate solution, it was impossible to determine the pH of the mixture at this stage. After two weeks the resulting mixtures were filtered. Samples of the filtrate were taken for chemical determinations of lime and alumina and for pH determinations.

The data obtained in this investigation are recorded in Table 9. Column 1 gives the number of the reaction mixtures and columns 2 and 3 the proportioned volumes (in milliliters) of aluminate and calcium hydroxide solutions used in the preparation of the mixtures. Columns 4 and 5 give the grams per liter of alumina initially in solution and at equilibrium, respectively. The same data respecting lime in solution are tabulated in columns 6 and 7. The molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , in the precipitate (column 12) was calculated from the data of columns 4, 5, 6, and 7. In Figure 14 the lime and alumina (expressed as grams per liter) at the start and at equilibrium are plotted against the volume composition of the solutions as given in columns 2 and 3. The pH values of the equilibrium solutions (column 11) are also plotted against this composition.

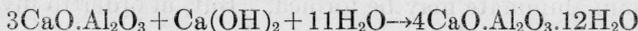
It is evident that increasing concentrations of calcium hydroxide result in the precipitation of increasing proportions of the total alumina and an increase in the pH. At a pH of 12.0, or above, the alumina is almost completely precipitated from solution. A portion of the lime is also precipitated with the alumina—presumably as a hydrated calcium aluminate. The molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3$ , in the precipitate, as computed from the composition of the solutions before and after precipitation, is recorded in column 12. The values are only approximate, since the computations involve a method of difference wherein the inherent errors may be fairly large. This is especially true of the values for the molar ratios of lime to alumina in the precipitate from mixtures Nos. 2 and 9, where the quantity of precipitate was very small. However, the molar ratio,  $\text{CaO}/\text{Al}_2\text{O}_3 = 4.13$ , of mixture No. 8 indicates that at the higher alkalinities a hydrated tetracalcium aluminate may be formed. But, in order to investigate the possible existence of such a compound, a new series of equilibrium mixtures was prepared from large volumes of aluminate and calcium

hydroxide solutions to obtain sufficient quantities of the precipitated material for more reliable chemical analyses.

Before discussing the results obtained, attention should be called to the remaining data of Table 9; that is, the relation between the pH of the equilibrium solutions as recorded in column 11 and the lime in the same solutions in excess of monocalcium aluminate,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , as given in column 9. The increase in pH is represented diagrammatically in Figure 13, which contains also the plotted values obtained heretofore for the less basic solutions obtained from the reaction of water on the calcium aluminates and high alumina cement. It is evident from Figure 13 that aluminic acid also behaves primarily as a monobasic acid at alkalinities higher than those heretofore studied in this investigation. This adds to the evidence in favor of the existence in aqueous solution of monocalcium aluminate, as brought out in the recent discussion of the constitution of aluminate solutions.

In the second series of reaction mixtures the aluminate solutions were obtained by filtering a mixture of high alumina cement and water which had stood a day. The clear filtrates were then mixed with the proportioned volume of clear calcium hydroxide solution, with the careful exclusion of the carbon dioxide of the air. As soon as the solutions were mixed, a "silken" precipitate appeared in each case, which settled after a day had elapsed. Four days later the bulk of the clear supernatant solution was siphoned from each mixture, with the careful exclusion of carbon dioxide of the air. Samples of the filtrates were taken for chemical analyses and for pH determinations. The mixture remaining was then filtered rapidly through a Büchner funnel. The precipitated material on the filter was pressed firmly between numerous sheets of filter paper and then washed with alcohol and ether. It was dried over anhydrous calcium chloride and analyzed for water (loss on ignition), alumina, and lime.

The analyses of the precipitate, together with the analyses and pH determinations of the resulting equilibrium solutions, are given in Table 10. It is seen that the molar ratio of lime to alumina in the precipitated material (column 13) increased with the pH of the equilibrium solution. At a  $\text{pH} > 12.0$ , this ratio is close to 4.0, indicating again that a tetracalcium aluminate may be formed. From the chemical analyses of the material, the composition apparently approaches that of a hydrated tetracalcium aluminate,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ . Le Chatelier<sup>58</sup> considered that a compound of this formula was formed in the setting of cement due to the reaction between anhydrous tricalcium aluminate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , and calcium hydroxide resulting from the hydrolysis of tricalcium silicate, as



<sup>58</sup> Le Chatelier, *Recherches Expérimentales sur la Constitution des Mortiers Hydrauliques*, pp. 61 and 67, Thèse, Paris; 1887. English translation also prepared by J. L. Mack, New York; 1905.

the hydrated tetracalcium aluminate being the stable form in the presence of an excess of lime. More recently Lafuma<sup>59</sup> prepared a material of the same composition,  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O}$ , by the reaction of lime upon a calcium aluminate solution. He gave no optical properties of his material other than that under the microscope the crystals appeared as fine needles.

TABLE 9.—Composition and pH of calcium aluminate—calcium hydroxide mixtures

No.	Composition of mixture		Total alumina in solution g $\text{Al}_2\text{O}_3$ per l		Total lime in solution g CaO per l		Molar ratio, CaO/ $\text{Al}_2\text{O}_3$ , in solution at equilibrium	Lime in solution in excess CaO/ $\text{Al}_2\text{O}_3$ , g CaO per l at equilibrium	Observed E. M. F. at equilibrium at 30°	pH at equilibrium at 30°	Molar ratio, CaO/ $\text{Al}_2\text{O}_3$ , in precipitate at equilibrium
	Aluminate solution at start	Calcium hydroxide solution at start	A At start	B At equilibrium	A At start	B At equilibrium					
1	2	3	4	5	6	7	8	9	10	11	12
	<i>ml</i>	<i>ml</i>									
1	1,000	0	0.3075	0.3075	0.3925	0.3925	2.32	0.2234	0.9380	11.55	-----
2	900	100	.2768	.2500	.4708	.4425	3.22	.3050	.9455	11.67	3.06
3	800	200	.2460	.1875	.5492	.4770	4.62	.3749	.9510	11.77	2.22
4	700	300	.2153	.1440	.6275	.5370	6.78	.4578	.9550	11.83	2.31
5	600	400	.1845	.1000	.7059	.5850	10.6	.5300	.9590	11.90	2.95
6	500	500	.1537	.0370	.7912	.5895	29.0	.5691	.9621	11.95	3.14
7	400	600	.1230	.0075	.8626	.6770	106.0	.6739	.9664	12.02	2.92
8	300	700	.0922	.0025	.9410	.7370	-----	.7356	.9697	12.08	4.13
9	200	800	.0615	None	1.0193	.9305	-----	.9305	.9743	12.15	2.48
10	0	1,000	-----	-----	1.1760	1.1760	-----	1.1760	.9830	12.30	-----

TABLE 10.—Composition and pH of calcium aluminate—calcium hydroxide mixtures and chemical analyses of the resulting precipitates

No.	Composition of mixture		Total alumina in solution, g $\text{Al}_2\text{O}_3$ per l at equilibrium	Total lime in solution, g CaO per l at equilibrium	Lime in solution in excess CaO/ $\text{Al}_2\text{O}_3$ , g CaO per l at equilibrium	Observed E. M. F. at equilibrium at 30°	pH at equilibrium at 30°	Analysis of precipitate (percentage composition)				Molar ratio, CaO/ $\text{Al}_2\text{O}_3$ in precipitate
	Aluminate solution at start	Calcium hydroxide solution at start						$\text{Al}_2\text{O}_3$	CaO	$\text{H}_2\text{O}$	Total	
	<i>Liters</i>	<i>Liters</i>										
1	10	2	0.3860	0.4600	0.2477	0.9440	11.65	26.56	35.69	37.36	99.61	2.44
2	8	4	.1300	.5875	.5160	.9585	11.89	24.42	37.65	36.77	98.84	2.80
3	6	6	.0770	.6600	.6168	.9625	11.96	19.02	40.49	39.60	99.11	3.87
4	4	8	.0250	.7470	.7332	.9675	12.04	18.71	40.50	39.85	99.06	3.93
5	2	10	.0000	.9940	.9940	.9755	12.17	18.75	41.40	39.63	99.81	4.01
Theoretical composition $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O}$ -----								18.82	41.34	39.84	100.00	4.00

