



Reactions of sugar solution on certain calcium aluminates and calcium alumino-ferrite
by William W Niven Jr

A THESIS Submitted to the Graduate Committee In partial fulfillment of the requirements for the
degree of Master of Science In Industrial Chemistry
Montana State University
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Abstract:

The Mechanisms of the reaction of sugar solution with the calcium aluminates, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ as related to the Merriman auger solubility test for Portland cement, here been studied. A similar study for $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ was also attempted but was not completed. Both aluminates reacted with sugar solution to form metastable solutions from which solid phase precipitated on standing. The ultimate products of hydrolysis of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ by sugar solution under the conditions examined were dissolved and precipitated hydrated calcium aluminate of the apparent composition, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and precipitated hydrated alumina, without the liberation of free calcium hydroxide at any stage of the reaction. The ultimate products of hydrolysis of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ by sugar solution were dissolved and precipitated hydrated alumina and calcium sucates, the sugar solution apparently completely hydrolysing the compound at the hydroxyl-ion concentrations obtaining in the tests and the calcium hydroxide thus liberated then combining with the sugar.

REACTIONS OF SUGAR SOLUTION ON CERTAIN
CALCIUM ALUMINATES AND CALCIUM ALUMINO-FERRITE

by

WM. W. HIVEN, Jr.

A THESIS

Submitted to the Graduate Committee

in

partial fulfillment of the requirements

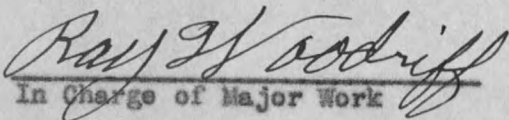
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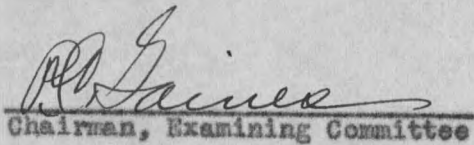
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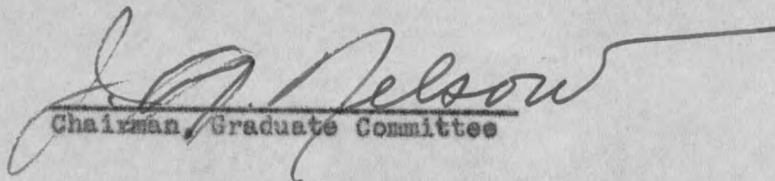
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I. ABSTRACT

The mechanisms of the reactions of sugar solution with the calcium aluminates, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, as related to the Merriman sugar solubility test for Portland cement, have been studied. A similar study for $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ was also attempted but was not completed. Both aluminates reacted with sugar solution to form metastable solutions from which solid phase precipitated on standing. The ultimate products of hydrolysis of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ by sugar solution under the conditions examined were dissolved and precipitated hydrated calcium aluminate of the apparent composition, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, and precipitated hydrated alumina, without the liberation of free calcium hydroxide at any stage of the reaction. The ultimate products of hydrolysis of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ by sugar solution were dissolved and precipitated hydrated alumina and calcium suerates, the sugar solution apparently completely hydrolyzing the compound at the hydroxyl-ion concentrations obtaining in the tests and the calcium hydroxide thus liberated then combining with the sugar.

II. INTRODUCTION

The problem of readily determining the degree to which equilibrium conditions have been attained in the kiln in the manufacture of Portland cement has yet to be satisfactorily solved. Quantitative chemical analyses and the standard physical tests of Portland cement cannot alone indicate whether equilibrium conditions were adequately approached and, frequently, the theoretical compound composition of the cement, as computed from the chemical analysis, may be only a rough approximation of the actual conditions.

The fact that existing methods for exact determination of true cement composition are not readily adaptable for routine application to the problem of determining cement quality has led to the development of the so-called "sugar solubility test" as proposed by Merriman (8, 9, 10)*, which is in effect an adaptation of earlier test methods for the determination of free lime in cement. This test has been incorporated into at least one contract specification for the purchase of Portland cement (12) and consists briefly of the following:

Fifteen grams of prepared cement are shaken for two hours with 100 ml of a 15% sugar (sucrose) solution, after which the suspension is filtered. A 25 ml aliquot of the filtrate is titrated with 0.5N hydrochloric acid, first to a phenolphthalein end point and then to a clear point. Cements which require more than 8.0 ml of acid to the phenolphthalein end point and more than 10.0 ml of acid to the clear point are considered objectionable.

*Numbers in parentheses refer to references listed at the end of this paper.

Merriman, from his studies of the effects of sugar solution on Portland cement, arrived in part at the following conclusions:

- (a) Unsound cement will be broken down almost completely by the sugar solution, whereas this condition is not observed with sound cements;
- (b) A cement having low reactivity with sugar solution has been calcined to the extent that it will remain reasonably stable in the presence of water during the operations of mixing and placing concrete;
- (c) A cement that has been appreciably prehydrated, either while in the form of clinker or by the addition of water during the final grinding, will exhibit high reaction with sugar.

Based on these conclusions, he has proposed that the action of sugar solution on cement may serve as an index of the degree of calcination and prehydration.

The Merriman sugar solubility test has been the subject of much controversy, with the result that considerable work has been done to determine its merits (1, 2, 16). However, no conclusive determinations have been made of the chemical reactions that take place between sugar solution and the various compound constituents of Portland cement. Based on a belief that no final conclusions as to the merits of the test can be reached until more is known of the chemistry of the test, it has been the purpose of the present investigation to determine as much of that chemistry as

available time would permit, without attempting to arrive at any conclusions as to the merits of the test itself. Due to the fact that the standard test for loss on ignition is considered a more adequate test for excessive pre-hydration of cement than the sugar solubility test, no special consideration has been given in the present investigation to the reactions between sugar solution and hydration products, other than the hydration products that normally form under the conditions of the test.

Portland cement is generally conceded to consist essentially of the compounds, $3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, in major proportions, and the minor but not insignificant constituents, CaSO_4 , MgO , free CaO , and alkalis, the latter probably in complex combination with calcium oxide and silica or alumina. In a few Portland cements, the compound, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, may exist and, since this compound is probably an intermediate in the kiln reaction between calcium oxide and alumina to form $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, it has also been considered in the present study.

When water is added to cement, hydrolysis or hydration of the various cement compounds results, with the formation chiefly of calcium hydroxide and hydrated silicates, aluminates and ferrites. Much work has been done on the nature of these reactions and only those results directly related to the results of the present investigation will be reviewed in the following applicable sections of this paper. In the case of reactions between sugar solution and the cement compounds, it is not necessarily to be expected that the same results will obtain, primarily because of secondary reactions between calcium hydroxide and sugar to form sucrates. The author has found in previous unpublished work that the reactions between $3\text{CaO}\cdot\text{SiO}_2$ and

$2\text{CaO}\cdot\text{SiO}_2$ and sugar solution are apparently no different than between water and these compounds. Standard 25 ml aliquots of extracts from sugar solubility tests on each of the pure silicates required only 1.50 ml and 1.30 ml, respectively, of standard acid to titrate to a phenolphthalein end point and there was no evidence of any unusual degree of reaction. On the other hand, there was much evidence to indicate extensive reactions between sugar solution and $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, not so much from the amounts of standard acid required to titrate 25 ml aliquots (3.50 ml and 11.70 ml, respectively, to phenolphthalein end points) as from the fact that marked gelatin occurred in the mixtures during the course of the tests. Based on the above information, the present investigation has been limited to $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, CaO , and Al_2O_3 .

At numerous points throughout the following discussion, the term "solution" is used, when pertaining to extracts obtained by the treatment of cement compounds with sugar and water. No attempt is made during the general discussions to differentiate between true solutions and colloidal solutions. For a detailed discussion of this aspect, as it pertains to the various compounds, reference is made to Section IX near the end of this paper.

