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The effects of calcium chloride upon the hydrolysis of pure compounds of cement

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UMI

THE EFFECTS OF CALCIUM CHLORIDE UPON THE HYDROLYSIS

OF PURE COMPOUNDS OF CEMENT

by

George Henry McIntosh

A Thesis Submitted to the Graduate Faculty

for the Degree of

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Approved:

In charge of Major Work

Head of Major Department

Dean of Graduate College

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INTRODUCTION

Innumerable substances have been used for a number of years as admixtures in Portland cement. Today the only compounds used as admixtures to any great extent are calcium sulfate and calcium chloride. It is a well-known fact that the presence of calcium sulfate not only retards the setting process but also gives an increase in the strength of the resulting cement. Calcium chloride is unlike calcium sulfate in its action on cement. It has been found to be particularly effective in accelerating the initial hardening and causes a pronounced increase in strength when used in small quantities. However, when used in larger quantities it increases the setting time seriously and therefore should be used with the greatest care. Duff A. Abrams[1] has made an intensive study on this subject and has found that up to 3 per cent of the weight of the cement the use of calcium chloride can be very advantageous.

A great deal of research has been carried out on the study of the catalytic effects not only of calcium chloride but many other compounds. From these studies many theories have been presented as to what happens when catalysts are used in cements,[9] [10] [20] [25] but as yet no very satisfactory answer has been given.

The purpose of this research was to study not the effects of calcium chloride on cement, but rather its effects on the pure bodies that go to make up a normal cement clinker. If the effects of calcium chloride upon these pure compounds are known, its action upon the cement itself can be much better understood.

REVIEW OF LITERATURE

The Constituents of Portland Cement

Cementing materials have been used since time immemorial but only since 1824 have they been the dominant form for all types of construction.[21] In that year Joseph Aspdin, a bricklayer at Leeds, England, mixed certain quantities of lime and clay and burned them in a kiln. After the burning the resulting mass was pulverized and used in making concrete. Because the concrete resembled a stone quarried on the Isle of Portland, he called his product "Portland Cement" and obtained a patent on its preparation.

Many studies were made on cement after the year 1824, but it was not until 1887 that the first scientific research was started on the composition of the material. Henri Le Chatelier[4] recognized that Portland cement clinker was a heterogeneous system of several clinker minerals. It was by means of the microscope that he was able to discover and postulate so many of the principles that are acknowledged as facts today.

As the result of his work[16] Le Chatelier concluded that the essential constituents of Portland cement were tricalcium silicate and dicalcium silicate. He described another compound

of lesser importance, believed to be present, as a deep brown alumina-ferrite of lime.

The work of Le Chatelier remained unknown until 1897 when A. E. Törnebohm,[4] in a short paper duplicated the work of Le Chatelier. In his paper Törnebohm claimed that cement clinker was composed of four minerals which he designated as alite, belite, celite, and felite. The description of these compounds corresponded to the compounds described by Le Chatelier with possibly the exception of felite, the composition of which was doubtful.

Although the conclusions of Le Chatelier and Törnebohm were not identical, they agreed well enough to furnish us with the foundation on which we today base our many theories and hypotheses of the structure and constitution of cement.

The work of Le Chatelier and Törnebohm was accepted as authoritative and was not extended very much until about the year 1915. It must not be forgotten, however, that many theories were advanced during the years 1897 to 1915. These theories were soon disproved when G. A. Rankin[22] applied the laws of equilibrium of heterogeneous systems to the problem of cement. By means of the Phase Rule a complete description of the ternary system lime-silica-alumina was given for the first time. The results of this research have led to the conclusion that a normal Portland cement clinker must consist of tricalcium silicate, dicalcium

silicate, tricalcium aluminate, pentacalcium trialuminate and free lime. Of these compounds the tricalcium silicate, dicalcium silicate and tricalcium aluminate are by far the most predominant in the cement clinker.

Closely associated with Rankin's in this work were several Americans including A. L. Day[8], E. S. Shepherd[24], F. E. Wright[23], E. D. Campbell[6] and A. H. White[26]. These men, working in the Geophysical Laboratory of the Carnegie Institute of Washington, studied the system lime-silica-alumina. Their work was so complete that it stands today with but few minor corrections.

While American investigators were working on the problem of the constitution of cement clinker, Germans likewise were doing a great deal of research on the same thing. Among these was Jänecke[14].

He reported that alite, the principal constituent in the clinker described by Le Chatelier and Törnebohm, contained the three constituents silica, alumina and lime, and must be considered a ternary compound. He investigated the region of the ternary diagram corresponding to Portland cement and reported a new compound with the formula $8CaO.Al_2O_3.2SiO_2$, which he named Jäneckeite.

This compound has been questioned and according to W. C. Hansen and his co-workers does not exist. However, its presence in cement clinker is still a point of dispute between

American and European workers.

At the present time there are several theories on the composition of cement clinker, but only two of them appear to be of importance. According to Dr. Hans Kühl[15] the principal constituents of cement are but two in number, namely, alite and celite. The formulas of these two constituents are as follows:

Alite = $3CaO.SiO_2 + 2CaO.Al_2O_3$,

Celite = $2CaO.Fe_2O_3 + 2CaO.Al_2O_3$.
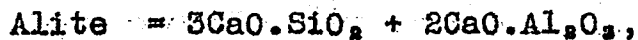
By means of X-ray methods L. T. Brownmiller and R. H. Bogue[5] have studied twenty-eight samples of commercial Portland cement clinker, representing many types of raw materials and processes of manufacture, both domestic and foreign. The results of their investigation by the X-ray method are in agreement with those obtained by the phase equilibria, and by chemical microscopic methods. Each supplements and confirms the other. Their findings indicate that the most abundant constituents in the clinker are tricalcium silicate and beta dicalcium silicate. Also that there are normally present, tricalcium aluminate, tetra calcium alumino ferrite and magnesia. They found that free lime is not normally present in amounts as great as 2.5 per cent.

Admixtures

The catalytic effect of various materials as admixtures in cement has been studied carefully by many researchers, but it still remains a mystery. The importance in the control of the setting properties of cement is of great interest, and consequently the use of various chemical compounds for the regulating of the setting process should be studied. D. A. Abrams[1] in his report upon calcium chloride gives a summary containing a great number of references to the use of calcium chloride upon cement and concrete. Dr. Kühl[15] has studied the catalytic effects of such compounds as the chlorides of Li, Na, K, NH_4, Cd, Sr, Ba, Cd, Al and Fe upon cement and found that they all accelerate the setting process as well as increase the strength. He also gives a list of compounds which retard the setting as well as those salts that are injurious to the strength of the cement.

E. J. Crane[7] has studied the effect of replacing calcium oxide by manganous oxide in Portland cement. He found that it was the soluble manganese compounds present and not the manganese silicates themselves that increased the rate of setting and final strength.

Little study has been made of the effect of various materials upon the pure compounds of cement. The action of $Ca(OH)_2$ and $NaOH$ upon the rate of hydrolysis of the compounds

that occur in cement has been studied by Lerch and Bogue[18].

The work of A. J. Hammer[11] was the first attempt to study the action of calcium chloride upon the constituents of cement. Microscopic methods were used in this study of the crystal formation when cement compounds were treated with calcium chloride solutions of varying concentrations. From this work it appeared that tricalcium silicate and dicalcium silicate reacted more rapidly with the calcium chloride than did tricalcium aluminate.

R. C. Sloane and his co-workers[25] have made a very extensive study of the rate of hydration of the cement bodies under the influence of calcium chloride. In this study were used three calcium chloride solutions of 2 per cent, 4 per cent and 8 per cent concentration. The compounds studied were tricalcium silicate, tricalcium aluminate and beta dicalcium silicate. The results of the work showed that calcium chloride accelerated the rate of hydration of the calcium silicates in cement, but retarded the hydration of tricalcium aluminate.

EXPERIMENTAL PROCEDURE

Preparation of the Cement Constituents

The compounds studied in this investigation were tricalcium aluminate, tricalcium silicate, beta dicalcium silicate and gamma dicalcium silicate. According to R. H. Bogue[3] more than eighty per cent of Portland cement is composed of these four compounds. Therefore the results obtained by the study of these compounds should give some indications as to how Portland cement would react under similar conditions.

The raw materials used in the preparation of these four compounds were silica, calcium carbonate and alumina. The calcium carbonate and alumina used were J. T. Baker's analyzed C. P. products. The materials were analyzed before the experiment was started. The silica was prepared from a technical grade of sodium silicate and hydrochloric acid. The acid was added until precipitation of the silicic acid was complete. The precipitate was washed by decantation until it gave no test for chlorides with silver nitrate. The precipitate was dried at 130° C. and finally ignited in platinum at 1000° C. The resulting product was ground to pass a 200 mesh and analysis showed it to contain 99.84 per cent silica.

The raw materials were all ground to pass 200 mesh before being used because R. K. Meade [19] has found that there is a

definite relationship between the variables, time, temperature and fineness, and the resulting clinker. When the materials are very finely ground, the combination will take place at a lower temperature or with less heating than when the materials are coarsely ground. Also, with materials of the same fineness the combination will take place more rapidly when the temperature is higher. As a result of this study Meade has developed a formula which is expressed as

$$A \times B \times C = D$$

where A represents time of burning, B the temperature, C fineness, and D a constant, namely, clinker.

The furnace used in preparing these compounds was a gas-fired crucible furnace. The high temperatures were easily attained as well as maintained by means of a gas-compressed air-oxygen blast burner. The gas was enriched with benzene.

All temperatures used in the preparation of these compounds were measured with a calibrated chromel-alumel thermo-couple when possible, or, in the case of higher temperatures, a calibrated Leeds and Northrup optical pyrometer.

Tricalcium aluminate

The tricalcium aluminate was made by mixing calcium carbonate with alumina in the proper proportions with distilled water. The resulting mixture was placed in an alundum crucible and the temperature slowly raised to 1375° C. This

temperature was maintained ± 20°C. for a period of four hours. After the heating the material was ground to pass a 200 mesh, thoroughly mixed, and refired for another period of four hours at the same temperature. It was then ground and mixed as before but analyzed before refiring. In case the analysis did not check the theoretical values for tricalcium aluminate, the sample was made up to this value by the addition of either alumina or calcium carbonate. The above procedure of mixing, grinding, and firing was repeated until the analysis checked the theoretical values. The calculated values of Al_2O_3 and CaO are 37.73% and 62.26% respectively. The values found were Al_2O_3, 38.12% and CaO, 62.27%.