A microscopic examination of several of the precipitates which had a molar ratio of lime to alumina close to 4 was undertaken in the present investigation. The material was found to be composed almost wholly of very minute crystals, apparently plates which often appeared as fibers or fine needles when turned on edge. These

<sup>59</sup> Lafuma, Recherches sur les aluminates de calcium et sur leurs combinaisons avec le chlorure et le sulfate de calcium. Thèse, Paris, p. 22, 1925. Also copies in Le Ciment, p. 174, May, 1925.

fibers showed positive elongation. It was very difficult to obtain exact indices, due to the fineness of grain of the crystals. The omega (or gamma) index was about  $1.532 \pm 0.005$  and the epsilon (or alpha) index about  $1.505 \pm 0.005$ . These values are approximately the same as those obtained for hydrated tricalcium aluminate, already described. No amorphous substances could be found, but the fineness of grain of the crystalline material and its tendency to form aggregates may have obscured small amounts of such materials. The samples examined showed no reaction with White's solution (used for the detection of "free" lime) after one hour of contact

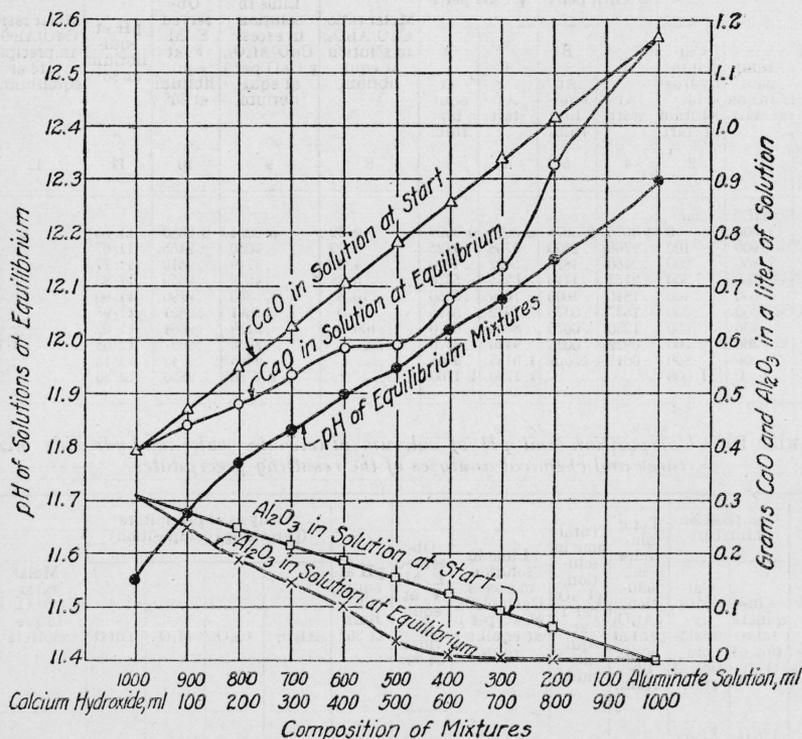


FIG. 14.—Showing the changes in the composition and pH of an aluminate solution attended by increasing concentrations of calcium hydroxide

with this reagent. The microscopic examination and the interpretation of such in the case of very fine grained material is very difficult. It would be of interest to establish more conclusively the identity of this and other hydrated calcium aluminates in future investigations. The use of X-ray patterns and other methods of attack may eventually throw more light upon this subject. The present study, however, indicates that a hydrated tetracalcium aluminate,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ , may be formed by the reaction of an excess of calcium hydroxide on a calcium aluminate solution if the pH of the resulting equilibrium solution becomes greater than 12.0.

## 2. REACTION OF CALCIUM SILICATES ON ALUMINATE SOLUTIONS

(A) REACTION OF TRICALCIUM SILICATE,  $3\text{CaO}\cdot\text{SiO}_2$ , ON ALUMINATE SOLUTIONS

From the study of the reaction of calcium hydroxide on an aluminate solution it was shown that increasing concentrations of calcium hydroxide result in the precipitation of increasing proportions of the total alumina, and that at a pH greater than 12.0 the alumina is practically all precipitated from solution as a hydrated calcium aluminate approaching, in composition,  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O}$ . Since calcium hydroxide is a product of the hydrolysis of tricalcium silicate, which occurs in Portland cement, it was decided to make up a series of mixtures of anhydrous tricalcium silicate and aluminate solutions to see if the resultant changes were actually analogous to those observed in the study of the reaction of increasing concentrations of calcium hydroxide on aluminate solutions. The procedure was to note the changes in the pH and chemical composition of an aluminate solution to which some anhydrous tricalcium silicate had been added. Accordingly, a series of reaction mixtures were prepared which contained 500 ml of an aluminate solution and 1 g anhydrous  $3\text{CaO}\cdot\text{SiO}_2$ , ground to a degree of fineness such that about 90 per cent passed a No. 200 sieve. The aluminate solution was prepared by shaking some high alumina cement with water, in the manner already described. This solution had a pH of 11.50 and contained 0.3110 g  $\text{Al}_2\text{O}_3$  and 0.3740 g CaO per liter. The reaction mixtures were kept in well-stoppered flasks which were placed in the air thermostat maintained at 30°. In order to get further information and to see whether or not the reactions occurring in the mixtures of the silicate with aluminate solutions may be in any way analogous to those proceeding in mixtures of this silicate with water, a second series of mixtures was likewise prepared, which consisted of 1 g  $3\text{CaO}\cdot\text{SiO}_2$  in 500 ml of distilled water. This new series also was placed in the air thermostat. The mixtures were shaken from time to time, and on successive days aliquots of the filtrates from separate reaction mixtures of both series were taken for analyses, and the dissolved alumina, lime, and the pH were determined.

It was observed that the particles of tricalcium silicate started to swell within 30 minutes after being placed in water. At the end of the first day they had swollen considerably. The swelling then continued more slowly, and at the same time increasing quantities of lime (calcium hydroxide) were dissolved as a result of the continued hydrolysis of this silicate. Accordingly, the pH of the solution increased. This is shown in the data of Table 11 and graphically represented in Figure 13, previously described.

However, the tricalcium silicate behaved differently in the aluminate solution than in water. In the aluminate solution there was no apparent swelling at the end of the first day. The material adhered

slightly to the bottom of the flask, such adherence increasing with time. After three days small spherulites of crystals—presumably a hydrated calcium aluminate—appeared on the bottom of the flask and after five days were visible on the walls of the container. The changes in the composition of the solutions are recorded in Table 12 and represented graphically in Figure 15. It can be seen that the pH increased slowly as time progressed, while the alumina in solution decreased, at first rapidly, and then more slowly, until it reached a value of about 0.02 g per liter. The latter value remained unchanged during the next 11 days.

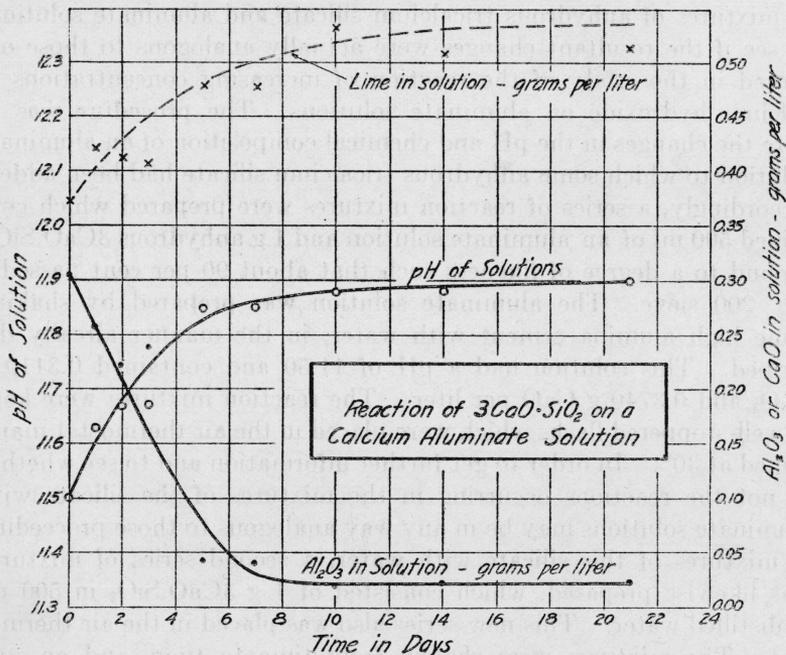


FIG. 15.—Showing the change in the composition and pH of an aluminat solution resulting from the hydrolysis of tricalcium silicate