III. GENERAL EXPERIMENTAL PROCEDURE

The compounds used were prepared from C. P. reagents, precipitated calcium carbonate being used as a source of calcium oxide. The pure cement compounds were prepared by mixing the reagents dry in theoretical proportions and calcining until no free lime was evident by the ammonium acetate test. In those cases where a small amount of free lime was desired in the compounds, the reagents were mixed as for the pure compounds but the calcining was stopped just short of complete equilibrium. It was believed that, in this way, conditions obtaining in cement containing free lime would be more nearly duplicated than would be the case if free lime were added to the pure compounds.

Series of tests were made as indicated by the mixing schedule in Table I. In the original Series 1 tests with calcium oxide and in the Series 2 tests with aluminum hydroxide, the oxide or hydroxide in the particular amounts

TABLE I. MIXING SCHEDULE

Series No.	Material added to sugar solution	Amounts added, g/100ml	For results see Table:
1	CaO	0.050 to 7.500	II and II-A
2	Al(OH) ₃	0.022 to 0.220	---
3	5CaO·3Al ₂ O ₃ (0.94% free CaO)	0.092 to 0.547	III
	5CaO·3Al ₂ O ₃ (no free CaO)	0.366 to 0.913	III
4	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ (0.84% free CaO)	0.184 to 4.564	IV
	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ (no free CaO)	0.914 to 4.566	IV
	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ (extra-burned)	2.283 to 4.565	IV
5	3CaO·Al ₂ O ₃ (2.04% free CaO)	0.047 to 1.371	V
	3CaO·Al ₂ O ₃ (no free CaO)	0.456 to 2.283	V

was mixed with 15 g of commercial-grade beet sugar previously dissolved in distilled water and diluted to 100 ml. When the aluminate compounds were mixed with sugar solution in a like manner, lumping of the compounds occurred because of rapid reaction with the sugar solution. In order to overcome this difficulty in all series of tests except Series 1 and 2, the compound in the particular amount was thoroughly mixed with 15 g of dry sugar, after which 100 ml of distilled water were rapidly added and the entire mixture vigorously shaken. The Series 1 tests with calcium oxide were then repeated, using the new method of mixing, because of slight differences in proportions of constituents.

Mixing of all tests was accomplished in 100 ml stoppered cylinders mounted on a wheel rotating at a speed of approximately 40 rpm. All tests were made at room temperature, $28^{\circ}\text{C} \pm 2^{\circ}$. Filtering difficulties inherent with the tests on the aluminates were avoided by separating the sugar extracts by centrifuging in all cases. Errors in composition of extracts due to selective absorption on the filter paper were also avoided in this manner. Calcium oxide was determined by titration with standard acid to a phenolphthalein end point in Series 1 and gravimetrically in the other series. Alumina and combined alumina and ferric oxide were determined gravimetrically and ferric oxide was determined volumetrically with standard titanous chloride solution and ammonium thiocyanate. Combined sugar in residues, when determined, was obtained by difference. The optical rotatory power of solutions was determined in a 200 mm tube by means of a wedge-type polarimeter accurate to 0.1%, Ventske scale. pH determinations were made electrometrically with an instrument accurate to 0.05. With reference to Note (2)

of Table II-A and Note (7) of Table V, the glass electrode for the meter was broken near the end of the investigation and no replacement was available in time. Results obtained with two other available meters could not be correlated with those obtained with the meter used throughout the investigation and therefore have been omitted as being of no value.

Further details of test procedures are given in the respective sections following.

IV. REACTIONS BETWEEN LIME AND SUGAR SOLUTION

Numerous texts on organic chemistry give mention to the reaction between calcium hydroxide and sucrose to form mono-, di-, and tricalcium sucates, the first two of which are soluble and the latter is insoluble in water. However, in spite of the importance of these reactions in the reclaiming of sugar from beet sugar molasses, little is apparently known of their details or of the structures of the sucates.

The results of the series of tests with freshly prepared calcium oxide and sugar solution are given in Tables II and II-A. Optical rotatory powers and pH values of the extracts from these tests are plotted in figure 1 against the corresponding amounts of dissolved calcium oxide.

Quantities of calcium oxide up to approximately 2.5 g gave clear solutions after only short periods of mixing. Increasing quantities of calcium oxide above 2.5 g gave increasing quantities of solid phase and, up to 7.5 g, gave increasing quantities of dissolved calcium oxide. Sufficient tests were made at each concentration of calcium oxide, with sufficiently long mixing periods, to assure that equilibrium was attained between the solid and solution phases, as evidenced by constant composition of the solution phase. The fact that the amount of dissolved calcium oxide continues to increase with increasing amounts of total calcium oxide, even above the point where a solid phase first exists in equilibrium, appears to be contradictory to the usual concepts of inter-phase relationships at equilibrium. All lime used was carefully calcined to avoid a "high-burned" condition and was entirely "sugar-soluble", as indicated by the fact that it went entirely into solution at concentrations below 2.5 g. Moreover, carbonation could not

TABLE II - RESULTS OF ORIGINAL TESTS WITH CaO AND SUGAR SOLUTION

No.	CaO added, g/100 ml.	Mixing time, hours	Residue	pH of extract	CaO dissolved, g/100 ml	Optical Rotation of extract, Vent- ske %/200 mm	Analysis of Residue	
							% Ca(OH) ₂	% Combined Sugar
1	2	3	4	5	6	7	8	9
1	0.000	---	---	6.60	---	57.7	---	---
2	0.050	2	None	10.95	0.050	57.2	---	---
3	0.100	2	None	11.25	0.100	57.0	---	---
4	0.500	2	None	11.90	0.500	55.3	---	---
5	1.000	2	None	12.00	1.000	53.4	---	---
6	1.500	2	None	12.10	1.500	51.3	---	---
7	1.900	2	None	12.15	1.900	49.9	---	---
8	2.500	8	Trace	12.15	2.500	48.1	Insufficient to analyze	
9	3.000	10	Increasing amount	12.20	2.93	47.4	Insufficient to analyze	
10	5.000	6-72	Increasing amount	12.30	3.43	45.3	94.1 1	5.9 1
11	7.500	6-72	Increasing amount	12.30	3.51	44.1	90.5 1	9.5 1

TABLE II-A
RESULTS OF TESTS WITH CaO AND SUGAR SOLUTION,
USING NEW MIXING METHOD.

No.	CaO dissolved, g/100 ml(1)	Mixing time, hours	pH of extract	Optical Rotation of extract, Ventske %/200 mm
1	2	3	4	5
1	0.000	-	6.60	52.6
2	0.044	1	10.90	52.4
3	0.094	1	11.20	52.2
4	0.134	1	11.30	52.0
5	0.179	1	11.45	51.8
6	0.208	1	11.50	51.6
7	0.426	1	11.65	50.7
8	0.649	1	11.80	49.7
9	0.870	1	11.90	48.8
10	1.349	2	(2)	47.2
11	1.804	2	(2)	45.6
12	2.235	2	(2)	44.3

Notes: (1) 15 g. sugar plus 100 ml water = 109.5 ml of solution. Amounts of CaO actually used have been reduced by the factor 100/109.5 to give the values shown in this column.

(2) Could not determine satisfactorily because glass electrode of pH meter was broken and no replacement was available in time. Results obtained with other available pH meters could not be correlated with those obtained by meter used throughout the investigation.