A test for free lime was made according to the method described by Lerch and Bogue[17]. The test was negative. The index of refraction of the material was 1.707 ± 0.002. This value checks that of W. C. Hansen[12] which is given as 1.710 ± 0.002.

Gamma dicalcium silicate.

The gamma dicalcium silicate was prepared by mixing calcium carbonate and silica in the proper proportions with distilled water and firing the mixture in an alundum crucible. The temperature of 1500°C. ± 20°C. was maintained for a period of four hours. On cooling, the sticks, which were very hard at high temperatures, crumbled or "dusted" completely. This crumbling is due to the inversion of the beta dicalcium sili-

cate to the gamma form, as described by Day and Shepherd[8].
The resulting compound was ground to pass a 200 mesh, mixed,
and refired at the same temperature for the same length of
time. After the second period of heating the compound was
ground and mixed. The analysis showed there was present
65.54% CaO and 34.92% SiO_2. The calculated values are 65.12%
CaO and 34.88% SiO_2. The compound gave a negative test for
free lime. Microscopic examination showed a pure product.
The angles of the crystals were not measured because the
crystals were too fine to be measured with the equipment
available.

Beta dicalcium silicate.

Beta dicalcium silicate was prepared by the method de-
scribed by Bates and Klein[2]. The raw materials were mixed
in the proper proportions as described in the preparation of
gamma dicalcium silicate, but one per cent of B_2O_3 was added
to prevent the inversion of the beta to the gamma form.
Alundum crucibles were not used because the compound stuck to
the crucible and became contaminated. The mixture was molded
into sticks with distilled water and dried in an oven at
130°C. These sticks were then fired for four hours at a
temperature of 1500°C. The sticks were removed from the fur-
nace while white hot and allowed to cool in the air as this
helped prevent dusting. The resulting compound was reground
and reheated a second time at the above temperature. After

this second heating an analysis showed the composition to be 65.43% CaO and 33.83% SiO_2. The theoretical values are 65.12% CaO and 34.88% SiO_2. A small amount of boric glass was found present upon microscopic examination. The compound gave a negative test for lime and showed strong birefringence.

Tricalcium silicate.

The tricalcium silicate was prepared according to the directions of Sloane and his co-workers[25]. A special procedure had to be used because calcium carbonate and silica mixed in the proper proportions and burned, as in the preparation of the other compounds described, produced some dead burned lime. Therefore it was necessary to make the compound in three steps. In the first mixture the calcium carbonate and silica were in the ratio of 2.3 CaO : $1SiO_2$. This mixture was burned at 1530° C. ± 20° C. for four hours, reground, analyzed, and enough $CaCO_3$ added to make the ratio 2.7 CaO : $1SiO_2$. This was fired as before, reground, analyzed, and enough $CaCO_3$ added to make the ratio 3CaO : $1SiO_2$. This mixture was reground and refired twice more at the same temperature for the same period of time. An analysis showed the composition to be 73.86% CaO and 26.50% SiO_2. The correct values are 73.69% CaO and 26.31% SiO_2. A microscopic test proved it to be a pure body. The compound showed weak birefringence and an index of refraction of N = 1.710 ± 0.002. The value given by Hansen[12] is N = 1.715 ± 0.002.

The Studies of the Rate of Hydrolysis

For the studies of the effects of calcium chloride upon the four cement compounds, namely, $3CaO.Al_2O_3$, $3CaO.SiO_2$, $\beta 2CaO.SiO_2$ and $\gamma 2CaO.SiO_2$ twelve calcium chloride solutions of the following concentrations were used:

Solution	Percentage
1	0.001
2	0.01
3	0.10
4	0.20
5	0.35
6	0.50
7	1.00
8	1.75
9	2.50
10	5.00
11	7.00
12	10.00

These solutions were prepared by weighing Mallinckrodt C. P. calcium chloride, the analysis on the bottle being:

CaO . . . . trace

Fe 0.001%

Other heavy metals 0.00%

SO_3 . . . . 0.02%

Assay $CaCl_2$ 95.00%

Effects of CaCl₂ upon the rate of hydrolysis.

Rate of hydrolysis in solution saturated with Ca(OH)₂.
The effects of the various concentrations of calcium chloride upon the four compounds studied were measured by the rate of hydrolysis. The first part of the experiment was a study of the rate of hydrolysis of the compounds in calcium chloride solutions saturated with Ca(OH)₂.

The amount of sample used was such that if complete hydrolysis of the compounds took place there would be formed 0.8226 grams of Ca(OH)₂. Equivalent quantities of the four compounds studied were used. These samples, twelve in number for each compound, were placed each in a carbon dioxide flask of 150 cc. capacity. To the flasks were added 100 cc. of the calcium chloride solutions of the concentrations mentioned above. The flasks were stoppered and shaken from time to time.

A duplicate series of samples was run to serve as a check. Also, pure Ca(OH)₂ was used in the same amount of each of the CaCl₂ solutions and in boiled distilled water as standards for comparison.

The OH ion concentration of the resulting solutions was determined at 25° C. by the electrometric method with a saturated calomel half cell, saturated agar-KCl bridge, and a platinum-platinum black electrode. The potentiometer used was a Leeds and Northrup Type K. The results of the experi-

ment are reported in the tables I, II, III, IV and V and graphically in figures I, II, III, IV and V. The values in the tables are in terms of pH.

TABLE I

Hydrolysis of 5CaO.Al₂O₃ in CaCl₂ Solutions

pH of solutions after one gram of the compound had been allowed

to react with 100 cc. of the CaCl₂ solutions

to give a saturated lime solution.

Time in Days	Number and Concentration of CaCl₂ Solutions												Distilled H₂O
	1	2	3	4	5	6	7	8	9	10	11	12	
	0.001%	0.01%	0.10%	0.20%	0.35%	0.50%	1.00%	1.75%	2.50%	5.00%	7.50%	10.00%	13
1/2	11.74	11.77	11.64	11.72	11.60	11.45	11.34	11.41	11.28	10.65	10.58	10.44	11.85
1	11.86	11.88	11.77	11.76	11.74	11.71	11.70	11.50	11.31	10.80	10.63	10.48	11.87
3	11.84	11.84	12.01	11.97	11.91	11.85	11.90	11.58	11.42	10.77	10.61	10.48	11.92
5	—	—	—	—	—	—	—	11.63	11.43	10.79	10.58	10.42	11.96
6	12.15	12.17	12.11	12.08	11.97	11.87	—	—	—	—	—	—	—
7	—	—	—	—	—	—	—	—	—	10.66	—	10.38	—
8	12.16	12.10	—	—	—	—	—	—	—	—	—	—	—
9	11.84	11.82	—	—	—	—	—	—	—	—	10.58	10.38	11.97
10	—	—	—	—	—	—	—	11.88	11.63	11.49	10.66	10.51	—
11	11.80	11.80	—	11.84	11.76	—	—	11.56	—	10.50	—	10.54	11.85
14	11.80	11.82	—	—	—	—	—	—	—	—	—	—	—

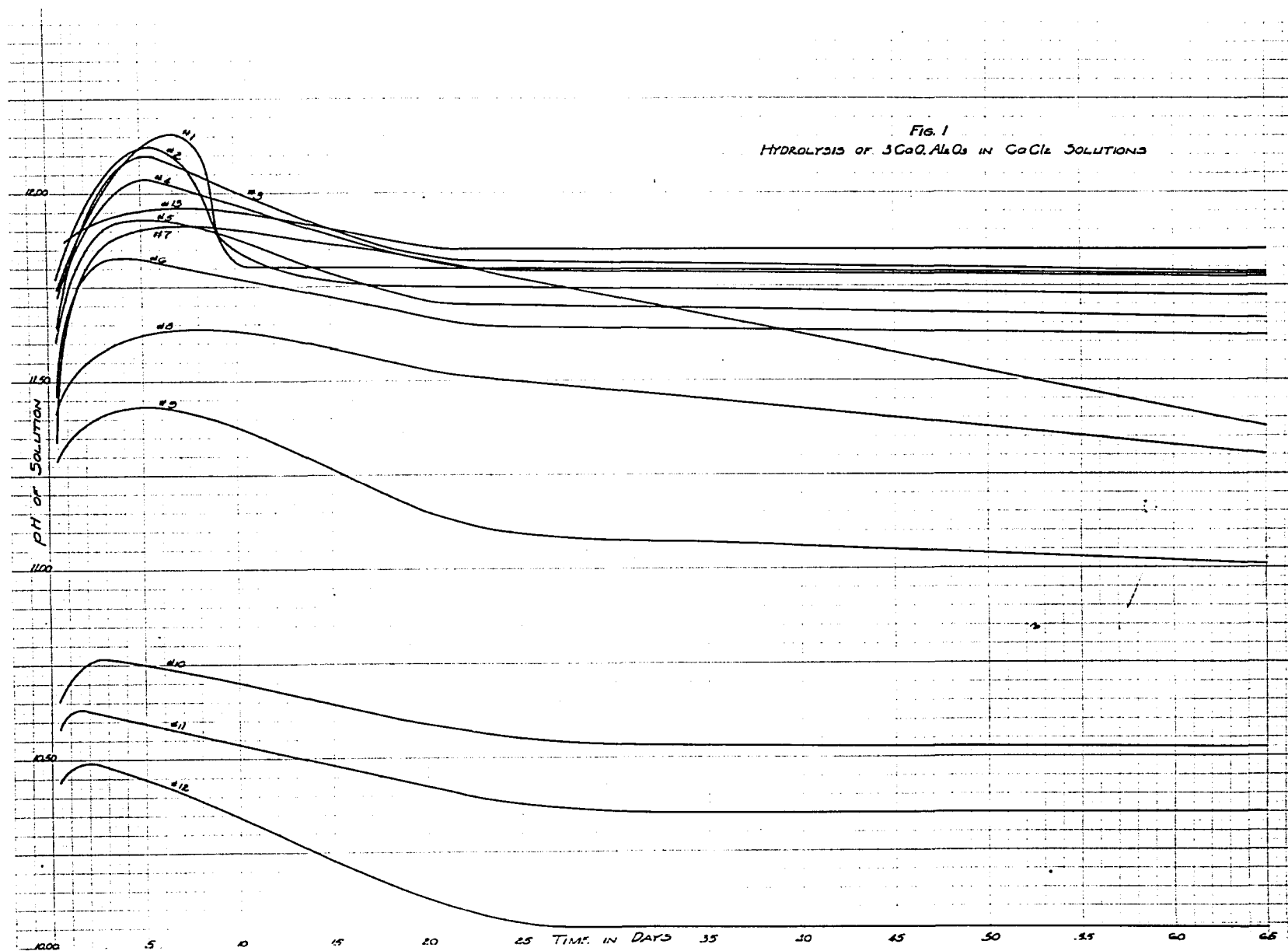|													
1/2	11.74	11.77	11.64	11.72	11.60	11.45	11.34	11.41	11.28	10.55	10.??	----	----
1	11.86	11.88	11.77	11.76	11.74	11.71	11.70	11.50	11.31	10.80	10.65	10.48	11.87
3	11.84	11.84	12.01	11.97	11.91	11.83	11.80	11.58	11.42	10.77	10.61	10.48	11.92
5	----	----	----	----	----	----	----	----	----	----	----	----	11.96
6	12.15	12.17	12.11	12.06	11.97	11.67		11.63	11.43	10.79	10.58	10.42	----
7	----	----	----	----	----	----	----	----	----	10.66		10.58	----
8	12.16	12.10	----	----	----	----	----	----	----	----	----	----	----
9	11.84	11.82	----	----	----	11.88	11.63	11.49	10.66	10.51	10.58	10.38	11.97
10	----	----	----	----	----	----	----	----	----	----	----	----	----
11	11.80	----	11.84	11.76	----	----	11.56	----	10.50	10.54	----	----	11.85
14	11.82	----	----	----	----	----	----	----	----	----	----	----	----
17	11.79	11.80	11.79	11.84	----	11.71	11.86	11.54	11.01	10.66	10.51	10.30	----
18	11.75	11.78	----	----	----	----	----	----	----	10.62	10.46	10.16	----
19	----	----	11.81	11.81	11.71	----	----	----	----	----	----	----	----
21	11.72	11.79	11.79	11.84	11.73	11.67	11.82	----	----	----	----	----	11.85
22	----	----	----	----	----	----	11.56	----	10.58	10.40	10.09	----	----
61	----	----	----	----	----	----	11.42	11.33	11.01	10.53	10.35	10.00	11.85
62	11.72	11.81	----	----	11.62	----	----	----	----	----	----	----	----
63	----	11.79	11.78	11.67	----	----	----	----	----	----	10.36	10.11	----
65	11.72	11.79	----	----	----	----	----	----	----	----	----	----	----