TABLE 11.—Hydrolysis of tricalcium silicate in water at 30°  
[1 g  $3\text{CaO} \cdot \text{SiO}_2$  per 500 ml water]

	Time	Lime in solution, g CaO per l	Observed E. M. F. at 30°	pH of solution at 30°
	Days			
No. 2.....	1	0.3829	0.9525	11.79
No. 3.....	2	.4150	.9547	11.83
No. 4.....	3	.4498	.9562	11.85
No. 5.....	5	.4734	.9579	11.88
No. 6.....	7	.5000	.9590	11.90
No. 7.....	10	.5110	.9590	11.90
No. 8.....	14	.5236	.9598	11.91
No. 9.....	21	.5500	.9615	11.94
No. 10.....	28	.5821	.9633	11.97

TABLE 12.—Hydrolysis of tricalcium silicate in aluminate solution at 30°  
[1 g 3CaO.SiO<sub>2</sub> per 500 ml aluminate solution]

	Time	Alumina in solution, g Al <sub>2</sub> O <sub>3</sub> per 1	Lime in solution, g CaO per 1	Lime in solution in excess CaO.Al <sub>2</sub> O <sub>3</sub> , g CaO per 1	Observed E. M. F. at 30°	pH of solu- tion at 30°
	<i>Days</i>					
No. 1.....	0	0.3110	0.3740	0.2030	0.9354	11.50
No. 2.....	1	.2575	.4235	.2819	.9430	11.63
No. 3.....	2	.2220	.4175	.2954	.9450	11.67
No. 4.....	3	.2400	.4100	.2780	.9451	11.67
No. 5.....	5	.0425	.4800	.4566	.9559	11.85
No. 6.....	7	.0410	.4790	.4564	.9560	11.85
No. 7.....	10	.0190	.5325	.5220	.9560	11.88
No. 8.....	14	.0240	.5063	.4935	.9578	11.88
No. 9.....	21	.0240	.5135	.5003	.9588	11.90

From the above data it is evident that the changes in the composition of the aluminate solutions in the presence of tricalcium silicate were analogous to those attended by increasing concentrations of calcium hydroxide, as previously recorded in Tables 9 and 10. Thus, by using a small quantity of tricalcium silicate, it was possible to follow the changes in the aluminate solutions, and such changes may be analogous to those occurring in the setting of Portland cement and which take place within a few minutes due to the relatively higher concentrations of calcium silicates. It has previously been observed that small amounts of alumina may be found in the solutions obtained by shaking Portland cement with water for a few minutes. At later periods the degree of alkalinity (pH > 12.0) of such solutions reaches a value sufficiently high to precipitate the alumina completely from solution.

(b) REACTION OF BETA DICALCIUM SILICATE,  $\beta$  2CaO.SiO<sub>2</sub> ON ALUMINATE SOLUTIONS

Klein and Phillips,<sup>60</sup> in their studies of the hydration of Portland cement, made up a series of mixtures of about three parts of beta dicalcium silicate (beta-orthosilicate) to one each of the following: Tricalcium aluminate, 5:3 calcium aluminate, and monocalcium aluminate. They noted that when these mixtures were placed on microscopic slides the aluminates started to hydrate soon after the addition of water to the material, with the formation of needles and plates of hydrated tricalcium aluminate in all mixes. They also observed some amorphous hydrated alumina in the mixtures of the beta dicalcium silicate with the 5:3 and 1:1 calcium aluminate. The silicate started to hydrate within two days with the formation of amorphous gelatinous material, which later covered the whole slide.

It will be recalled that the formation of hydrated tricalcium aluminate and hydrated alumina in the setting of the 5:3 and 1:1 calcium aluminates is in agreement with the conclusion of the present investigation, which also gives the additional information that the

<sup>60</sup> B. S. Tech. Paper No. 43, p. 42.

hydrated alumina and hydrated tricalcium aluminate result from the decomposition of metastable monocalcium aluminate solutions formed in the early periods of the reaction.

Klein and Phillips also state, "No reason for the behavior of the aluminates in hastening the hydration of beta-orthosilicate has been found, other than it is simply a case of the silicate being more soluble in the aluminate solution than in water, and that a saturated solution is formed with subsequent precipitation of the amorphous hydrated silicate."

It seemed that further light might be thrown upon this question by following the changes in the pH and chemical composition of an aluminate solution to which some beta-calcium orthosilicate had been added, and comparing these changes to those which take place in mixtures of water and the same silicate. The method of procedure was essentially the same as that already described in the investigation of the reaction of the tricalcium silicate.

The anhydrous  $\beta 2\text{CaO} \cdot \text{SiO}_2$  was ground to a degree of fineness such that about 90 per cent passed a No. 200 sieve. The aluminate solution had a pH of 11.48 and contained 0.3125 g  $\text{Al}_2\text{O}_3$  and 0.3580 g CaO per liter. In this manner the following series of reaction mixtures were then prepared and kept in well-stoppered flasks which were placed in the air thermostat, maintained at 30°.

Series A. 1 g  $\beta 2\text{CaO} \cdot \text{SiO}_2$  to 500 ml water.

Series B. 2 g  $\beta 2\text{CaO} \cdot \text{SiO}_2$  to 500 ml water.

Series C. 5 g  $\beta 2\text{CaO} \cdot \text{SiO}_2$  to 500 ml water.

Series D. 1 g  $\beta 2\text{CaO} \cdot \text{SiO}_2$  to 500 ml aluminate solution.

Series E. 2 g  $\beta 2\text{CaO} \cdot \text{SiO}_2$  to 500 ml aluminate solution.

Series F. 5 g  $\beta 2\text{CaO} \cdot \text{SiO}_2$  to 500 ml aluminate solution.

The above mixtures were shaken occasionally, and at different time intervals aliquot portions of the filtrates from separate reaction mixtures were taken for analyses and pH determinations.

It may be recalled that the tricalcium silicate started to swell within 30 minutes after being placed in water. No swelling of the dicalcium silicate, however, was noted until after 28 days, when this material then adhered to the bottom of the flask and appeared slightly swollen. Simultaneously, the lime liberated to the solution increased with a consequent increase in pH. This is shown in the data of Table 13 and graphically represented in Figure 13, previously described. The mixtures containing the higher percentage of dicalcium silicate gave the higher pH values.

In the aluminate solutions the dicalcium silicate was apparently still more inert. This silicate under these conditions did not swell even at the later periods, and the material has shown no tendency to adhere or "set" even after an elapse of two years. Furthermore, the composition and the pH of the aluminate solution, in which the

silicate was placed, remained practically unchanged, as can be observed from the data of Table 13. This indicates that the dicalcium silicate has hydrolyzed but little in such solutions, since it has been shown previously that calcium hydroxide (a product of the hydrolysis of the silicates in water) reacts with an aluminate solution with the continuous precipitation of alumina (as a hydrated aluminate) and an increase in the pH as the quantity of calcium hydroxide is increased. The repression of the hydrolysis of the dicalcium silicate by the aluminate solution is shown even more clearly by a comparison of Tables 13 and 14. Even after one takes into consideration the lime which might have been removed from the aluminate solution in the precipitation of hydrated tricalcium aluminate, there is still a marked difference in the lime dissolved by the water over that liberated to the aluminate solution. For example, in Table 14 it is seen that the alumina precipitated from solution 11, of the D series, after 60 days was 0.3125–0.2860, or 0.0265 g per liter. This should remove 0.0437 g of CaO if  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot(\text{H}_2\text{O})$  were precipitated. The actual decrease of CaO was but 0.3580–0.3445, or 0.0135 g per liter. This means that 0.0437–0.0135, or 0.0302 g was supplied by the hydrolysis of the  $2\text{CaO}\cdot\text{SiO}_2$ . When compared to the lime given up to the water (see Table 13, A series, No. 11), after the same lapse of time, of 0.1950 g per liter, it can be seen that there is a difference of 0.1950–0.0302 or 0.1648 g. This difference is even greater in those mixtures containing a higher percentage of dicalcium silicate.