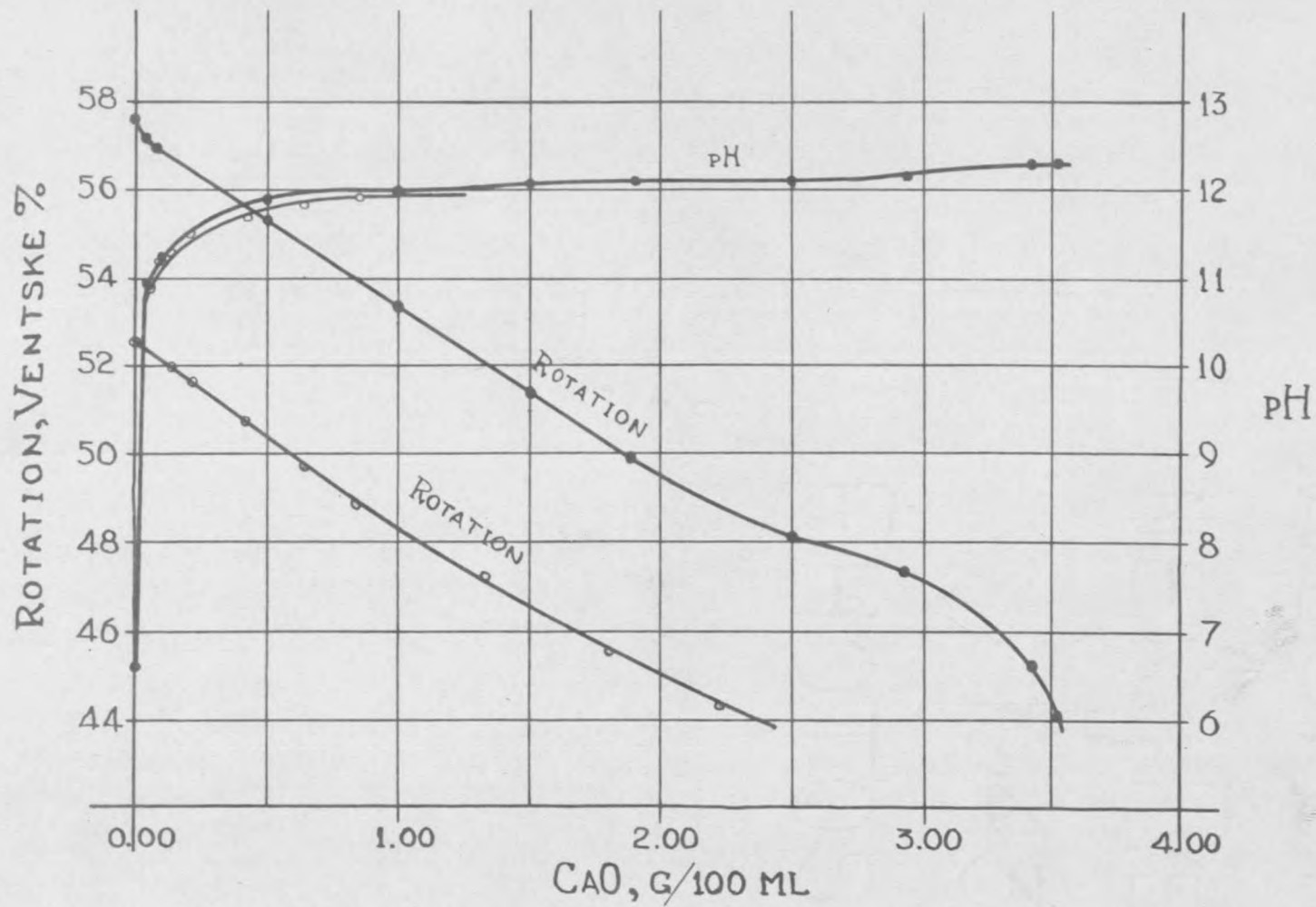


FIGURE 1

RELATIONSHIP OF DISSOLVED LIME (CaO) TO SUGAR CONTENT AND pH.

LEGEND: •-ORIGINAL MIXING METHOD ; ○- NEW MIXING METHOD.

have taken place during the mixing. This same condition has been previously observed by Doubourg (13) in connection with a study of the solubility of calcium hydroxide in aqueous sugar solutions in contact with increasing excesses of the solid phase. The only apparent explanation is that, in the presence of greater excesses of solid lime, there is a shift in the equilibrium in the solution between monocalcium sucate and dicalcium sucate toward the formation of greater proportions of the latter. However, this matter was not pursued further in the present investigation, the main purpose in studying the lime solubilities being to determine the effects of dissolved lime on the optical rotatory powers and pH values of the solutions.

The maximum concentration of dissolved calcium oxide of 3.51 g per 100 ml corresponds to 4.64 g of calcium hydroxide. This latter value agrees well with the solubilities reported by Weisberg (14) and by Cameron and Patten (13), when computed to a comparable basis, but is considerably higher than the value reported by Reinders and Van Gelder (13), for tests made under similar conditions.

Residues from the Series 1 tests with the original mixing method were analyzed in the following manner:

The residues obtained from the first centrifuging were washed three times with small amounts of concentrated ammonium hydroxide in the centrifuge tubes, recentrifuging and decanting after each washing. The residues were then dried at 100°C, transferred to weighed Gooch crucibles, and washed again with small portions of concentrated ammonium hydroxide until constant weights were obtained after dry-

ing at 100°C. All operations outside the drying oven were conducted as rapidly as possible to minimize carbonation and, during drying, carbon dioxide-free air was passed through the oven. Solid calcium hydroxide was found by test to be insoluble in the concentrated ammonium hydroxide and lime-sugar solutions were unaffected by the reagent. Absolute ethyl alcohol, as a possible washing agent, was found to cause a precipitate of undetermined composition (probably a calcium sucate) to be formed from the extracts.

The weighed washed residues were dissolved in a measured excess of standard hydrochloric acid, the excess then being back-titrated to a phenolphthalein end point with standard sodium hydroxide solution. The weight of calcium hydroxide in the residues was obtained from the amount of acid required to react with the sample, and the weight of combined sugar in the residues was then obtained by difference, assuming that tricalcium sucate has the formula $3\text{CaO} \cdot \text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{H}_2\text{O}$, as reported by MacKenzie (7).

The formula of hydrated lime, when dried at 100°C, was checked by adding an excess of water to weighed samples of calcium oxide and drying to constant weight at 100°C. The formula was found to be exactly $\text{CaO} \cdot \text{H}_2\text{O}$ or $\text{Ca}(\text{OH})_2$.

As indicated in Table I, starting amounts of 5.0 g. and 7.5 g of calcium oxide yielded residues containing $5.9 \pm 1\%$ and $9.5 \pm 1\%$ of combined sugar, respectively. Lesser amounts of calcium oxide yielded residues too small in amount to be satisfactorily analyzed for sugar; however, it is reason-

able to expect that even the smaller residues contained slight amounts of combined sugar. Therefore, the solid phase in equilibrium with the lime-sugar solution may be considered to consist chiefly of calcium hydroxide, together with relatively small proportions of tricalcium sucrate, in the range of concentrations and under the conditions covered by the present investigation.

The curves in figure 1 for optical rotatory power versus amount of dissolved lime are primarily of importance in connection with similar curves obtained with the cement compounds, insofar as the present investigation is concerned, and will be discussed in greater detail later. The decrease in rotatory power noted with increased amounts of dissolved lime, prior to the point where a solid phase is present at equilibrium, must be due entirely to a lesser rotatory power of dissolved combined sugar, as compared to that of dissolved free sugar. It is not considered that sugar combined in solution as sucrate has lost all its rotatory power because of the fact that even the solutions containing the maximum amount of dissolved lime show pronounced rotation. This property should serve therefore as a means of detecting hydrolysis of cement compounds by sugar solution to liberate calcium hydroxide. The plots for rotatory power give approximately straight lines up to the point where solid phase appears. The concentration of dissolved lime where solid phase first persists at equilibrium coincides approximately with a mol ratio of lime to sugar of 1:1. This would indicate that initial formation of dicalcium sucrate and probably also of tricalcium sucrate takes place prior to the complete tying-up of all sugar molecules as monocalcium sucrate. Apparently, a monocalcium sucrate molecule can com-

bine more readily with additional lime to form a more basic sucrate than can a free sugar molecule combine with lime to form monocalcium sucrate. However, further consideration of this possible reaction mechanism has not been considered pertinent to the present investigation.