Fig. 1
HYDROLYSIS OF 3CaO.Al₂O₃ IN CaCl₂ SOLUTIONS

TABLE II

Hydrolysis of 3CaO.SiO₂ in CaCl₂ Solutions

pH of solutions after 0.8450 grams of the compound had been allowed
to react with 100 cc. of the CaCl₂ solutions to
give a saturated lime solution

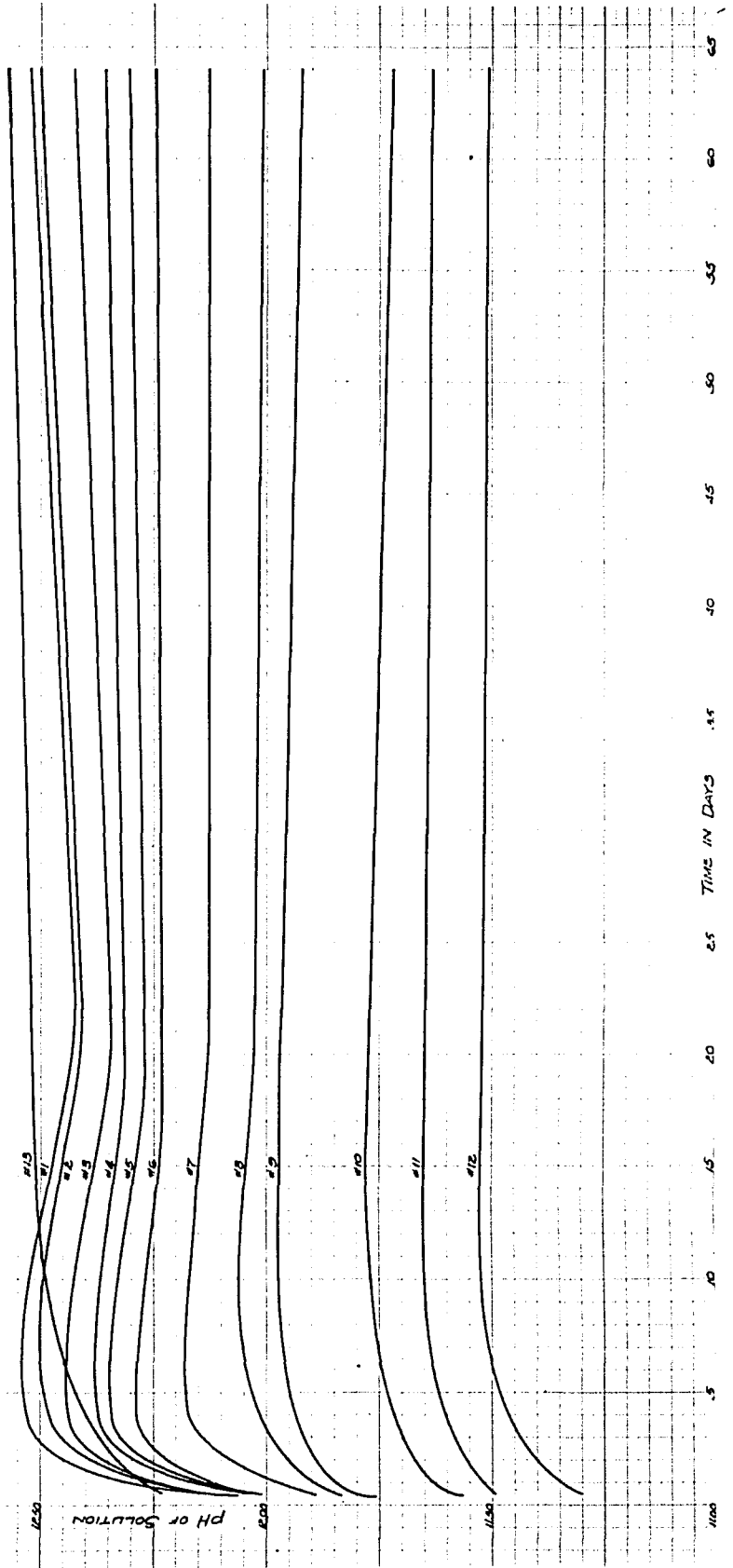| Time in Days | Number and Concentration of CaCl₂ Solutions | | | | | | | | | | | | Distilled H₂O |
	1	2	3	4	5	6	7	8	9	10	11	12	13
	0.001%	0.01%	0.10%	0.20%	0.35%	0.50%	1.00%	1.75%	2.50%	5.00%	7.50%	10.00%	
1/2	12.06	12.10	12.10	12.04	12.02	12.00	11.88	11.83	11.75	11.56	11.46	11.30	12.23
1	12.23	12.19	12.15	12.09	12.04	11.96	11.92	11.89	11.84	11.64	11.52	11.33	12.26
3	12.55	12.52	12.43	12.36	12.33	12.28	12.16	12.04	11.98	11.70	11.64	11.48	----
5	12.49	12.43	12.43	12.36	12.33	12.29	12.17	12.00	11.92	11.71	11.58	11.46	12.42
10	12.38	12.41	12.36	12.33	12.28	12.25	12.13	12.03	11.97	11.77	11.65	11.53	12.49
11	12.38	12.41	12.38	12.33	12.27	12.23	12.13	12.01	11.95	11.77	11.66	11.52	----
17	12.45	12.52	12.37	12.35	12.30	12.26	12.15	12.06	11.99	11.78	11.65	11.54	12.51
18	12.52	12.49	12.36	12.38	12.29	12.25	12.15	12.06	11.98	11.79	11.67	11.53	----
21	----	12.41	12.38	12.33	12.29	12.24	12.14	12.03	----	----	----	----	12.55
22	12.41	12.41	12.37	12.33	12.28	12.24	12.13	12.03	11.95	11.76	11.64	11.50	----
23	----	----	----	----	----	----	----	----	11.97	11.76	11.64	11.52	----
62	12.17	12.52	12.43	12.36	12.31	12.25	12.13	12.01	----	----	----	----	12.57
63	12.52	12.49	12.43	12.36	12.31	12.24	12.13	12.01	11.92	11.73	11.64	----	----

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Fig. 2
Hydrolysis of 3 CaO.SiO₂ in CaCl₂ Solutions

TABLE III

Hydrolysis of Beta 2CaO.SiO$_2$ in CaCl Solutions

pH of solutions after 0.9562 grams of the compound had been allowed

to react with 100 cc. of the CaCl$_2$ solutions to

give a saturated lime solution.