It is realized that the above results throw but little light on the problem regarding the rôle played by the dicalcium silicate in the processes of setting and hardening of Portland cement. Undoubtedly, both hydrolysis and hydration of dicalcium silicate are concerned in such processes, but which of these is of the more importance is not known. The above experiments would indicate that the dicalcium silicate does not hydrolyze (that is, liberate calcium hydroxide) as readily in a calcium aluminate solution as in water and that the separate particles of the silicate have but little tendency to adhere and "set" in an aluminate solution.

On the other hand, Klein and Phillips concluded from microscopical observations that the dicalcium silicate hydrates more readily in mixtures containing the various anhydrous aluminates than in water. Evidently, then, the presence of an excess of the aluminates is a factor of moment. Bates<sup>61</sup> found that tricalcium aluminate, when used to replace about 19 per cent of the dicalcium silicate (which is approximately the amount of aluminate present in Portland cement), adds somewhat to the strength of the latter at later periods. Apparently the whole problem is complicated, and the answer of the apparent hastening of the hydration of the dicalcium silicate may be found to

<sup>61</sup> B. S. Tech. Paper No. 78; see Tables 2 and 5.

be more than simply a case of the silicate being relatively more soluble in the aluminate solution than in water.

It would be of interest to study further the setting and hardening of beta dicalcium silicate in the presence of each of the calcium aluminates as well as in aluminate solutions of different composition than the one used in the above investigation.

TABLE 13.—Hydrolysis of beta dicalcium silicate in water at 30°

A SERIES. 1 g 2CaO·SiO<sub>2</sub> PER 500 ml WATER

	Time	Lime in solution g CaO per l	Observed E. M. F. at 30°	pH of solution at 30°
	<i>Days</i>			
No. 2.....	1	0.1114	0.9048	11.00
No. 3.....	2	.1162	.9127	11.13
No. 4.....	3	.1169	.9138	11.15
No. 5.....	5	.1184	.9149	11.16
No. 6.....	7	.1169	.9153	11.17
No. 7.....	10	.1162	.9152	11.17
No. 8.....	14	.1177	.9145	11.16
No. 9.....	21	.1169	.9142	11.15
No. 10.....	28	.1177	.9152	11.17
No. 11.....	60	.1950	.9354	11.51

B SERIES. 2 g 2CaO·SiO<sub>2</sub> PER 500 ml WATER

No. 3.....	2	0.1232	0.9160	11.18
No. 10.....	28	.2367	.9450	11.66

C SERIES. 5 g 2CaO·SiO<sub>2</sub> PER 500 ml WATER

No. 3.....	2	0.1560	0.9250	11.33
No. 10.....	28	.4664	.9570	11.87

TABLE 14.—Hydrolysis of beta dicalcium silicate in aluminate solution at 30°

D SERIES. 1 g 2CaO·SiO<sub>2</sub> PER 500 ml ALUMINATE SOLUTION

	Time	Alumina in solution g Al <sub>2</sub> O <sub>3</sub> per l	Lime in solution g CaO per l	Lime in solution in excess CaO·Al <sub>2</sub> O <sub>3</sub> g CaO per l	Observed E. M. F. at 30°	pH of solution at 30°
	<i>Days</i>					
No. 1.....	0	0.3125	0.3580	0.1761	0.9338	11.48
No. 2.....	1	.3050	.3555	.1877	.9355	11.51
No. 3.....	2	.3040	.3480	.1808	.9352	11.51
No. 4.....	3	.2950	.3430	.1807	.9344	11.49
No. 5.....	5	.3010	.3500	.1844	.9363	11.52
No. 6.....	7	.2995	.3520	.1873	.9363	11.52
No. 7.....	10	.2970	.3480	.1846	.9354	11.51
No. 8.....	14	.2875	.3520	.1937	.9362	11.52
No. 9.....	21	.2900	.3450	.1855	.9355	11.51
No. 10.....	28	.2895	.3480	.1888	.9359	11.52
No. 11.....	60	.2860	.3445	.1882	.9350	11.50

E SERIES. 2 g 2CaO·SiO<sub>2</sub> PER 500 ml ALUMINATE SOLUTION

No. 3.....	2	0.2930	0.3405	0.1793	0.9348	11.50
No. 10.....	28	.2700	.3460	.1975	.9356	11.51

F SERIES. 5 g 2CaO·SiO<sub>2</sub> PER 500 ml ALUMINATE SOLUTION

No. 3.....	2	0.2755	0.3450	0.1935	0.9350	11.50
No. 10.....	28	.2780	.3450	.1921	.9364	11.52

## IV. CALCIUM CHLOR-ALUMINATES

## 1. ELECTROMETRIC TITRATION STUDY OF ALUMINUM CHLORIDE WITH CALCIUM HYDROXIDE AND AN INVESTIGATION OF CALCIUM CHLOR-ALUMINATES

In the discussion of the constitution of aluminate solutions it was shown how previous investigators, by the construction of titration curves from electromotive-force measurements, had brought out the salient characteristics of monobasic aluminic acid. The earlier studies were, for the most part, electrometric titrations of aluminum salts with alkalis. It seemed desirable, therefore, to make a complete electrometric titration of an aluminum salt with calcium hydroxide, with the belief that additional information would be obtained relative to the constitution of the calcium aluminates in aqueous solutions. Chronologically, this study was completed before the investigation of the reaction of water on the calcium aluminates, herein previously described, was started. In fact, the electrometric titration study laid the foundation for many of the methods of procedure which were later to be applied to the more general problem. In the meantime, Britton<sup>62</sup> published the results of his electrometric titrations of aluminum salts with alkaline earth hydroxides, including a titration of aluminum sulphate with calcium hydroxide. It is gratifying to find a general agreement in the results of his investigation with those of this laboratory. However, since the present study deals more extensively with the reactions at the higher alkalinities (that is,  $\text{pH} > 10.0$ ) and involves a consideration of the formation of the calcium chlor-aluminates in an electrometric titration study of aluminum chloride with calcium hydroxide, additional knowledge of the reaction of the aluminates has been obtained. Furthermore, the investigation herein described also presents the changes in the composition of the solutions resulting from the precipitation of the solid phases during the titration, together with the chemical composition and optical properties of the hydrated calcium chlor-aluminate.

Several preliminary titrations were made from continuous electrode measurements carried out in a bottle into which were led the hydrogen electrodes as previously described, the gas inlet and outlet, a goose-neck siphon from the saturated calomel half cell, a motor-driven glass stirrer, and a burette tip. The other parts of the potentiometric system have already been described. However, in the more alkaline regions it was found that the potentials, obtained after each addition of calcium hydroxide, were not constant. The drift was of uncertain nature and was undoubtedly due to properties of the solid phases precipitating from solution and the general complexity of the proc-

<sup>62</sup> J. Chem. Soc. (London), p. 422; 1927.

esses occurring. Similar drifts of potential have been noted by Theriault and Clark<sup>63</sup> in their electrometric titrations concerning the studies of the relation of the hydrogen-ion concentrations to the formation of floc in alum solutions.

Consequently, a series of mixtures consisting of varying amount of aluminum chloride and calcium hydroxide were prepared and set aside in well-stoppered flasks, and, after equilibrium had been reached on standing, an electrometric titration curve was obtained by measuring the potentials of aliquot portions of each mixture separately transferred to the electrode vessel, following the procedure formerly described. The alumina remaining in solution after equilibrium had been attained was also determined from separate aliquots.

All materials were first purified with the greatest of care, and the solutions of  $\text{AlCl}_3$  and  $\text{Ca}(\text{OH})_2$  used in the preparation of the above mixtures were both 0.043 *N*.