As was the case in connection with the curve for optical rotatory power, the curves in figure 1 for pH versus dissolved lime are of primary importance in the present investigation only in connection with consideration of reactions with the cement compounds and will be discussed in greater detail later.

V-REACTIONS BETWEEN ALUMINUM HYDROXIDE AND
SUGAR SOLUTION

Because of the amphoteric nature of hydrated alumina, the possibility of a reaction between aluminum hydroxide and sugar solution was considered. A series of tests (Series 2) was therefore made, involving freshly precipitated aluminum hydroxide and sugar solution. However, no evidence of a reaction was obtained. Both the optical rotatory power and the pH of the extracts from increasing amounts of aluminum hydroxide remained unchanged from the corresponding values for the original pure sugar solution, from which the conclusion is drawn that, at least at the low hydroxyl-ion concentration existing in these solutions, aluminum hydroxide is not sufficiently basic to combine with sugar.

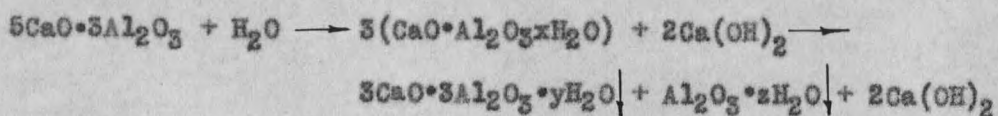
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VI. REACTIONS BETWEEN $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ AND SUGAR SOLUTION

Wells (15) reports that water reacts with $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ to form a metastable solution of monocalcium aluminate, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, plus dissolved calcium hydroxide, and that, upon standing, a solid phase appears consisting of hydrated tricalcium aluminate plus hydrated alumina. These reactions can be represented as follows:



The results of tests with $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and sugar solution are shown in Table III. No significant differences were noted between the results obtained with $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ containing 0.94% free lime and the results obtained with the compound containing no free lime. The compound, in the various amounts, was mixed for the times indicated with the sugar solution. The clear extracts obtained from centrifuging these mixtures were then tested for optical rotatory power, pH, dissolved alumina and dissolved lime.

Below concentrations of approximately 0.228 g of the aluminate per 100 ml of solution, the aluminate was found to entirely dissolve within a mixing time of 6 hours and no solid phase separated from the extracts on standing. Concentrations of the aluminate from 0.228 g to 0.686 g per 100 ml of solution resulted in substantially complete solution of the aluminate; however, at the higher concentrations, secondary precipitation reactions set in prior to 6 hours, thus rendering complete solution impossible. Therefore, tests were made with different mixing times, as indicated in Table III, at each of the higher concentrations in order to determine the composition of extracts prior to the occurrence of the secondary reactions. In the tests with the higher concentrations of aluminate and shorter mixing periods,

TABLE III - RESULTS OF TESTS WITH $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ AND SUGAR SOLUTION

No. (1)	5CaO- 3Al ₂ O ₃ added, g/100ml (2)	Mix- ing time, hrs. (3)	Total dis- solved, g/100ml (4)	Composition of Extract						Mol-Rat. of pre- cipitate CaO/Al ₂ O ₃ (11)	pH of Extract		Optical Rota- tion of Extract, Ventske % per 200 mm	
				Al ₂ O ₃ , g/100ml		CaO, g/100ml		Mol-Ratio, CaO/Al ₂ O ₃			A	B	A	B
				A(3)	B(3)	A	B	A	B					
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	0.092	6	0.092	0.048	No ppt	0.044	No ppt	1.67	No ppt	No ppt	10.50	No ppt	52.6	No ppt
2	0.228	6	0.228	0.119	No ppt	0.109	No ppt	1.67	No ppt	No ppt	10.35	No ppt	52.6	No ppt
3	0.365	6	0.337	0.166	0.121	0.171	0.132	1.88	1.98	1.58	10.95	(5)	52.2	52.2
3-a	0.366	4½	0.344	0.176	(4)	0.168	(4)	1.73	(4)	(4)	11.00	(4)	52.3	(4)
4	0.412	6	0.389	0.195	0.122	0.194	0.142	1.81	2.12	1.27	11.00	(5)	52.3	52.3
5	0.457	6	0.442	0.227	0.124	0.215	0.141	0.72	2.06	1.28	11.00	(5)	52.4	52.4
5-a	0.458	4½	0.429	0.219	(4)	0.210	(4)	1.74	(4)	(4)	11.05	(4)	52.3	(4)
5-b	0.458	4	0.414	0.217	0.133	0.197	0.138	1.65	1.89	1.25	11.00	10.70	52.2	52.0
6	0.547	6	0.514	0.261	0.128	0.253	0.143	1.76	2.04	1.49	11.05	(5)	52.4	52.4
6-a	0.550	4½	0.497	0.248	0.113	0.249	0.124	1.82	1.99	1.61	11.05	10.95	52.2	51.6
6-b	0.549	4	0.489	0.257	0.147	0.232	0.154	1.64	1.90	1.29	11.05	10.85	52.2	51.5
7-a	0.686	2	0.459	0.241	0.131	0.218	0.140	1.64	1.95	1.29	10.95	10.85	52.4	52.0
8-a	0.913	2	0.574	0.297	0.151	0.277	0.161	1.69	1.94	1.44	11.00	10.95	52.3	51.0
Averages				0.130		0.142		1.72	1.99	1.39	10.86			

Notes: (1) Numbers not followed by letters are for tests using $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ containing 0.94% free CaO. Other tests are with $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ containing no free CaO.
 (2) 15 g sugar plus 100 ml water = 109.5 ml solution. Amounts of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ actually used have been reduced by the factor 100/109.5 to give the values shown in this column.
 (3) Column A for original extracts; Column B for extracts after precipitation.
 (4) Extracts spilled after precipitation.
 (5) Insufficient extract to determine.

equilibrium probably was not attained in the initial solution process.

Use of amounts of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ in excess of 0.228 g per 100 ml of solution resulted in metastable extracts containing increasing amounts of dissolved lime and alumina, from which solid gelatinous material separated on standing. The greater the amount of the aluminate used, the sooner did the solid phase appear.

To compare the compositions of the original extracts with those of the extracts obtained after secondary precipitation had taken place, portions of the original extracts were set aside in tightly stoppered flasks. Completeness of precipitation was determined by centrifuging the material at intervals and then setting aside the new clear extracts. This process was repeated until new extracts were obtained, from which no further precipitation would occur. A total period of two weeks was found sufficient in all cases.

The mol ratio, CaO to Al_2O_3 , of the original $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ is 1.67. As indicated in column 9 of Table III, the values of this mol ratio in the original extracts ranged from 1.64 to 1.88, with an average value of 1.72. In general, the longer the mixing period the higher the mol ratio, which fact is indicative that some secondary reaction probably took place during the longer mixing periods. Therefore, the difference between the average ratio of 1.72 and the value of 1.67 for the original aluminate may be considered negligible, and the statement may be made that, prior to the occurrence of secondary precipitation, there is no change in mol ratio between the solution phase and the solid aluminate.