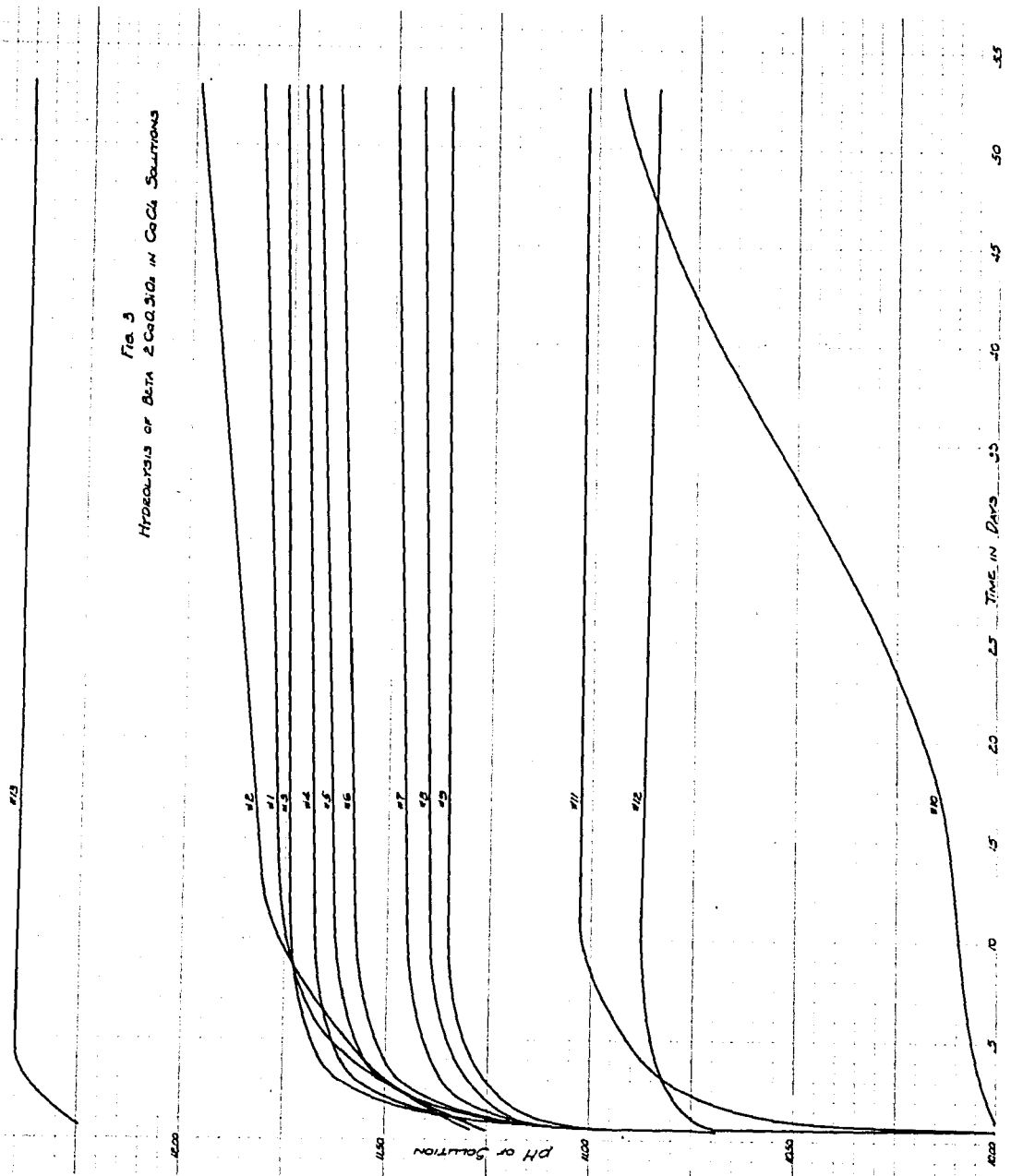| Time in Days	Number and Concentration of CaCl$_2$ Solutions												Distilled H$_2$O
	1	2	3	4	5	6	7	8	9	10	11	12	13
	0.001%	0.01%	0.10%	0.20%	0.35%	0.50%	1.00%	1.75%	2.50%	5.00%	7.50%	10.00%	
1/2	11.25	11.29	11.08	11.00	10.91	10.89	10.78	10.69	11.45	9.98	9.98	9.73	----
1	11.33	11.35	11.10	11.24	11.21	11.16	11.17	11.12	11.06	9.99	10.33	10.75	12.27
2	11.34	11.26	11.25	11.50	11.41	11.38	11.32	11.28	11.21	9.99	10.80	10.80	12.30
3	----	----	11.29	----	----	----	----	----	----	----	----	----	----
5	11.63	11.59	11.69	11.64	11.59	11.54	11.41	----	----	10.03	10.89	10.82	12.40
7	----	11.63	----	----	----	11.54	11.43	11.36	11.30	10.08	10.96	----	----
9	----	11.72	11.70	11.66	11.61	11.55	11.44	11.39	11.32	10.07	10.99	----	12.40
11	11.75	11.82	11.72	11.67	11.62	11.57	11.45	11.40	11.32	10.10	11.03	10.89	12.40
51	----	----	11.77	11.72	11.69	11.64	11.50	11.44	11.36	10.90	11.02	10.78	12.40
53	11.83	11.99	11.77	11.73	11.69	11.64	11.49	11.43	11.37	10.98	11.03	10.91	12.40

Fig. 3

Hydrolysis of Beta 2CaO.SiO₂ in CaCl₂ Solutions

TABLE IV

Hydrolysis of Gamma 2CaO.SiO$_2$ in CaCl$_2$ Solutions

pH of solutions after 0.9562 grams of the compound had been allowed

to react with 100 cc. of the CaCl$_2$ solutions to

give a saturated lime solution.

| Time in Days | Number and Concentration of CaCl$_2$ Solutions | | | | | | | | | | | | Distilled H$_2$O |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
	0.001%	0.01%	0.10%	0.20%	0.35%	0.50%	1.00%	1.75%	2.50%	5.00%	7.50%	10.00%	
1/2	11.15	11.13	10.96	10.88	10.75	10.66	10.50	10.43	10.35	9.71	9.65	9.45	---
1	11.15	11.18	10.97	10.90	10.78	10.69	10.54	10.48	10.36	9.73	9.66	9.47	12.26
2	11.24	11.23	10.99	10.90	10.78	10.66	10.50	10.46	10.37	9.70	9.62	9.44	12.31
6	11.22	11.23	10.97	10.91	10.78	10.66	10.52	10.48	10.37	9.74	9.68	9.50	12.41
9	11.24	11.26	10.99	10.92	10.77	10.64	10.48	10.48	---	9.71	9.68	9.50	12.40
12	11.22	11.24	10.97	10.90	10.78	10.61	10.48	10.44	10.36	9.71	9.67	9.49	12.40
50	11.95	11.85	11.93	11.84	11.73	10.64	10.47	11.57	11.18	9.74	9.72	9.53	12.40
53	---	---	---	11.87	11.73	---	10.51	11.53	11.57	9.74	9.65	9.51	12.40

Fig. 4
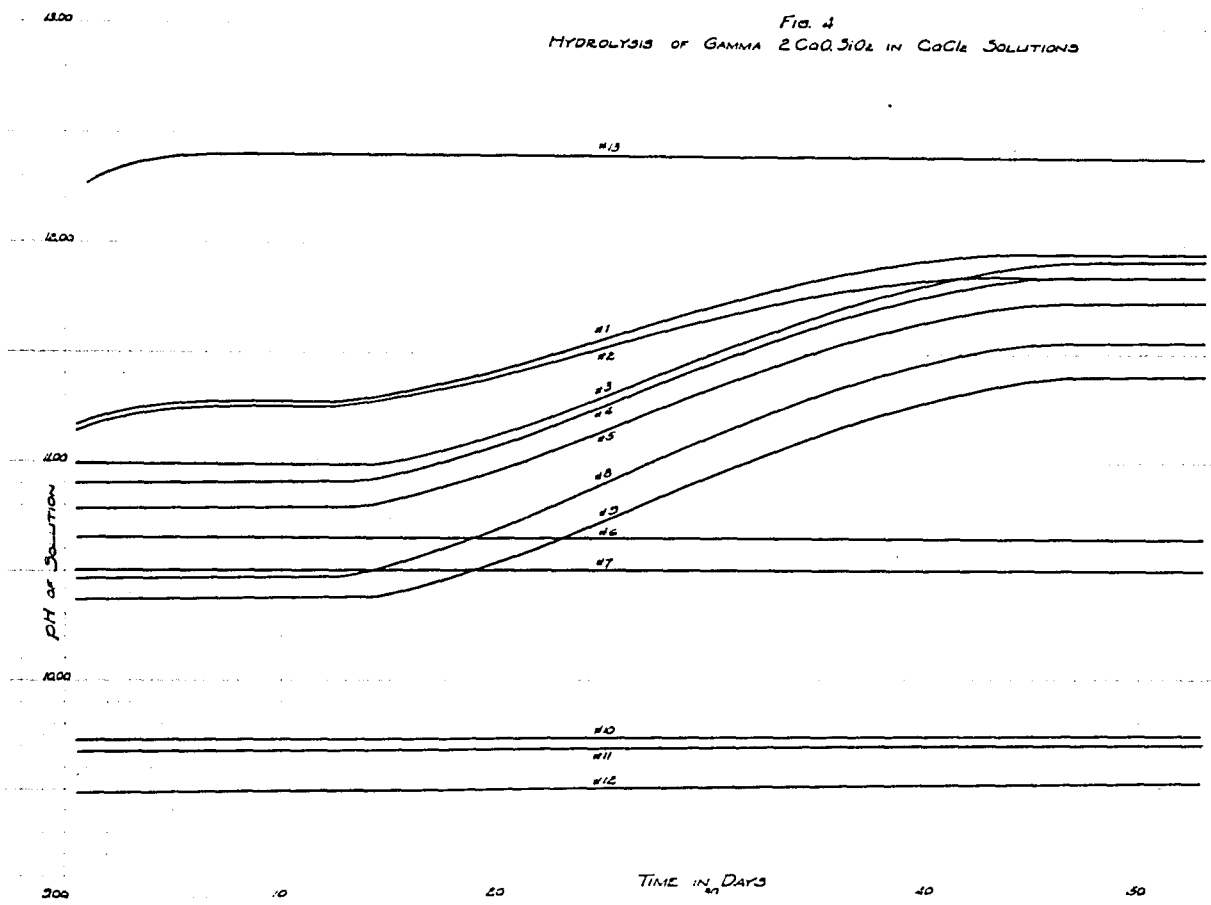HYDROLYSIS OF GAMMA 2 CaO.SiO₂ IN CaCl₂ SOLUTIONS

TABLE V

Change in pH on Placing Ca(OH)$_2$ in CaCl$_2$ Solutions

pH of solution after 0.8568 grams of Ca(OH)$_2$ had been allowed

to react with 100 cc. of the CaCl$_2$ solutions

to give a saturated lime solution.