TABLE 15.—*Electrometric titration of  $\text{AlCl}_3$  with  $\text{Ca}(\text{OH})_2$* 

No.	Composition of equilibrium mixture		Mols CaO per mol $\text{Al}_2\text{O}_3$ in mixture	Total alumina at start, g $\text{Al}_2\text{O}_3$ per l	Alumina in solution at equilibrium, g $\text{Al}_2\text{O}_3$ per l	Observed E. M. F. at equilibrium at 30°	pH at equilibrium at 30°	Remarks
	$\text{AlCl}_3$ (0.043 <i>N</i> ) at start	$\text{Ca}(\text{OH})_2$ (0.043 <i>N</i> ) at start						
	<i>ml</i>	<i>ml</i>						
1	1,000	0	0.00	0.7300	0.7300	0.4667	3.71	Solution clear.
2	900	100	.33	.6570	.6570	.4726	3.81	Do.
3	800	200	.75	.5840	.5840	.4763	3.87	Do.
4	700	300	1.29	.5110	.5110	.4825	3.97	Do.
5	600	400	2.00	.4380	.4380	.4766	3.87	Do.
6	550	450	2.45	.4015	.4015	.4810	3.95	Do.
7	530	470	2.66	.3869	.3860	.4816	3.96	Faint opalescence.
8	520	480	2.77	.3796	.3510	.4951	4.16	Distinct opalescence.
9	510	490	2.88	.3723	None.	.5935	5.82	Floc of $\text{Al}(\text{OH})_3$ .
10	500	500	3.00	.3650	None.	.7290	8.07	Do.
	500	500	3.00	.3650	None.	.7158	7.85	Do.
	500	500	3.00	.3650	None.	.7388	8.23	Do.
11	475	525	3.32	.3453	.0750	.8870	10.70	Do.
12	450	550	3.67	.3285	.0850	.8958	10.85	Do.
13	440	560	3.82	.3219	.0950	.9061	11.02	Decreasing amount of floc.
14	430	570	3.98	.3139	.1560	.9000	10.92	Do.
15	420	580	4.13	.3066	.3066	.9015	10.94	Floc disappeared, solution clear.
16	410	590	4.31	.2993	.2993	.9103	11.09	Solution clear.
17	400	600	4.50	.2930	.2930	.9163	11.19	Do.
18	380	620	4.90	.2774	.2774	.9258	11.34	Do.
19	360	640	5.33	.2628	.2480	.9290	11.40	First precipitation of chlor-aluminate.
20	350	650	5.57	.2555	.1880	.9320	11.45	Precipitate of chlor-aluminate.
21	300	700	7.00	.2190	.1110	.9402	11.59	Do.
22	250	750	9.00	.1825	.0525	.9477	11.71	Do.
23	200	800	12.00	.1460	.0200	.9582	11.88	Do.
24	150	850	17.00	.1095	.0060	.9615	11.94	Do.
25	100	900	27.00	.0750	Trace.	.9682	12.05	Do.
26	50	950	57.00	.0365	None.	.9724	12.12	Do.
27	0	1,000				.9818	12.29	Solution clear.

<sup>63</sup> U. S. Pub. Health Rep., 38, p. 181; 1923.

The data obtained in this investigation are recorded in Table 15. Column 1 gives the number of the reaction mixture and column 2 and 3 the proportioned volumes (in milliliters) of the 0.043 *N.*  $\text{AlCl}_3$  and 0.043 *N.*  $\text{Ca}(\text{OH})_2$  used in their preparation. Column 4 gives the mols  $\text{CaO}$  per mol  $\text{Al}_2\text{O}_3$ , figured from the volume and normality relations of the  $\text{AlCl}_3$  and  $\text{Ca}(\text{OH})_2$ . Columns 5 and 6 contain the grams per liter of alumina initially in solution and at equilibrium, respectively. The observed e. m. f. and computed pH of the equilibrium solutions are recorded in columns 7 and 8. In Figure 16 the alumina (expressed as grams per liter) at the start and at equilibrium is plotted against the volume composition of the solution as given in

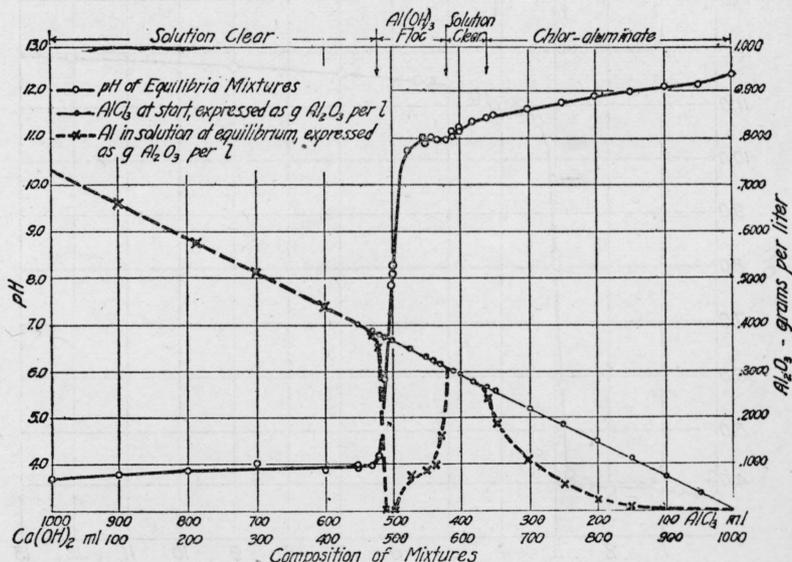


FIG. 16.—Electrometric titration curve of aluminum chloride with calcium hydroxide, showing the regions in which the different phases are separately precipitated

columns 2 and 3 of Table 15. The pH values of the equilibrium solutions are also plotted against this composition. In Figure 17 the pH values are plotted against the mols  $\text{CaO}$  per mol  $\text{Al}_2\text{O}_3$  as recorded in column 4 of the same table.

If these curves are compared with those published by previous investigators,<sup>64</sup> there will be found a general agreement in the main features, particularly in the regions less alkaline than pH 10.0. However, it appears advisable to discuss briefly some of the salient factors pertaining to the reactions at the lower alkalinities for a more complete understanding of the subsequent changes occurring in the

<sup>64</sup> Hildebrand, *J. Am. Chem. Soc.*, **35**, p. 864; 1913; Blum, *ibid.*, **35**, p. 1499; 1913; Theriault and Clark, *U. S. Pub. Health Rep.*, **38**, p. 181; 1923; Britton, *J. Chem. Soc. (London)*, p. 422; 1927.

solutions more alkaline than pH 10.0. Thus, an aqueous solution of  $\text{AlCl}_3$  is distinctly acid, as shown by a pH of 3.71 for the 0.043 *N* solution. As 0.043 *N*  $\text{Ca}(\text{OH})_2$  of pH 11.29 was added to this solution, the pH of the resulting mixture at first increased but slightly and the solutions remained clear; only opalescence was produced, even after the addition of 2.66 equivalents of  $\text{Ca}(\text{OH})_2$  per atom of aluminum had been added. This is represented in Table 15 by mixture No. 7, which contained 530 ml  $\text{AlCl}_3$  and 470 ml  $\text{Ca}(\text{OH})_2$ . The opalescence increased when more  $\text{Ca}(\text{OH})_2$  was added, until a floc of  $\text{Al}$

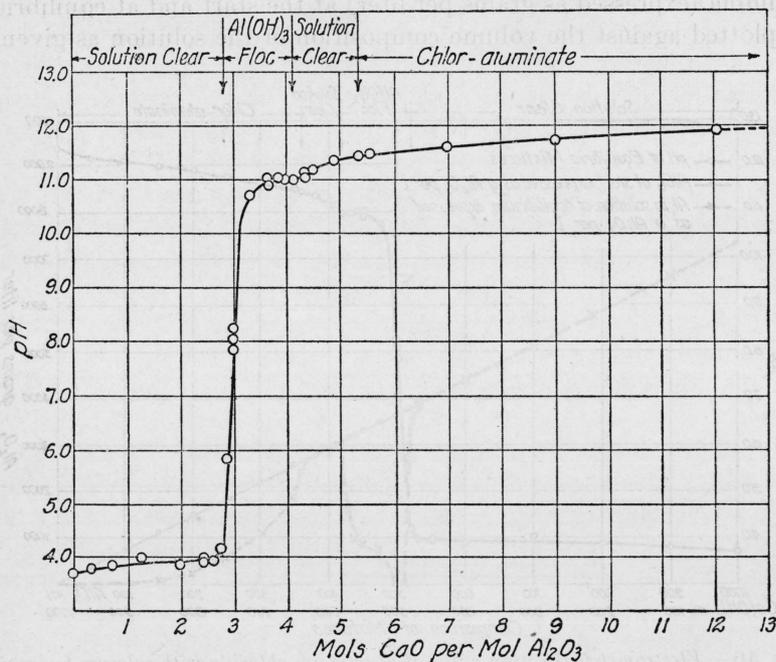
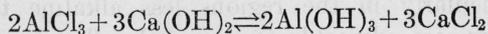