With reference to Column 14 of Table III, varying amounts of dissolved

$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ had no effect on the optical rotatory power of the original extracts, the rotatory power of a solution consisting only of 15 g of sugar and 100 ml of water being 52.5%, Ventske scale. From the effects of dissolved lime on the rotatory power of sugar solution, as noted in Section IV, above, this constancy of rotatory power of sugar extracts from $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ is considered conclusive evidence that no free lime was formed in the extracts by the hydrolysis of the aluminate, and that the calcium oxide existed in the extracts combined with alumina.

All extracts from which solid phase separated on standing had approximately the same composition after equilibrium was attained, the average composition being 0.142 g of calcium oxide and 0.130 g of alumina per 100 ml of solution. The mol ratio, CaO to Al_2O_3 , in these extracts after precipitation was in every case equal to approximately 2.00, the actual average value being 1.99. As was the case for the original extracts, the optical rotatory power of the extracts after precipitation was unchanged from that of the pure sugar solution. Therefore, no free lime was formed in the extracts during the precipitation process and all the dissolved calcium oxide must have existed in molecular combination with alumina.

The various values of the pH of the extracts have been plotted in figure 2 against the corresponding amounts of dissolved calcium oxide, along with similar values for CaO -sugar solutions from figure 1 for comparison. The pH of the original $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ extracts approaches a limiting value of 11.00 to 11.05. The pH of the extracts after precipitation is fairly constant, the average of the five determinations made being 10.86. Slight but definite reductions in pH were brought about by the secondary reactions. An explanation of the fact that the $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ extracts exhibit considerable

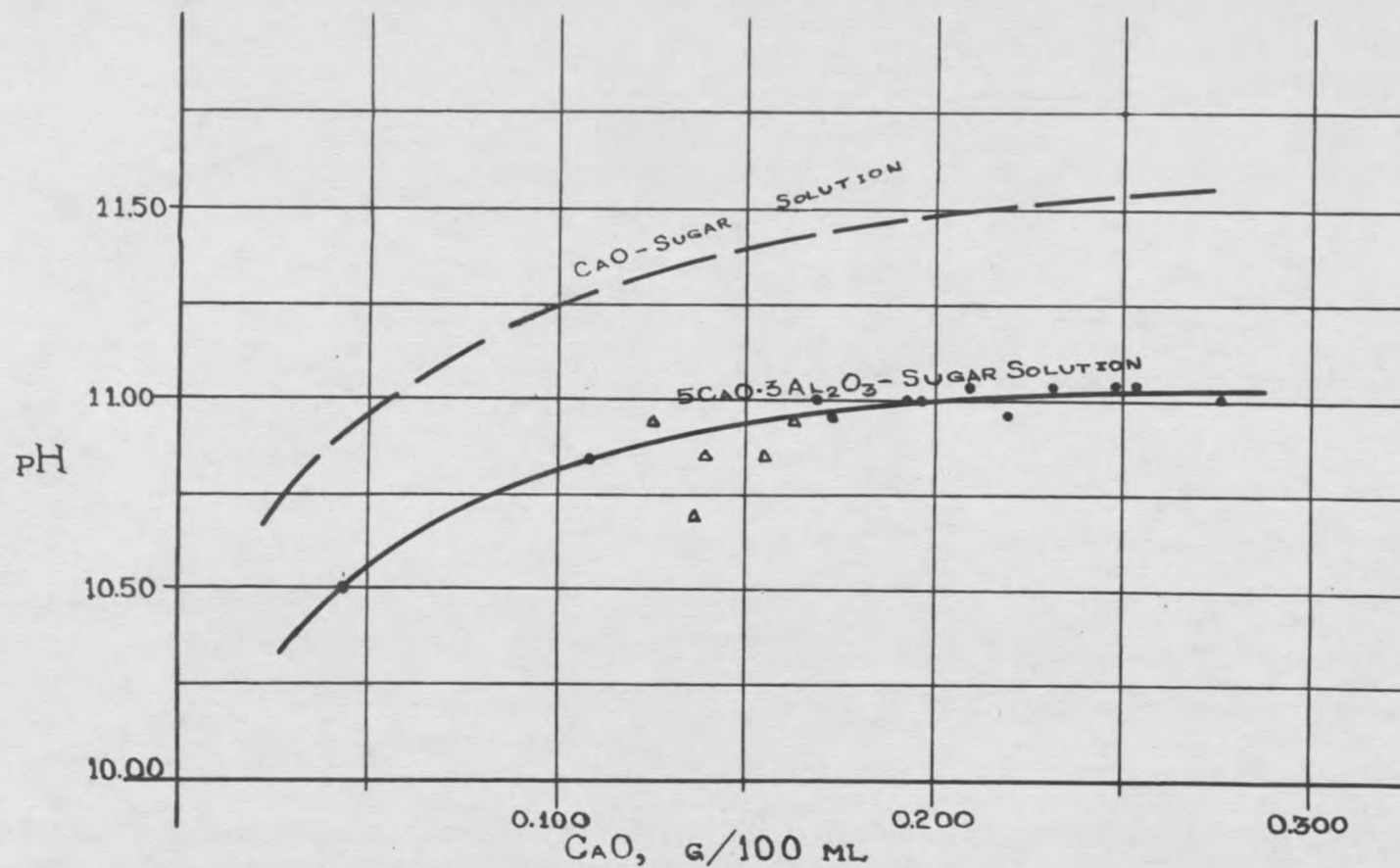


FIGURE 2

CALCIUM OXIDE CONTENT OF EXTRACT VS pH

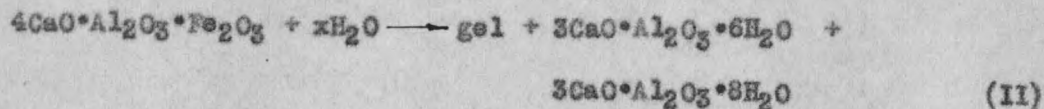
LEGEND: •-RESULTS FROM ORIGINAL EXTRACTS.
 Δ-RESULTS FROM EXTRACTS AFTER PRE-
 CIPITATION. (NOT INCLUDED IN CURVE)

hydroxyl-ion concentration, even though the aluminate is not hydrolyzed to give free calcium hydroxide, will be given in Section IX-A, below.

The mol ratios, CaO to Al_2O_3 , of the precipitates formed from the original extracts, as shown in column 11 of Table III, are rather erratic, undoubtedly due to the fact that they were determined by difference and the fact that the amounts of precipitate formed were small with resultant large error in the ratio from relatively small analytical error. The average of the values, which vary over a range from 1.25 to 1.61, is 1.39. Direct analysis of the residues was not attempted because of difficulties and errors to be expected in purifying the small amounts of such a gelatinous material. In view of the consistent results obtained in the determinations of the mol ratios of the extracts, both before and after precipitation, it is to be expected that the mol ratio of the precipitates will have a constant value. Since the mol ratio of the extracts increased from 1.72 (average value) to 1.99 (average value) during the precipitation process, a mol ratio of 1.39 (average value) should be a close approximation for the precipitates. This corresponds to a proportion of calcium oxide to alumina of 4 mols to 3 mols, and all the lime must be in combination with alumina, although all alumina is not necessarily in combination with lime. A final summarization of the reactions involved between $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and sugar solution will be given in Section IX-C, below.

VII. REACTIONS BETWEEN $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ AND SUGAR SOLUTION

Lapin (4) reports that water reacts with $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ to form a gel and crystalline hydrated tricalcium aluminate, which process may be represented as follows:



The number of molecules of water of hydration in the tricalcium aluminate, as reported by Lapin, is probably very susceptible to the conditions of formation.