Time in Days	| Number and Concentration of CaCl$_2$ Solutions											
	1 0.001%	2 0.01%	3 0.10%	4 0.20%	5 0.35%	6 0.50%	7 1.00%	8 1.75%	9 2.50%	10 5.00%	11 7.50%	12 10.00%
1/2	12.38	12.28	12.34	12.30	12.25	12.21	12.11	12.00	11.87	11.73	11.61	11.46
1	12.51	12.44	12.40	12.35	12.26	12.23	12.12	12.00	11.92	11.72	11.60	11.46
2	12.38	12.38	12.34	12.30	12.24	12.20	12.11	12.00	11.92	11.73	11.61	11.47
3	12.39	12.39	12.34	12.30	12.25	12.21	12.11	11.99	11.91	11.72	11.59	11.46
4	12.44	12.44	12.38	12.35	12.30	12.25	12.14	12.02	11.95	11.75	11.63	11.48
9	12.42	12.41	12.37	12.33	12.26	12.22	12.13	12.02	11.93	11.73	11.61	11.48
13	12.37	12.39	12.35	12.30	12.24	12.22	12.11	11.94	11.93	11.74	11.61	11.48
19	12.37	12.39	12.35	12.30	12.24	12.22	12.11	11.94	11.93	11.74	11.61	11.48
21	12.37	12.39	12.35	12.30	12.24	12.22	12.11	11.94	11.93	11.74	11.61	11.48

Fig. 5
CHANGE IN pH ON PLACING Co(OH)₂ IN CoCl₂ SOLUTIONS
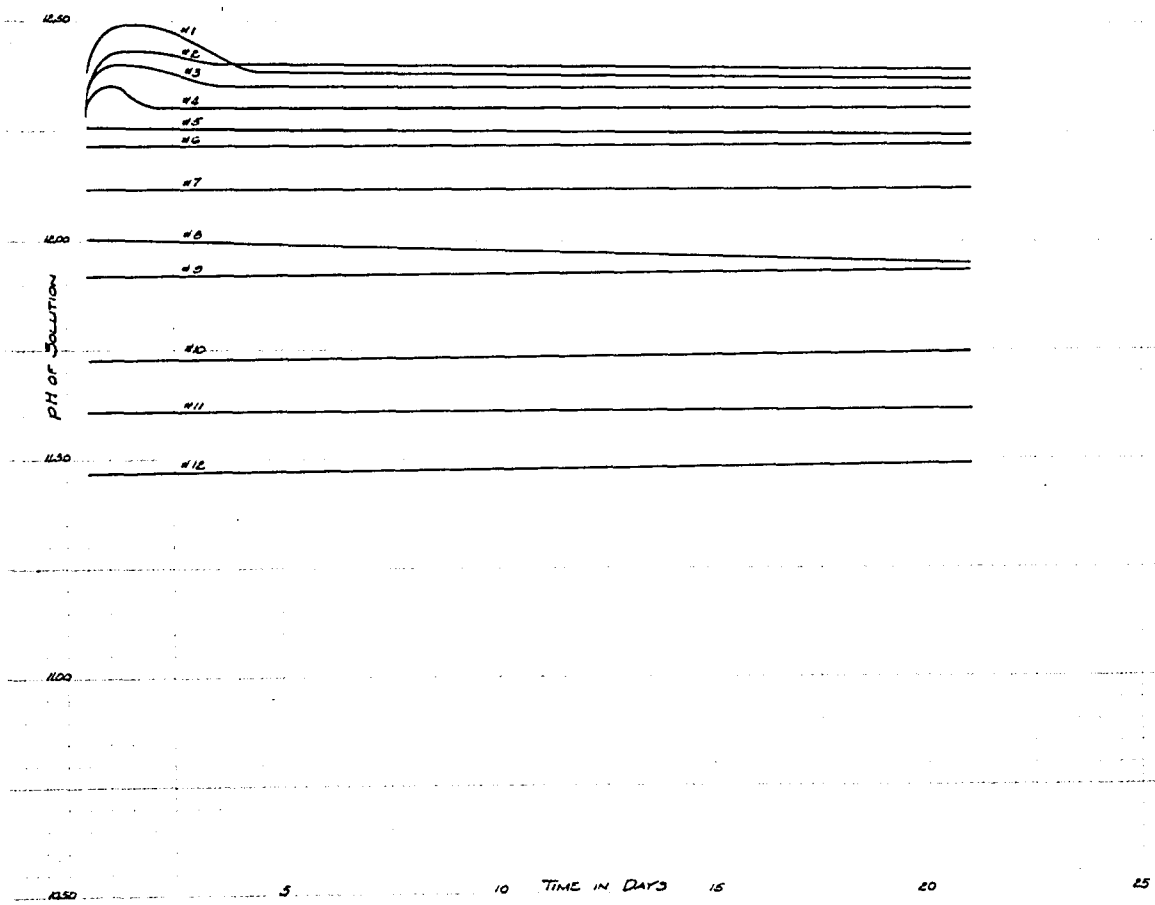
Rate of hydrolysis when solutions were not saturated with
Ca(OH)$_2$. In this part of the experiment the procedure given
under "Rate of hydrolysis in solution saturated with Ca(OH)$_2$"
above was duplicated with the exception of the size of the
samples used. Instead of having 0.8226 grams of Ca(OH)$_2$ pre-
sent per 100 cc. of the calcium chloride solution, there was
but 0.1000 grams of Ca(OH)$_2$ present, assuming that there was
a complete hydrolysis of the compounds. This amount of Ca(OH)$_2$
was not enough to saturate the solutions if allowance is made
for the decrease in the solubility of the Ca(OH)$_2$ in dilute
calcium chloride solution[27].

A standard of comparison was made by using the same weight
of pure Ca(OH)$_2$ in the same amount of the calcium chloride
solutions and in boiled distilled water.

The results reported in terms of pH are given in tables
VI, VII, VIII, IX and X, and plotted graphically in figures
VI, VII, VIII, IX and X.

TABLE VI

Hydrolysis of 3CaO.Al$_2$O$_3$ in CaCl$_2$ Solutions

pH of solutions after 0.160 grams of the compound had been allowed to react

with 100 cc. of the CaCl$_2$ solutions to

give an unsaturated lime solution.

Time in Days	Number and Concentration of CaCl$_2$ Solutions												Distilled H$_2$O
	1	2	3	4	5	6	7	8	9	10	11	12	13
	0.001%	0.01%	0.10%	0.20%	0.35%	0.50%	1.00%	1.75%	2.50%	5.00%	7.50%	10.00%	
1/2	11.49	11.58	11.41	11.39	11.24	11.20	10.92	10.73	10.62	9.93	10.01	9.99	11.84
1	11.65	11.68	11.46	11.45	11.29	11.24	10.97	10.79	10.67	10.06	10.16	10.07	11.85
2	11.65	11.68	11.49	11.45	11.31	11.26	10.99	10.80	10.68	10.15	10.21	10.11	11.85
4	11.67	11.71	11.52	11.46	11.35	11.31	11.07	10.88	10.72	10.27	10.27	10.12	11.86
7	11.71	11.75	11.52	11.42	11.34	11.26	11.07	10.83	10.71	10.26	10.26	10.00	11.85
11	11.83	11.85	11.61	11.47	11.38	11.26	11.06	10.81	10.65	10.26	10.31	10.00	11.85
19	11.70	11.76	11.54	11.38	11.29	11.21	11.02	10.81	10.72	10.26	10.24	10.01	11.85
24	11.70	11.76	11.54	11.38	11.29	11.21	11.02	10.81	10.72	10.26	10.24	10.01	11.85

Fig. 6
HYDROLYSIS OF 3CaO.Al₂O₃ IN CaCl₂ SOLUTIONS

#13

#2

#1

#3

#4

#5

#6

#7

#8

#9

#10

#11

#12

PH OF SOLUTION

12.00

11.50

11.00

10.50

10.00

TIME IN DAYS

5   10   15   20   25

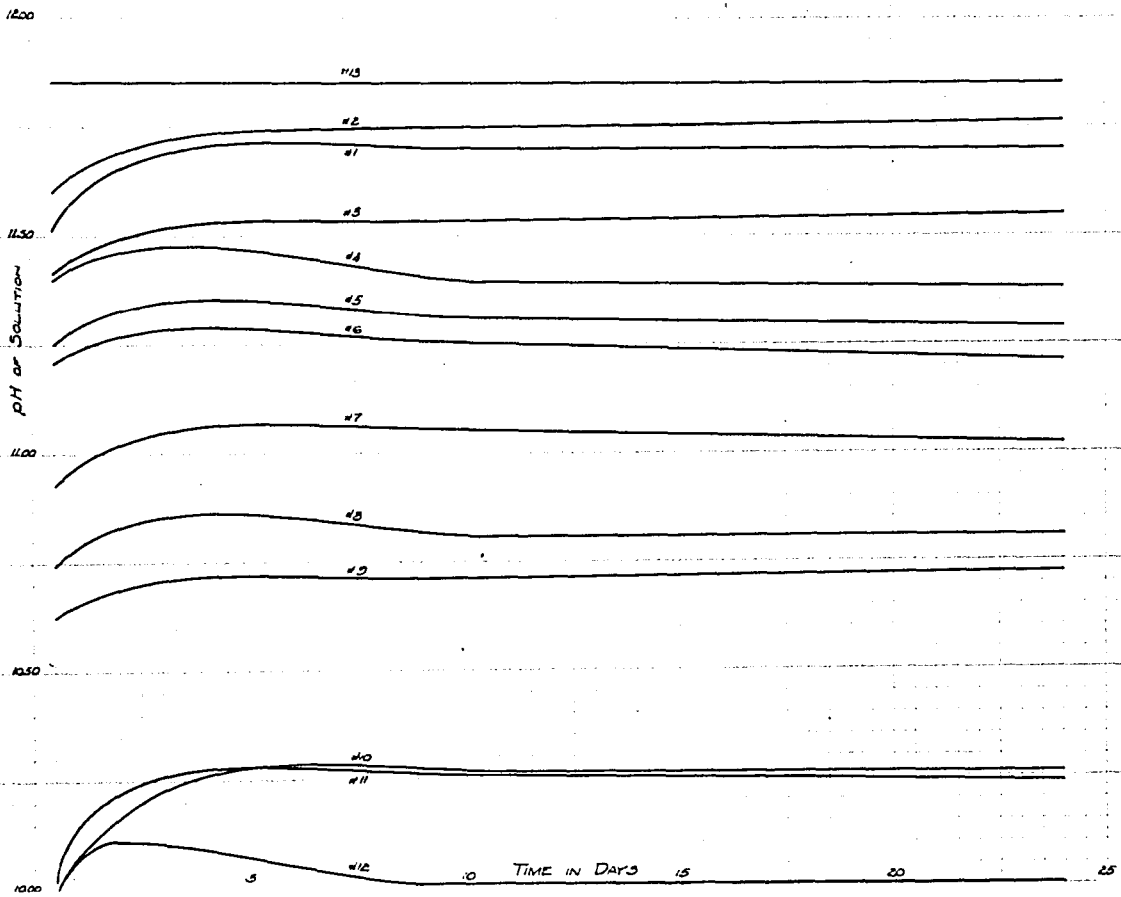## TABLE VII

Hydrolysis of $3CaO.SiO_2$ in $CaCl_2$ Solutions

pH of solutions after 0.1357 grams of the compound had been allowed to react with 100 cc. of the $CaCl_2$ solutions to give an unsaturated lime solution.