FIG. 17.—Electrometric titration curve of aluminum chloride with calcium hydroxide, showing the pH values as a function of the mols CaO added per mol  $\text{Al}_2\text{O}_3$

$(\text{OH})_3$  gradually appeared at a pH of 5.82 when 2.88 equivalents of  $\text{Ca}(\text{OH})_2$  had been added. When three mols  $\text{Ca}(\text{OH})_2$  had been added to two of  $\text{AlCl}_3$  (mixture No. 10 of 500 ml  $\text{Ca}(\text{OH})_2$ :500 ml  $\text{AlCl}_3$ ) the pH had increased to 8.0. This represents just enough  $\text{Ca}(\text{OH})_2$  to complete the reaction



The rate of floc formation was greater at pH 8.0 than at pH 5.82. This was also noted by Miller,<sup>65</sup> who showed, furthermore, that coagulation was dependent not only upon the concentration of the hydro-

<sup>65</sup> U. S. Pub. Health Rep., 40, p. 351; 1925.

genions, but also upon the anions present. Thus, the sulphate ion has a stronger coagulating effect than the chloride ion. In general, however, the "precipitation" in the sense of the chemical formation of  $\text{Al}(\text{OH})_3$  (which at first may not actually coagulate) begins at pH 4.0 and is complete before pH 8.0. Appreciable resolution of the floc of  $\text{Al}(\text{OH})_3$  occurs soon after pH 8.0 is passed. Blum has shown that an appreciable amount of alumina was always found dissolved in any solution in which the pH is greater than 9.0 but was a minimum between pH 6.5 and 7.5, points approximately defined by the color change of methyl red and of rosolic acid. The  $\text{Al}(\text{OH})_3$  redissolved completely when approximately another equivalent of  $\text{Ca}(\text{OH})_2$  had been added, the redissolving being indicated by a slight inflection of the titration curve at a pH of about 10.9. This again indicates the existence in aqueous solution of monocalcium aluminate,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  or  $\text{Ca}(\text{AlO}_2)_2$ , and the aluminate ion,  $\text{AlO}_2^-$ .

From this point the pH increased slowly as more  $\text{Ca}(\text{OH})_2$  was added to the clear aluminate solution. At a pH of about 11.4 a purely crystalline precipitate containing calcium, aluminum, and chlorine began to separate. Further increasing concentrations of calcium hydroxide resulted in the precipitation of increasing proportions of the total alumina and a gradual increase in the pH, until at a pH of 12.0, or above, the alumina was again almost completely precipitated from solution.

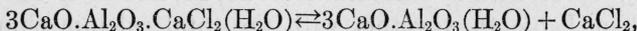
The mixtures containing the crystalline precipitates were filtered rapidly through a Büchner funnel in a cabinet free from carbon dioxide. The precipitated material on the filter paper was pressed firmly between numerous sheets of paper, dried in a desiccator over anhydrous calcium chloride, and analyzed for alumina, lime, chlorine, and water (loss on gentle ignition over a Bunsen burner). The analyses of the precipitated material from the proportionate volumes of  $\text{AlCl}_3$  and  $\text{Ca}(\text{OH})_2$ , represented by mixtures Nos. 20, 21, and 22 of Table 15, are recorded in Table 16, together with the total calcium chloride (expressed in terms of normality) in solution directly upon mixing. The composition of the precipitate was calculated from the analyses on the assumptions that a computed portion of calcium was combined with all of the chlorine as  $\text{CaCl}_2$ , and the remainder was present as  $\text{CaO}$  in a hydrated calcium chlor-aluminate. Evidently these assumptions were valid, since the compositions then totaled very close to 100 per cent.

TABLE 16.—Analysis of precipitates from  $AlCl_3:Ca(OH)_2$  mixtures

	No. (see Table 15)		
	21	22	23
Composition of mixture:			
$AlCl_3$ 0.043 <i>N</i> .....ml.	600	500	400
$Ca(OH)_2$ 0.043 <i>N</i> .....do.	1,400	1,500	1,600
Normality $CaCl_2$ in mixture.....	0.0129	0.0107	0.0086
pH of mixture.....	11.59	11.71	11.88
Composition of precipitate:			
$Al_2O_3$ .....	18.76	18.70	18.89
$CaO$ .....	31.01	32.56	33.17
$CaCl_2$ .....	15.98	14.78	13.32
$H_2O$ .....	34.25	34.12	34.66
Total.....	100.00	100.16	100.04
Molar ratio $CaCl_2/Al_2O_3$ .....	.78	.73	.66
Molar ratio $CaO/Al_2O_3$ .....	3.00	3.16	3.19
Molar ratio $H_2O/Al_2O_3$ .....	10.32	10.32	10.37

<sup>1</sup>  $H_2O$  by difference.

Kühl and Ulbrich<sup>66</sup> have shown that when solutions of aluminum chloride and calcium hydroxide interact precipitates containing chlorine may be formed in which the  $CaCl_2$  content varies appreciably from  $1/2$  to 1 mol for each mol of  $Al_2O_3$ . However, since the precipitates contain in addition about three mols  $CaO$  for each mol  $Al_2O_3$ , they have suggested as the limits for the composition of the precipitates,  $3CaO.Al_2O_3.1/2CaCl_2$  and  $3CaO.Al_2O_3.1CaCl_2$ . It should be noted that the composition of the precipitates as given in Table 16 fall within these limits. However, the molar ratio  $CaCl_2/Al_2O_3$ , in these precipitates decreased with a simultaneous decrease in the total concentration of chloride ( $CaCl_2$ ) in the mixture. This suggests the idea that the chlor-aluminate,  $3CaO.Al_2O_3.CaCl_2(H_2O)$ , may be partially decomposed into  $CaCl_2$  and  $3CaO.Al_2O_3(H_2O)$  (hydrated tri-calcium aluminate) according to the following equation:

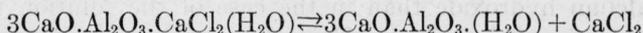


in which case the products of the reaction would be a mixture of the chlor-aluminate and aluminate with a chemical composition falling within the above limits, depending upon the extent of decomposition. If this explanation is correct, then increasing concentrations of  $CaCl_2$  should force the reaction from right to left, and there should be some definite concentration of  $CaCl_2$  above which  $3CaO.Al_2O_3.CaCl_2(H_2O)$  would be a stable phase. This was found to be the case, as will be shown in the following study of the formation and composition of calcium chlor-aluminates resulting from the reaction of calcium chloride or calcium aluminate solutions.

<sup>66</sup> Zement, 14, pp. 859-861, 880-882, 898-901, 917; 1925.