The results of tests with $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and sugar solution are shown in Table IV. The results obtained from the compound containing 0.84% free calcium oxide are distinctly different from those obtained with the compound containing no free lime. This is no doubt indicative that, in so complex a molecule as that of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ where there are two different acidic constituents (Al_2O_3 and Fe_2O_3) and two kinds of coordinating atoms (Al-atoms and Fe-atoms), complete equilibrium in calcination is very essential. The mechanism of the formation of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ might well be that of formation of, first, a calcium aluminate and a calcium ferrite and, second, the interaction of these latter compounds to form the complex $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. If such is the case, determination of free lime is less a measure of the completeness of calcination in this instance than it is for the calcium aluminates.

In view of the possibility that a negative free lime test might not imply complete calcination of the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, a portion of the material containing 0.84% free calcium oxide was heated for two successive periods

of 7 hours each at 1250°C , whereas a heating period of two hours at this temperature was sufficient to just eliminate all free lime. Tests Nos. 9-c, 9-d, and 10-c in Table IV pertain to this so-called "extra burned" material. In this connection, it is of at least passing interest to note that $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, upon long heating at 1250°C , underwent a decrease in volume of approximately one-third of that of the original dry powder, but that, upon cooling to room temperature, the material "dusted" and returned to its original volume. This phenomenon, which took place considerably below the fusion point, has not been previously reported in the literature to the writer's knowledge.

The test procedure for this series was substantially the same as that for $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, except for the additional analyses for ferric oxide. In this connection, determinations were made of the possible reducing effect of sucrose on ferric salts by mixing known quantities of ferric sulphate with sugar solution. No evidence of reduction to the ferrous condition was found.

As indicated in Table IV, no appreciable reaction occurred between apparently pure $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ and sugar solution below amounts of 2.28 g of the solid compound per 100 ml of sugar solution. However, the decided dissimilarity between results with 2.28 g. and more of the material calcined just to the point of elimination of free calcium oxide and results obtained with the "extra-burned" material brings up a question as to the true natures of these materials. Both materials were prepared from the same supply of partially calcined stock, contained no free lime after calcination, and received identical treatment except for the difference in length of calcining. The

TABLE IV - RESULTS OF TESTS WITH $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ AND SUGAR SOLUTION

No. (1)	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ added, g/100 ml (2)	Mixing time, hours (3)	Total dis- solved, g/100 ml (4)	Composition of Extract								Mol-Ratio- $\text{CaO}/\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ in precipitate (13)	pH of Extract		Optical Rotation of Extract, Ventske % per 200 mm		
				Al_2O_3 , g/100 ml		Fe_2O_3 , g/100ml		CaO , g/100ml					Mol Ratio $\text{CaO} / \text{Al}_2\text{O}_3 / \text{Fe}_2\text{O}_3$	A	B	A	B
				A (3)	B(3)	A	B	A	B	A	B						
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
1	0.184	6	0.018	0.002	(4)	0.000	(4)	0.016	(4)	-----	-----	-----	9.85	(4)	52.6	(4)	
2	0.275	6	0.025	0.004	(4)	0.000	(4)	0.021	(4)	-----	-----	-----	10.05	(4)	52.5	(4)	
3	0.366	6	0.047	0.019	(4)	0.000	(4)	0.028	(4)	-----	-----	-----	10.15	(4)	52.4	(4)	
4	0.458	6	0.054	0.021	(4)	0.001	(4)	0.033	(4)	-----	-----	-----	10.25	(4)	52.6	(4)	
5	0.684	6	0.087	0.049	(4)	0.001	(4)	0.037	(4)	1.38/1.00/0.01	-----	-----	10.40	(4)	52.3	(4)	
6	0.915	6	0.119	0.060	(4)	0.007	(4)	0.052	(4)	1.58/1.00/0.08	-----	-----	10.55	(4)	52.4	(4)	
6-a	0.914	5	0.003	0.000	(4)	0.000	(4)	0.003	(4)	-----	-----	-----	10.05	(4)	52.3	(4)	
6-b	0.914	8	0.008	0.000	(4)	0.000	(4)	0.008	(4)	-----	-----	-----	10.05	(4)	52.5	(4)	
7	1.368	6	0.191	0.093	0.082	0.013	0.013	0.085	0.081	1.67/1.00/0.09	1.79/1.00/0.11	Insufficient	10.75	10.65	52.6	52.7	
7-a	1.370	5	0.005	0.000	(4)	0.000	(4)	0.005	(4)	-----	-----	-----	10.10	(4)	52.6	(4)	
7-b	1.371	8	0.008	0.000	(4)	0.000	(4)	0.008	(4)	-----	-----	-----	10.15	(4)	52.5	(4)	
8	1.828	6	0.288	0.126	0.099	0.031	0.026	0.131	0.111	1.89/1.00/0.16	2.04/1.00/0.17	1.35/1.00/0.10	10.80	10.50	52.0	52.0	
8-a	1.826	5	0.008	0.001	(4)	0.0005	(4)	0.008	(4)	-----	-----	-----	10.15	(4)	52.5	(4)	
8-b	1.826	8	0.016	0.005	(5)	0.0005	(5)	0.011	(5)	-----	-----	-----	10.20		52.5		
9	2.285	6	0.393	0.162	0.133	0.050	0.048	0.181	0.153	2.03/1.00/0.19	2.09/1.00/0.23	1.76/1.00/0.04	10.95	10.85	52.0	51.6	
9-a	2.283	5	0.019	0.005	(4)	0.0005	(4)	0.013	(4)	-----	-----	-----	10.20	(4)	52.5	(4)	
9-b	2.284	8	0.090	0.053	(5)	0.001	(5)	0.036	(5)	1.23/1.00/0.01	(5)	(5)	10.40		52.5		
9-c	2.283	8	0.329	0.167	(6)	0.019	(6)	0.143	(6)	1.56/1.00/0.08	(6)	(6)	10.75	(6)	52.1	(6)	
9-d	2.283	8	0.310	0.152	(6)	0.019	(6)	0.139	(6)	1.66/1.00/0.08	(6)	(6)	10.75	(6)	52.0	(6)	
10	4.564	6	0.793	0.319	0.164	0.107	0.083	0.367	0.217	2.09/1.00/0.21	2.38/1.00/0.32	1.76/1.00/0.10	11.00	10.75	51.0	49.4	
10-a	4.566	5	0.226	0.118	0.092	0.011	0.009	0.097	0.079	1.49/1.00/0.06	1.57/1.00/0.07	1.29/1.00/0.04	10.75	10.45	52.0	52.4	
10-b	4.566	8	0.258	0.137	0.101	0.013	0.011	0.108	0.085	1.44/1.00/0.06	1.56/1.00/0.07	1.17/1.00/0.03	10.75	10.50	52.1	52.4	
10-c	4.565	5	0.628	0.310	(6)	0.040	(6)	0.278	(6)	1.63/1.00/0.08	(6)	(6)	10.80	(6)	52.0	(6)	

- Notes: (1) Numbers not followed by a letter are for tests using $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ containing .84% free CaO . Other tests are with $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ containing no free CaO . See comments in test for differences between Nos. 9-c, 9-d, 10-c and 9-a, 9-b, 10-a, 10-b.
- (2) 15g sugar + 100ml water = 109.5ml of solution. Amounts of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ actually used have been reduced by the factor 100/109.5 to give the values shown in this column.
- (3) Column A for original extracts; Column B for extracts after precipitation.
- (4) No precipitate formed. (6) Insufficient time available to permit the precipitation reaction to reach equilibrium.
- (5) Slight amount of crystalline precipitates, insufficient to analyze, collected on bottom and walls of flask.

material calcined for the shorter period is definitely the more stable in the presence of sugar solution, as evidenced by its decidedly lower solubilities for given mixing periods. Facilities and time were not available for determining whether either of these materials was truly pure $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. It is considered that a petrographic or X-ray diffraction examination is necessary for this purpose. It might be that the phenomenon of volume-change and "dusting" mentioned above for the extra-burned material is evidence of an unstable combination of the constituents (at high temperature with resultant shrinkage) followed by decomposition into an aluminate and a ferrite (at low temperature with resultant "dusting"). In any event, the extra-burned material more closely resembles the material containing 0.84% free calcium oxide, insofar as its reaction with sugar solution is concerned, than it does the material calcined just to the point of elimination of free lime.