Time in Days	Number and Concentration of $CaCl_2$ Solution												Distilled H_2O
	1	2	3	4	5	6	7	8	9	10	11	12	13
	0.001%	0.01%	0.10%	0.20%	0.35%	0.50%	1.00%	1.75%	2.50%	5.00%	7.50%	10.00%	
1/2	11.77	11.77	11.65	11.63	11.57	11.51	11.42	11.38	11.30	11.09	11.00	10.85	11.82
1	11.78	11.77	11.65	11.64	11.59	11.53	11.44	11.40	11.35	11.16	11.07	10.93	11.90
2	11.83	11.82	11.73	11.68	11.62	11.56	11.47	11.42	11.36	11.18	11.09	10.93	11.93
3	11.94	11.92	11.75	11.72	11.62	11.58	11.48	11.43	11.37	11.20	11.11	10.96	11.94
8	12.03	11.97	11.82	11.77	11.70	11.64	11.55	11.52	11.43	11.25	11.14	10.99	11.94
12	11.90	11.89	11.77	11.75	11.70	11.65	11.56	11.46	11.44	11.25	11.14	11.02	11.94
18	11.90	11.90	11.79	11.75	11.72	11.64	11.58	11.49	11.47	11.25	11.14	11.02	11.94
20	11.90	11.90	11.79	11.75	11.72	11.64	11.58	11.49	11.47	11.25	11.14	11.02	11.94

Fig. 7
HYDROLYSIS OF 3CaO.SiO₂ IN CaCl₂ SOLUTIONS

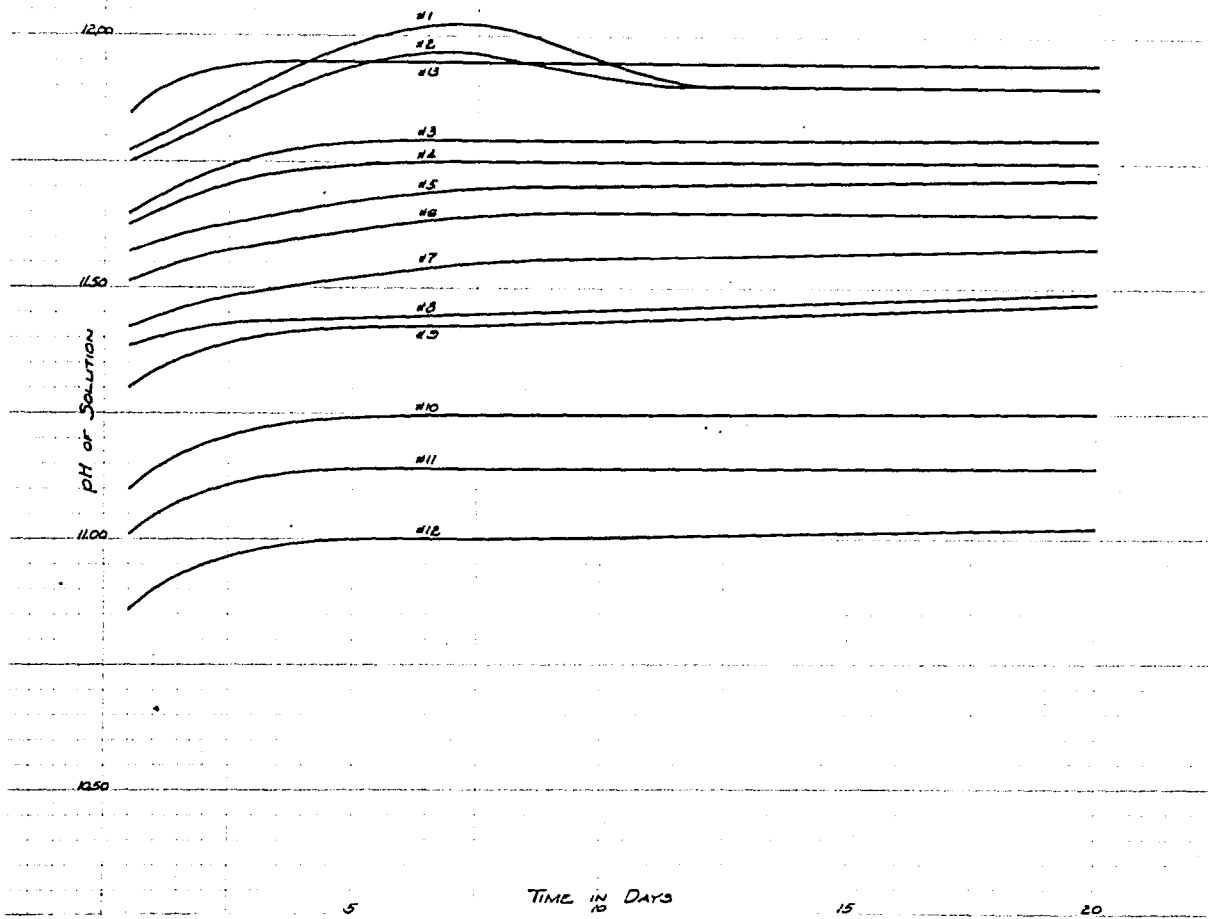## TABLE VIII

Hydrolysis of Beta 2CaO.SiO$_2$ in CaCl$_2$ Solutions

pH of solutions after 0.1536 grams of the compound had been allowed to react with 100 cc. of the CaCl$_2$ solutions to give an unsaturated lime solution.

Time in Days	Number and Concentration of CaCl$_2$ Solutions												Distilled H$_2$O
	1	2	3	4	5	6	7	8	9	10	11	12	13
	0.001%	0.01%	0.10%	0.20%	0.35%	0.50%	1.00%	1.75%	2.50%	5.00%	7.50%	10.00%	
1/2	10.97	11.00	10.77	10.70	10.62	10.49	10.40	10.30	10.21	9.79	9.71	9.50	11.17
2	11.35	11.24	10.94	10.88	10.67	10.59	10.45	10.35	10.30	9.79	9.65	9.43	11.28
4	11.13	11.14	10.93	10.84	10.74	10.65	10.53	10.42	10.33	9.78	9.70	9.44	11.34
7	11.22	11.21	10.97	10.88	10.76	10.69	10.47	10.51	10.39	9.78	9.69	9.43	11.34
11	11.22	11.21	10.94	10.85	10.79	10.66	10.55	10.68	10.71	9.77	9.67	9.38	11.34
16	11.22	11.21	10.94	10.83	10.79	10.66	10.56	10.92	10.82	9.80	9.69	9.38	11.34
19	11.22	11.21	10.94	10.83	10.79	10.66	10.56	10.92	10.82	9.80	9.69	9.38	11.34
24	11.22	11.21	10.94	10.83	10.79	10.66	10.56	10.92	10.82	9.80	9.69	9.38	11.34