## 2. CALCIUM CHLOR-ALUMINATE FROM THE REACTION OF CALCIUM CHLORIDE ON ALUMINATE SOLUTIONS

It has been shown that calcium aluminate solutions are formed from the reaction of water upon the anhydrous calcium aluminates or high alumina cement, and that the alumina in these solutions is apparently combined with a portion of the lime as monocalcium aluminate with the remainder of the lime existing in solution as calcium hydroxide. Also, in the electrometric titration study of  $\text{AlCl}_3$  and  $\text{Ca}(\text{OH})_2$ , it was shown that under certain conditions sparingly soluble calcium chlor-aluminates are precipitated. Therefore, it was concluded that such chlor-aluminates might also be obtained by the addition of calcium chloride to an aluminate solution, provided there was also sufficient calcium hydroxide in solution to supply the necessary three mols  $\text{CaO}$  required in the precipitation of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot X\text{CaCl}_2(\text{H}_2\text{O})$ . Furthermore, it can be seen that the pH of the solutions must decrease if the chlor-aluminates are precipitated in this manner with the removal of a portion of the calcium hydroxide from solution. Finally, a study of the subsequent changes attended by increasing concentrations of calcium chloride should supply the additional information as to the concentration of calcium chloride necessary for the sole formation of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2(\text{H}_2\text{O})$ , as previously discussed in relation to the equation



Consequently, an aluminate solution was prepared and analyzed according to the procedure previously described. This solution contained 0.3005 g  $\text{Al}_2\text{O}_3$  and 0.3985 g  $\text{CaO}$  per liter, respectively, which gave a pH of 11.52. A crystalline precipitate was formed immediately upon the addition of weighed quantities of C. P. calcium chloride to separate portions of this aluminate solution in each case. After several days the resultant mixtures, which had been kept in well-stoppered flasks, were filtered with the aid of suction. The precipitated material was dried and analyzed by methods heretofore described, and the pH of the filtrate was determined.

From columns 1 and 2 of Table 17 it is seen that the pH of the aluminate solutions decreased with increasing concentrations of calcium chloride, until about 3 per cent of this salt had been added, after which it remained constant with further increasing concentrations of calcium chloride. This is shown graphically in Figure 18. Undoubtedly this decrease in pH is due to the continuous removal of a portion of the calcium hydroxide from solution as increasing quantities of the calcium chlor-aluminate are precipitated.

Table 18 shows that the per cent  $\text{CaCl}_2$  in the precipitate is a direct function of the total amount of  $\text{CaCl}_2$  in the mixture. When the normality of the  $\text{CaCl}_2$  in the mixture is greater than 0.5 (equiva-

lent to about 3 per cent  $\text{CaCl}_2$  by weight) the composition of the precipitated material agrees very closely to that of a calcium chlor-aluminate hydrate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ , as shown in the following analysis:

	Theoretical composition	From actual analysis
$\text{Al}_2\text{O}_3$ .....	18. 16	18. 44
$3\text{CaO}$ .....	29. 97	29. 67
$\text{CaCl}_2$ .....	19. 77	19. 60
$10\text{H}_2\text{O}$ .....	32. 10	32. 30
Total.....	100. 00	100. 01

Microscopic examination showed that this chlor-aluminate was composed wholly of crystals as thin hexagonal plates with the following refractive indices:  $\omega = 1.550 \pm 0.003$  and  $\epsilon = 1.535 \pm 0.003$ . The plates were uniaxial negative. The chlor-aluminate from the mixtures of  $\text{AlCl}_3$  and  $\text{Ca}(\text{OH})_2$  has essentially the same optical properties, although the indices varied slightly in the different samples, as did those of the tricalcium aluminate previously studied. However, the indices of the latter were in all cases lower than those of the chlor-aluminate.

Calcium chloride was also added to other aluminate solutions containing relatively more alumina (as monocalcium aluminate) and less "free" calcium hydroxide than in the case of the solution used in the experiment just described. Two phases precipitated from such solutions; one a hydrated chlor-aluminate as described above, and the other hydrated alumina similar to that precipitated from the metastable calcium aluminate solutions, and previously described. It was evident from the chemical analyses of the aluminate solutions to which the calcium chloride was added that the "free" calcium hydroxide was insufficient for the sole formation of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ . It is evident, therefore, that the resultant composition of the precipitate depends upon the composition of aluminate solution as well as upon the total concentration of calcium chloride in the resultant mixture.

Lafuma<sup>67</sup> has prepared a calcium chlor-aluminate of the composition,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 18\text{H}_2\text{O}$ , by the addition of about 5 per cent  $\text{NaCl}$  or  $\text{CaCl}_2$  and 4 g  $\text{CaO}$  to an aluminate solution, with the subsequent removal of excess  $\text{CaO}$  by dilution with a 5 per cent  $\text{NaCl}$  solution until the resulting solution contained about 0.5 g  $\text{CaO}$  per liter. This formula differs from that of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$  as previously obtained by Friedel<sup>68</sup> and more recently found in the investigation herein described only in the degree of hydration.

<sup>67</sup> Lafuma, Recherches sur les aluminates de calcium et sur leurs combinaisons avec le chlorure et le sulfate de calcium. Thèse, Paris, p. 52; 1925.

<sup>68</sup> Bull. Soc. Franc. Mineral. 19, p. 122; 1897.

Poisson<sup>69</sup> concluded that the formula of the calcium chlor-aluminate was  $2(3\text{CaO}\cdot\text{Al}_2\text{O}_3)\cdot\text{CaCl}_2(\text{H}_2\text{O})$  or  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 0.5\text{CaCl}_2(\text{H}_2\text{O})$ . Lafuma has criticised his work and thinks that Poisson analyzed a partially decomposed chlor-aluminate. Also, from the present work herein described, it appears that Lafuma's criticism is well founded. It is hoped that further investigations may throw more light upon the reactions of the chlor-aluminates.

TABLE 17.—Showing decrease in pH of aluminate solution as a function of the concentration of chloride

Total grams chloride per liter	pH of solutions after addition of chlorides					Analyses of solutions before and after addition MgCl <sub>2</sub>	
	CaCl <sub>2</sub>	MgCl <sub>2</sub>	BaCl <sub>2</sub>	NaCl	NH <sub>4</sub> Cl	Al <sub>2</sub> O <sub>3</sub> g per l	CaO g per l
0.0.....	11.52	11.52	11.52	11.52	11.52	0.3435	0.4060
0.5.....	11.37	10.81					
1.0.....	11.28	8.98					
2.0.....	10.97	8.11				None.	3960
5.0.....	10.56	7.85				None.	3900
10.0.....	10.39	8.11				None.	3970
20.0.....	10.05		11.37		7.89	None.	4010
23.5.....		7.14					
30.0.....	9.81			11.27			
50.0.....	9.84						
50.0.....	9.78						
50.0.....	9.80						

TABLE 18.—Showing the per cent CaCl<sub>2</sub> in the calcium chlor-aluminates as a function of the CaCl<sub>2</sub> in the mixtures

Total grams CaCl <sub>2</sub> per liter (approximate)	Normality CaCl <sub>2</sub> (approximate)	CaCl <sub>2</sub> in calcium chlor-aluminate
		<i>Per cent</i>
0.47.....	0.0086	13.32
0.5.....	.0090	13.41
0.6.....	0.0107	14.78
0.72.....	0.0129	15.98
1.0.....	.018	16.43
2.0.....	.036	17.35
5.0.....	.090	16.29
10.0.....	.180	18.62
20.0.....	.360	18.06
30.0.....	.560	19.25
50.0.....	.901	19.60

<sup>1</sup> From mixtures AlCl<sub>3</sub> and Ca(OH)<sub>2</sub> (see Table 16).

### 3. REACTION OF OTHER CHLORIDES ON ALUMINATE SOLUTIONS

An investigation was also made of the effect of barium, magnesium, sodium, and ammonium chlorides upon a calcium aluminate solution. This solution contained 0.3435 g Al<sub>2</sub>O<sub>3</sub> and 0.4060 g CaO per liter and had a pH value of 11.52.

Weighed quantities of C. P. magnesium chloride were first added to aliquots of this solution, and later the resultant mixtures were

<sup>69</sup> Ciment, 6, p. 108; 1910.

examined in the manner described in the study of the calcium chlor-aluminates. The addition of increasing quantities of  $MgCl_2$  reduced the pH of aluminate solution from 11.52 to 7.14, the successive reductions being in each case lower than those affected by the addition of corresponding amounts of  $CaCl_2$ . These reductions are recorded in Table 17 and graphically represented in Figure 18. Also, from columns 7 and 8 of Table 17 it may be noted that, although the precipitation of alumina was complete at concentrations of  $MgCl_2$  in excess of 2 g per liter at pH values less than 8.11, yet but traces of lime were precipitated, or accluded with the alumina.