The rate of the initial reaction between the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ materials and sugar solution is slow, as compared to that between either $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and sugar solution discussed in Section VI or $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ to be discussed in Section VIII, below. There is no evidence of complete solution, either true or colloidal, at any concentration, even with the smallest amounts of the material used in the investigation. The amount of material dissolved is a function of the length of the mixing period but, as indicated in columns 5, 7, and 9 of Table IV, the initial reaction is not one of solution of the original material as such. The proportion of ferric oxide going into solution is, in all cases, much less than the corresponding proportions of alumina and calcium oxide. Likewise, the ratios of calcium oxide to alumina

are not the same in the extracts as in the original materials.

Evidence of the hydrolysis of all three types of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ material investigated comes from the very limited amounts of ferric oxide dissolved, the changes in mol ratio of calcium oxide to alumina in the original extracts as indicated in column 11 of Table IV, and the reductions in optical rotatory power of the extracts with increasing amounts of total dissolved calcium oxide as indicated in column 16 of Table IV.

In figure 3, the rotatory power and pH values of extracts from $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ material containing no free lime have been plotted against the corresponding amounts of total dissolved calcium oxide per 100 ml of solution. Figure 4 is similar to figure 3, except that it is for material containing 0.84% free calcium oxide. Both of these figures illustrate the substantially complete hydrolysis of that portion of the $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ material that is dissolved, as evidenced by the fact that the reductions in rotatory power of the original extracts with increasing amounts of total dissolved calcium oxide are approximately the same as those for CaO-sugar solutions. With reference to figure 4 and the seemingly unusual reductions in rotatory power of the extracts after precipitation, reference is made to the explanation in Section VIII, below, of a similar phenomenon in the case of extracts from $3\text{CaO}\cdot\text{Al}_2\text{O}_3$.

The results shown in columns 11 and 12 of Table IV for the mol ratios, CaO to Al_2O_3 , of the extracts before and after secondary precipitation, and the values shown in column 13 for similar mol ratios of the precipitates, show definite trends with changes in amounts of starting materials. However, the significance of these results cannot be properly evaluated in view of

the questionable nature of the materials tested. Final summarization of the reactions between pure $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and sugar solution is not possible from the results of the present investigation.

PERMANENT RECORD

SOUTHWORTH, D.D. U.S.A.

25% SODIUM CHLORIDE

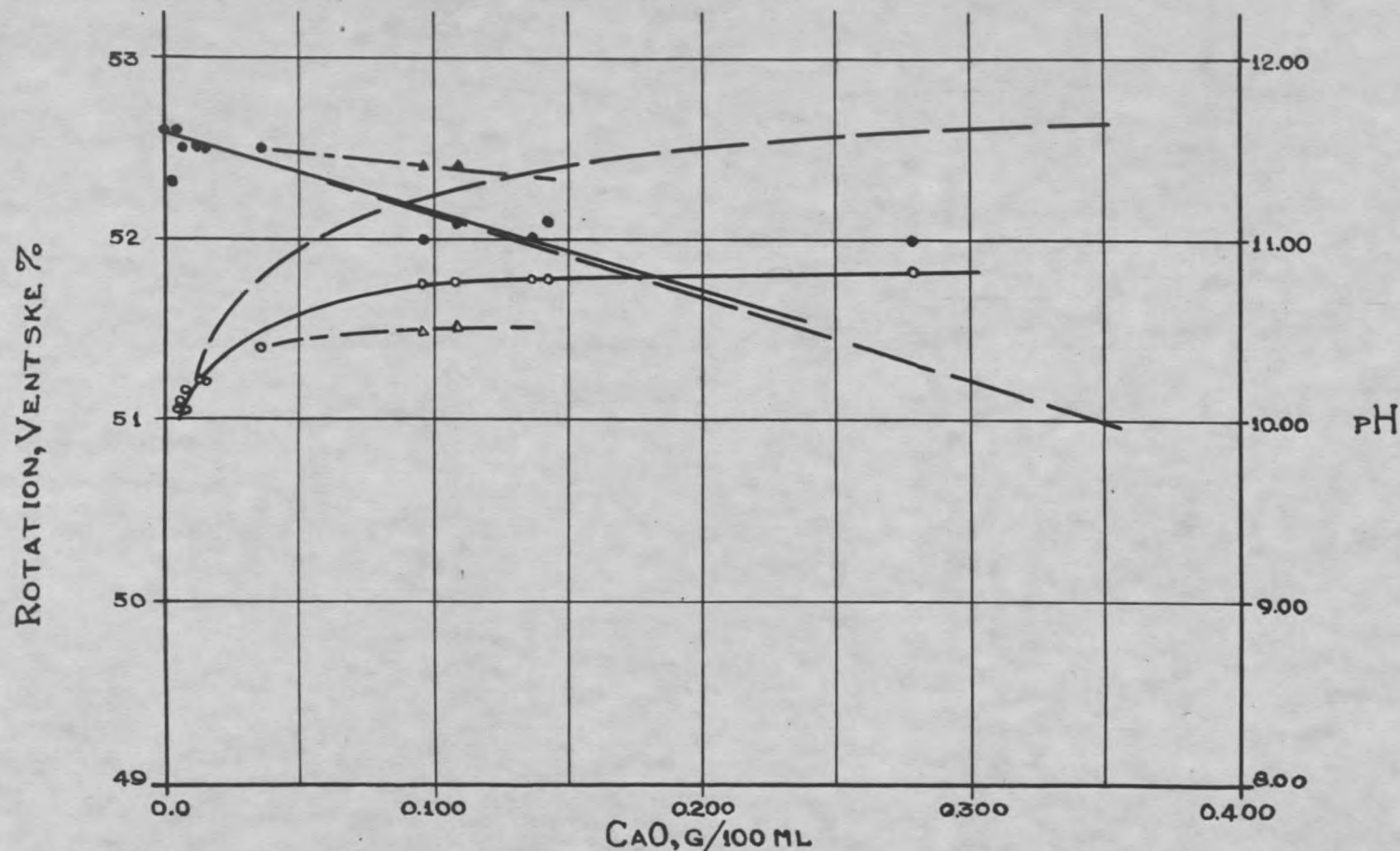


FIGURE 3

SUGAR CONTENT AND pH. CaO CONTENT OF EXTRACT FROM $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$

LEGEND: —●— ROTATION OF ORIGINAL EXTRACTS
 -▲- ROTATION OF EXTRACTS AFTER PRECIPITATION
 —○— pH OF ORIGINAL EXTRACTS
 -△- pH OF EXTRACTS AFTER PRECIPITATION
 ——— CaO-SUGAR SOLUTION