Fig. 8
HYDROLYSIS OF BETA 2 CoO.SiO₂ IN CoCl₂ SOLUTIONS

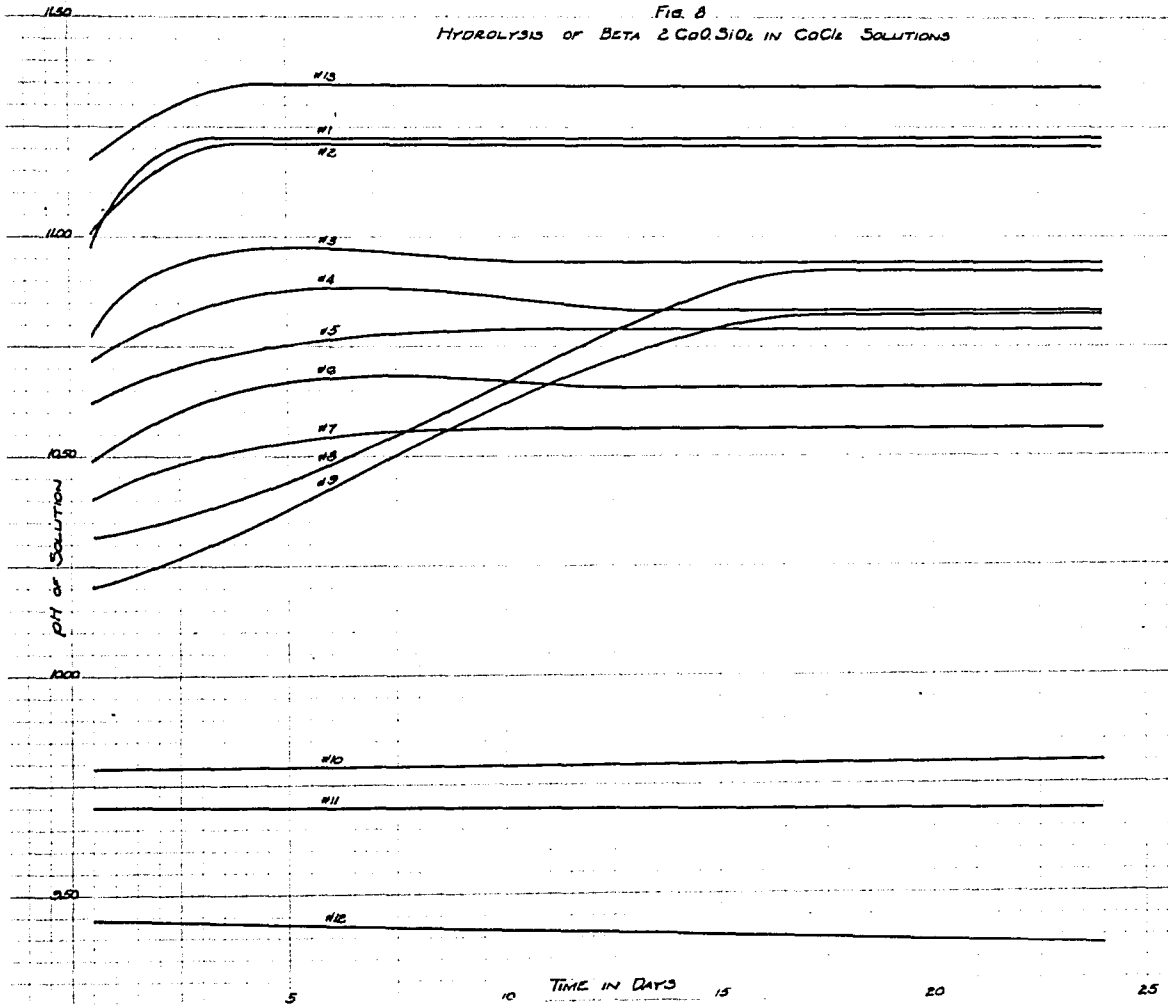## TABLE IX

Hydrolysis of gamma 2CaO.SiO$_2$ in CaCl$_2$ Solutions

pH of solutions after 0.1536 grams of the compound had been allowed
to react with 100 cc. of the CaCl$_2$ solutions to
give an unsaturated lime solution.

| Time in Days | Number and Concentration of CaCl$_2$ Solutions | | | | | | | | | | | | Distilled H$_2$O |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
	0.001%	0.01%	0.10%	0.20%	0.35%	0.50%	1.00%	1.75%	2.50%	5.00%	7.50%	10.00%	
1/2	10.87	10.98	10.70	10.58	10.41	10.35	10.21	10.06	10.01	9.55	9.38	9.20	11.09
1	10.48	10.86	10.61	10.52	10.30	10.30	10.21	9.94	9.82	9.37	9.15	9.20	11.18
2	10.79	10.98	10.68	10.62	10.45	10.36	10.36	10.20	10.10	9.53	9.47	9.23	11.18
3	10.76	10.99	10.68	10.63	10.46	10.35	10.36	10.23	10.11	9.51	9.44	9.20	11.18
6	10.78	11.08	10.68	10.67	10.44	10.40	10.39	10.23	10.13	9.53	9.47	9.22	11.18
10	10.58	11.00	10.59	10.64	10.42	10.39	10.38	10.23	10.13	9.53	9.49	9.22	11.18
15	10.49	11.06	10.61	10.65	10.41	10.40	10.37	10.23	10.12	9.52	9.47	9.22	11.18
24	10.49	11.06	10.61	10.65	10.41	10.40	10.37	10.23	10.12	9.52	9.47	9.22	11.18

Fig 9
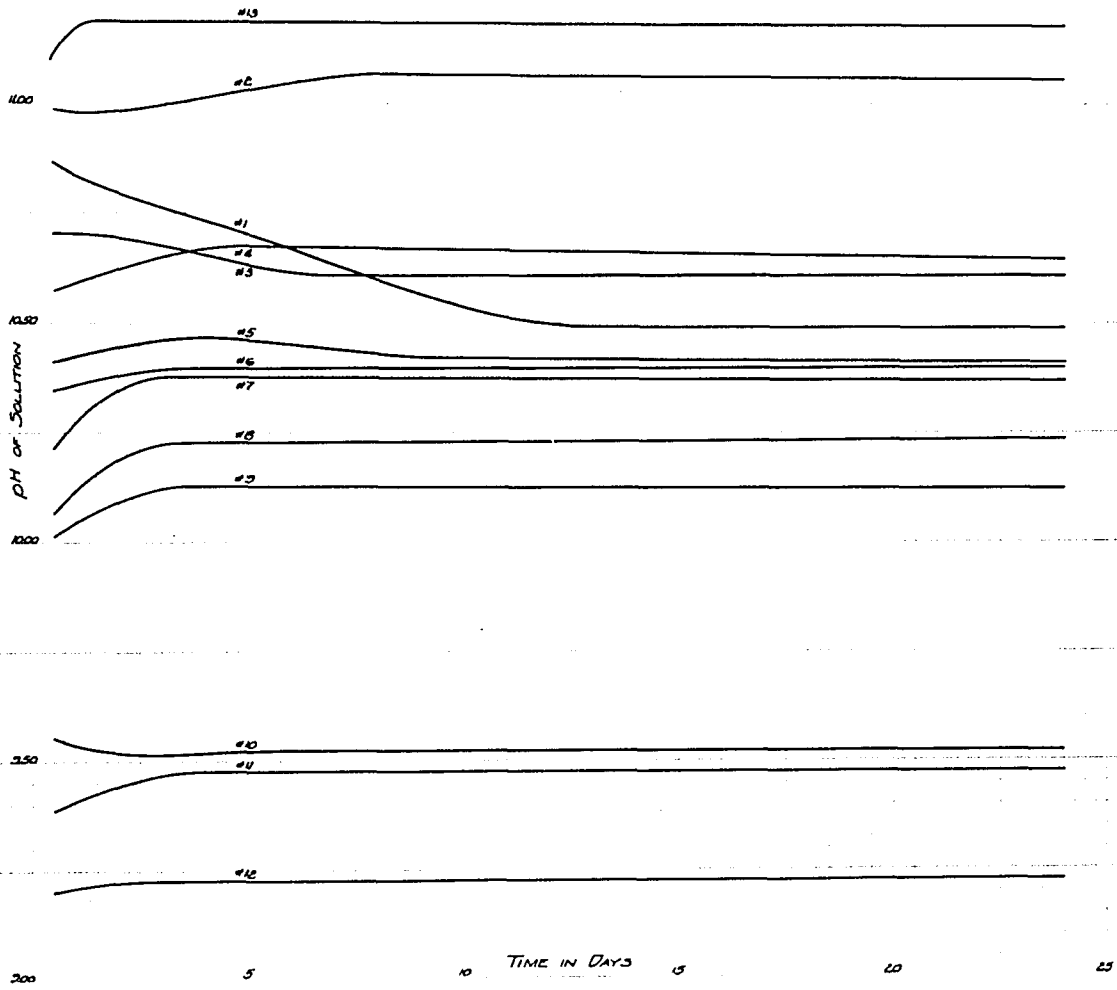HYDROLYSIS OF GAMMA 2CaO.SiO₂ IN CoCl₂ SOLUTIONS

TABLE X

Change in pH on Placing Ca(OH)$_2$ in CaCl$_2$ Solutions

pH of solution after 0.1376 grams of Ca(OH)$_2$ had been allowed

to react with 100 cc. of the CaCl$_2$ solutions to

give an unsaturated lime solution.

Time in Days	Number and Concentration of CaCl$_2$ Solutions											
	1 0.001%	2 0.01%	3 0.10%	4 0.20%	5 0.35%	6 0.50%	7 1.00%	8 1.75%	9 2.50%	10 5.00%	11 7.50%	12 10.00%
1/2	12.27	12.27	12.23	12.19	12.18	12.12	12.01	11.92	11.84	11.60	11.46	11.28
1	12.32	12.32	12.29	12.26	12.19	12.13	12.03	11.92	11.85	11.60	11.47	11.29
2	12.29	12.31	12.27	12.23	12.19	12.14	12.04	11.93	11.85	11.60	11.46	11.28
8	12.27	12.27	12.26	12.21	12.19	12.15	12.04	11.93	11.86	11.63	11.46	11.28
11	12.29	12.29	12.28	12.23	12.19	12.14	12.04	11.93	11.86	11.62	11.46	11.28
15	12.29	12.29	12.28	12.23	12.19	12.14	12.04	11.93	11.86	11.62	11.46	11.28
21	12.29	12.29	12.28	12.23	12.19	12.14	12.04	11.93	11.86	11.62	11.46	11.28