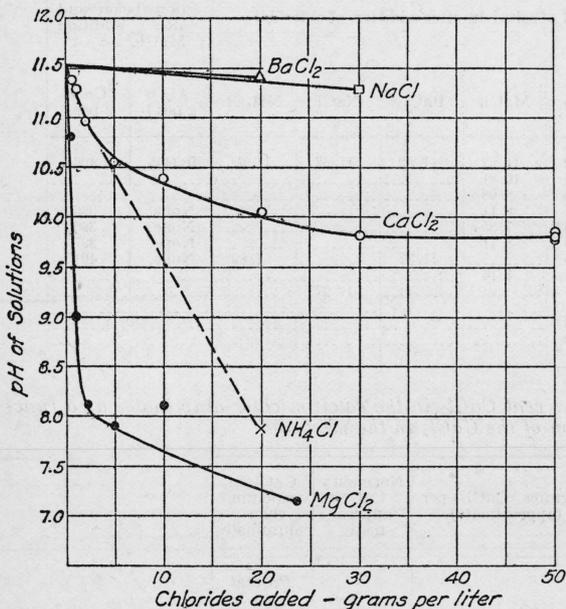


FIG. 18.—Curves showing the decreases in the pH of an aluminate solution attended by the addition of various chlorides

Apparently little or no calcium chlor-aluminate is precipitated by the addition of this quantity of  $MgCl_2$ . Whether this compound is formed at concentrations of  $MgCl_2$  less than 2 g per liter could not be ascertained, since the precipitate was colloidal and could not be filtered readily. Microscopic examination of the filterable precipitates showed the absence of any crystals which resembled calcium chlor-aluminate.

The material appeared to be amorphous and was found by chemical analysis to contain both aluminum and magnesium (presumably as hydrated oxides). It was found previously from the electrometric titration of  $AlCl_3$  with  $Ca(OH)_2$  that hydrated alumina is precipitated from solution as the stable phase at the pH between 7.14 and 8.11, the values attained by the addition of more than 2 g of  $MgCl_2$  per liter. Apparently, then, the  $MgCl_2$  reacts with the "free"  $Ca(OH)_2$  of the aluminate solution to form insoluble magnesium hydroxide, the calcium chloride remaining in solution. The hydroxyl ions are thus removed from the field of action to such an extent that the alumina, which has been in solution as an aluminate, pre-

precipitates also as the hydroxide. The precipitate is thus a mixture of aluminum and magnesium hydroxides.

It was found upon the addition of sodium or barium chloride to the calcium aluminate solution that a small quantity of calcium chlor-aluminate was precipitated gradually and that the pH of the solution was but slightly decreased. This indicates that barium chlor-aluminate is more soluble than calcium chlor-aluminate. It has also been shown that both the concentration of calcium chloride and "free" calcium hydroxide are factors of moment in the precipitation of the calcium chlor-aluminates. This accounts for the small amount of this compound being precipitated, since the quantity of calcium chloride which could be formed by the reaction between the calcium hydroxide and sodium or barium chlorides is too limited. The addition of either  $\text{CaCl}_2$  or  $\text{Ca}(\text{OH})_2$  to the mixtures resulted in the formation of increasing amounts of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ .

Ammonium chloride, on the other hand, reacted more like magnesium chloride on the aluminate solutions. The addition of 2 g  $\text{NH}_4\text{Cl}$  to a liter of the aluminate solution resulted in a decrease in pH from 11.52 to 7.89 with the complete precipitation of the aluminum as the hydroxide. Analysis of the filtrate showed that no calcium was precipitated. The reaction of the ammonium chloride on the calcium aluminate solution may be explained as follows: The ammonium chloride reacts with the calcium hydroxide of the aluminate solutions to form ammonium hydroxide, which is but slightly ionized. The ionization is further repressed by the "common ion effect" of the  $\text{NH}_4^+$  of the additional ammonium chloride to such an extent that the hydroxyl-ion concentration becomes sufficiently low to cause the formation of the insoluble aluminum hydroxide. The lime is converted to calcium chloride and remains in solution.

## V. SUMMARY

This investigation included the study of the mechanism of the reaction of water on a high alumina cement and the following anhydrous calcium aluminates: Monocalcium aluminate, 3:5 calcium aluminate, 5:3 calcium aluminate, and tricalcium aluminate.

Since the addition of water to tricalcium aluminate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , produces a very vigorous reaction, the changes in the composition of the resulting aqueous solutions could not be followed in the case of this aluminate. Previous investigations have indicated that its setting is due to the formation of hydrated tricalcium aluminate.

On the other hand, since the activity of the other aluminates and high alumina cement toward water is distinctly less than that shown

by the tricalcium aluminate, it was possible to follow the mechanism of the reaction in the formation and decomposition of the metastable calcium aluminate solutions. During the early periods of the reaction a portion of the lime and alumina in each case passed into solution as the calcium salt of monobasic aluminic acid. The total concentration of this aluminate depended upon the chemical composition of the anhydrous aluminate or cement from which it was formed, as well as upon the time of reaction. However, these monocalcium aluminate solutions were metastable and soon decomposed with precipitation of a portion of the lime and alumina. The molar ratio of the lime to the alumina remaining in solution after precipitation increased and was attended in each case by an increase in the pH from about 11.1 to 11.75.

Identical changes in the metastable solutions took place when filtered from the reaction mixture. Part of the lime and alumina likewise precipitated from these clear metastable solutions and resulted in "equilibrium" solutions similar to those obtained when the aluminate or high alumina cement had been left in contact with the water for long periods. In both cases equilibrium apparently was reached only after several weeks had elapsed.

Chemical analyses and microscopic examinations of the material precipitated from the metastable solutions indicated that hydrated alumina and hydrated tricalcium aluminate were precipitated as equilibrium was approached. The pH of the aqueous solution in equilibrium with these two solid phases, hydrated alumina and hydrated tricalcium aluminate, is approximately 11.75.

The constitution of the aluminates in solution was reviewed in the light of previous investigations, where it has been shown that aluminum hydroxide is an amphoteric electrolyte and, as an acid, is primarily monobasic. Calculations based upon electrometric measurements and chemical analyses are submitted which indicate that the alumina exists in solution as the calcium salt of monobasic aluminic acid, and that the quantity of "free" calcium hydroxide in excess of this salt is the determining factor of the pH. The conclusion of Slade, Blum, and Heyrovsky that aluminic acid is a relatively strong monobasic acid has been confirmed.

It has been shown that the more concentrated monocalcium aluminate solutions are metastable, since they are supersaturated with respect to the more insoluble form of aluminic acid (hydrated alumina) as well as to the hydrated tricalcium aluminate.

An investigation has been made of the subsequent changes in the aluminate solutions attended by increasing concentrations of calcium hydroxide. As the concentration of calcium hydroxide is increased, increasing proportions of the total alumina are precipitated, until at a pH of 12.0 or above the alumina is completely precipitated from

solution. Some lime is also precipitated with the alumina. The molar ratio, lime to alumina in the precipitated material, increases with an increase in pH. A tetracalcium aluminate of the composition,  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O}$ , appears to be formed at a pH above 12.0.

Analogous changes in the aluminate solutions are affected by the calcium hydroxide liberated by the hydrolysis of tricalcium silicate in such solutions. The hydrolysis of beta dicalcium silicate appears to be greatly inhibited by an aluminate solution.

A study of the electrometric titration of  $\text{AlCl}_3$  with  $\text{Ca}(\text{OH})_2$  has been made. The precipitation of aluminum as the hydroxide is complete between pH 6.0 and 7.5, a confirmation of the conclusions of Blum. Appreciable resolution of the aluminum hydroxide occurs in solutions in which the pH is greater than 9.0. The alumina redissolves completely at a pH of 10.9. At the higher alkalinities a calcium chlor-aluminate is formed. This aluminate may also be prepared by the reaction of calcium chloride on an aluminate solution; its chemical composition depends upon the composition of the aluminate solution and the concentration of calcium chloride. If the concentration of the latter exceeds 3 per cent, the composition of the chlor-aluminate approaches  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ . The optical properties of this compound have been determined.

Barium chlor-aluminate appears to be more soluble than calcium chlor-aluminate. Ammonium chloride and magnesium chloride both decompose calcium aluminate solutions, with the precipitation of aluminum hydroxide by the ammonium chloride and of a mixture of aluminum and magnesium hydroxides by the magnesium chloride.

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