Fig. 10

Change in pH on Placing Ca(OH)₂ in CaCl₂ Solutions
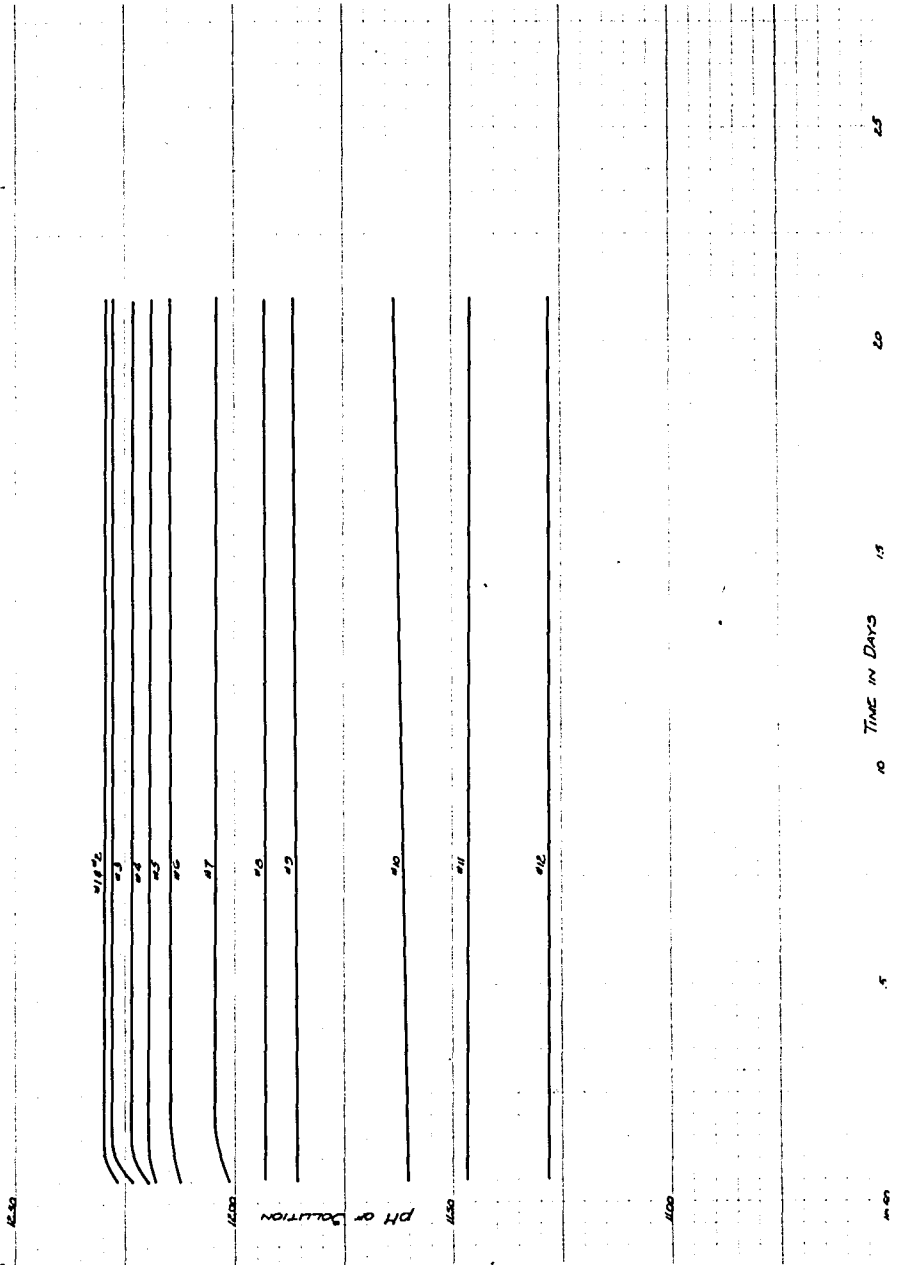
DISCUSSION

The experiments described have been a study of the hydrolysis of the pure constituents that occur in Portland cement when treated with calcium chloride solutions. In the first part of the work the hydrolysis was brought about in the presence of quantities of water or calcium chloride solutions somewhat similar to that present in a properly tempered mortar or concrete. In other words, if the complete hydrolysis of the compounds took place, a high concentration of lime would have been present reaching saturation such as would be present in a mortar. Thus the results of these experiments should be applicable to the actual procedure in industry.

In the last part of the work described, dilute solutions were used. This part of the experiment was carried out more or less to have a comparison of results for the first part of the experiment. The amount of sample used was such that the resulting solutions were not saturated with lime, if it is assumed that complete hydrolysis took place. Therefore the results do not have any great bearing on what takes place in actual practice.

A study of the results obtained in the first part of the experiment as given in the tables I, II, III, IV and V and in the figures with corresponding numbers is very interesting.

These show that the hydrolysis of tricalcium aluminate and tricalcium silicate is accelerated with dilute calcium chloride solutions. In the case of tricalcium aluminate the pH was greater in calcium chloride solution than in water as can be seen by comparing curves 1, 2, 3, 4 and 5 with curve 13. This shows that calcium chloride solutions up to a concentration of 0.35 per cent of calcium chloride have increased the rate of hydrolysis while stronger solutions of the same salt retarded the rate of hydrolysis as shown by curves 6 to 12 inclusive.

A study of table II shows that the hydrolysis of tricalcium silicate is increased by calcium chloride solution of 0.35 per cent concentration for the first three days and for five days by solutions of 0.10 per cent concentration. The solutions of higher concentrations have a retarding effect, as was true with tricalcium aluminate.

The results given in tables III and IV and illustrated graphically in figures III and IV show that calcium chloride solutions of all concentrations studied retarded the hydrolysis of beta dicalcium silicate and gamma dicalcium silicate.

Tricalcium aluminate differs from the silicates in its reaction with calcium chloride as shown by a study of the data. In the hydrolysis a maximum pH is attained, after which the value of the pH decreases. This shows that the OH ion concentration is decreased; that is, calcium hydroxide is being taken from the solution. One can explain this by the fact that the $3CaO.Al_2O_3$ reacts with the calcium chloride or calcium

hydroxide present to form a double salt such as $3CaO.Al_2O_3$. $CaCl_2.XH_2O$. The calcium chloride in this compound can be replaced by calcium hydroxide, calcium nitrate or calcium iodide. These double salts crystallize from the solution and so decrease the calcium hydroxide present and lower the pH of the solution.

Table V and the corresponding graph show the effect of calcium hydroxide upon the calcium chloride solutions used in this study. There is no explanation for the irregularities in the first few readings of the curves 1, 2, 3 and 4. It will be noticed from a study of this table that the pH of the solutions gradually decreased as the concentration of the calcium chloride increased. One would expect this from the work of Zahorsky[27] in which he reported that the solubility of calcium hydroxide is increased in calcium chloride solutions stronger than 5 per cent. Apparently what happened in this experiment was a combination of the calcium hydroxide with the calcium chloride and that lowered the pH of the solution.

The results of the last part of the experiment are given in tables VI, VII, VIII, IX and X and presented graphically in the figures with the same numbers. A study of these results shows that only in the case of tricalcium silicate did the calcium chloride solutions accelerate the hydrolysis of the compounds studied. The pH became constant sooner in these solutions than in the concentrated solutions studied in

the first part of the experiment. The action of calcium
hydroxide on the calcium chloride solutions was practically
the same as it was in the first part of the experiment.

The results of the above study can be very well applied
to what happens in the action of calcium chloride on cement.
There are many theories on this subject but only two of them
will be discussed.

According to L. Forsen[9], when cement clinker is treated
with water it reacts to form hydrates of calcium aluminate
and calcium silicate. These hydrates are in turn hydrolyti-
cally decomposed to a state of equilbrium. The resulting
silicates form negative colloids while the aluminates form
positive colloids. The presence of a retarder such as calcium
sulfate prevents the rapid setting of the clinker which would
naturally take place by the reciprocal coagulation of the
positive and negative colloids.

". . .In the presence of retarders the aluminate component
is precipitated from the solution as a crystallized double
salt $3CaO.Al_2O_3.CaX_2.XH_2O$, where X may be sulfate (one half
mole) Cl, Br, I, ClO_3, NO_3, NO_2 or OH. Normally the setting
of cement begins with the formation and coagulation of the
silicates as soon as the necessary concentration of the Ca ion
is reached. The addition to cement of compounds which combine
with lime increases the strength of the cement. This removes
the lime from solutions, and the solubility of the colloidal
silicates is increased. The compounds that combine with lime

in this way are $CaCl_2$, $AlCl_3$, $CaBr_2$, $Ca(NO_3)_2$, $3CaO.Al_2O_3$ and $5CaO.Al_2O_3$. . ."[9].

Dr. Kühl[15] also explains the setting process in very much the same way as Forsen. He considers, ". . .The hardened cement mortar as an unstable gel consisting of dicalcium hydrosilicate, tricalcium hydroaluminate, hydrated lime, and calcium ferrites of unknown composition. All of these constituents tend slowly to pass over into the crystalline form, although the transformation requires a period of some years before it can be observed and some decades before it is complete. We are ignorant of the order in which the different gel compounds assume a microcrystalline structure. Probably the calcium hydroxide and calcium hydroaluminate are first affected, followed only at a later stage by the gradual transformation of calcium hydrosilicate. . ."[15]

The action of calcium chloride in accelerating the setting process and the increased strength of the resulting cement can be explained as follows: The calcium chloride, as our experiments show, increases the rate of hydrolysis of the compounds in the clinker. The Ca ion concentration is very soon attained at which the colloidal silicates are formed and coagulation of these takes place. As soon as coagulation starts the setting effect in cement is manifest. Thus this initial process is speeded up by the presence of small amounts of calcium chloride. The excess lime formed by the hydrolysis of the tricalcium silicate must unite with the excess calcium

chloride present to give an increased strength. The strength of a Portland cement is attributed to the formation and interlocking of the crystalline bodies that separate out during the hardening process.

CONCLUSIONS

The data obtained in this study definitely show that dilute solutions of calcium chloride cause a marked increase in the rate of hydrolysis of tricalcium aluminate and tricalcium silicate. In the case of beta dicalcium silicate and gamma dicalcium silicate all concentrations of the calcium chloride solutions studied retarded the rate of hydrolysis.

It is a well-known fact that when a small amount of calcium chloride is used as an admixture in cement, it accelerates the setting process, and the final strength of the cement is increased. The normal setting process, according to the colloidal theory of cement, begins with the coagulation of the colloidal silicates and aluminates present. A certain Ca ion concentration is necessary before this process takes place. Therefore, the catalytic effect of the calcium chloride on cement is to increase the rate of hydrolysis of the compounds in the clinker resulting in the rapid attainment of the Ca ion concentration necessary for the setting process. The transformation of these coagulated silicates and aluminates into crystalline bodies gives the strength to the cement.

SUMMARY

1. Calcium chloride is the only compound of practical importance used as an admixture in Portland cement to accelerate the setting process.

2. The present conception of the constitution of Portland cement clinker is best given in the work of Dr. Hans Kühl representing the German idea and the work of Broumiller and Bogue representing the American view.

3. Methods are given for the preparation of tricalcium silicate, tricalcium aluminate, beta dicalcium silicate and gamma dicalcium silicate.

4. The rate of hydrolysis of the constituents of cement were studied by the electrometric method.

5. The results of the studies on the concentrated calcium hydroxide solutions showed that small amounts of calcium chloride accelerated the rate of hydrolysis of the tricalcium aluminate and tricalcium silicate, but retarded the hydrolysis of beta dicalcium silicate and gamma dicalcium silicate.

6. In solutions not saturated with calcium hydroxide, calcium chloride retarded the rate of hydrolysis of all the compounds studied.

7. The data show that calcium chloride combines with calcium hydroxide.

8. The action of calcium chloride in the setting processes of cement is explained by the theories of L. Forsen and Hans Kühl.

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