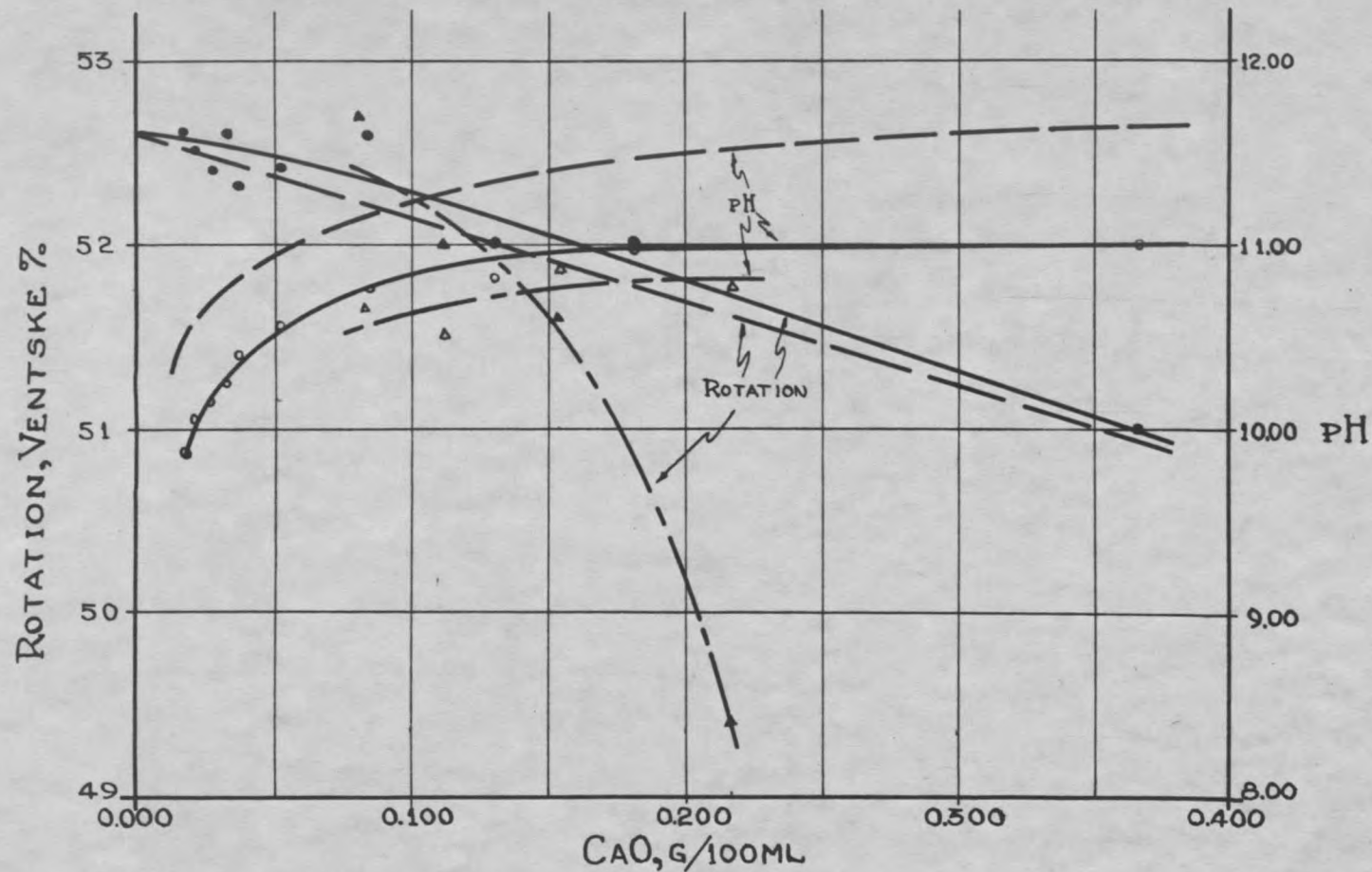


FIGURE 4

SUGAR CONTENT AND pH VS. CaO CONTENT OF EXTRACT FROM $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ AND FREE LIME.

LEGEND:
 —●— ROTATION OF ORIGINAL EXTRACTS
 -▲- ROTATION OF EXTRACTS AFTER PRECIPITATION
 —○— pH OF ORIGINAL EXTRACTS
 -△- pH OF EXTRACTS AFTER PRECIPITATION
 ——— CaO - SUGAR SOLUTION

VIII. REACTIONS BETWEEN $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ AND SUGAR SOLUTION

Wells (15) reports that water reacts with $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ so rapidly that the progress of the reaction cannot be followed experimentally. However, Klein and Phillips (3) report that the setting of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ is due to the formation of the hydrate without the formation of hydrated alumina. Irrespective of whether or not hydrolysis of the compound occurs when it first comes in contact with water, it is apparent that the final aluminate precipitate is the same as that obtained from the other calcium aluminates as reported by Wells (15), namely, the hydrated tricalcium aluminate. This most basic of the calcium aluminates known to exist in the system $\text{CaO}-\text{Al}_2\text{O}_3$ therefore must be the most stable in the presence of water.

The results of tests with $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and sugar solution are shown in Table V. No appreciable difference is noted between test results obtained with the aluminate containing 2.04% free calcium oxide and results obtained with the aluminate containing no free calcium oxide, undoubtedly due to the high reactivity of the aluminate itself.

The test procedure for this series was the same as that for $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, except that the sugar was ground to a powder prior to weighing and mixing with the compound, in order to assure more intimate mixing and further reduce the tendency to lump when water is added.

Quantities of the aluminate up to 0.913 g per 100 ml of sugar solution went entirely into solution within 15 minutes. However, a solution of 0.913 g of the aluminate started secondary precipitation shortly after the 15-minute mixing period, necessitating that the pH and polarimetry determinations be made very rapidly. In view of the fact that 15 minutes was about the mini-

TABLE V - RESULTS OF TESTS WITH $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ AND SUGAR SOLUTION

No. (1)	3CaO· Al ₂ O ₃ added, g/100ml (2)	Mix- ing time, hrs. (3)	Total dis- solved, g/ 100ml (4)	Composition of Extract						Mol-Rat. of Pre- cipitate, CaO/Al ₂ O ₃ (11)	pH of Extract		Optical Rota- tion of Extract, Ventske % per 200 mm	
				Al ₂ O ₃ , g/100ml		CaO, g/100ml		Mol-Ratio, CaO/Al ₂ O ₃			A	B	A	B
				A(3)	B(3)	A	B	A	B					
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	0.047	$\frac{1}{4}$	0.047	0.018	No ppt	0.029	No ppt	3.00	No ppt	No ppt	10.50	(7)	52.8	52.7
2	0.092	$\frac{1}{4}$	0.092	0.035	No ppt	0.057	No ppt	3.00	No ppt	No ppt	10.75	10.60	52.7	52.7
3	0.229	$\frac{1}{4}$	0.229	0.086	0.085	0.143	0.141	3.00	----	----	11.10	11.00	52.5	52.3
4	0.458	$\frac{1}{4}$	0.458	0.173	0.171	0.285	0.284	3.00	----	----	11.30	11.30	52.2	52.2
4-a	0.456	$\frac{1}{4}$	0.456	0.172	0.171	0.284	0.267	3.00	----	----	11.30	(7)	52.1	52.2
5	0.899	$\frac{1}{4}$	0.899	0.339	0.176	0.560	0.343	3.00	3.55	2.42	11.35	11.35	51.7	49.6
5-a	0.913	$\frac{1}{4}$	0.913	0.345	0.165	0.568	0.318	3.00	3.50	2.53	11.40	(7)	51.7	49.1
6	1.371	(4)	1.371(5)	0.517	0.161	0.854	0.345	3.00	3.89	2.59	(6)	(7)	(6)	47.0
6-a	1.370	(4)	1.370(5)	0.517	0.146	0.853	0.313	3.00	3.90	2.64	(6)	(7)	(6)	45.8
7-a	2.283	(4)	(6)	(6)	0.115	(6)	0.280	(6)	4.41	----	(6)	(7)	(6)	38.5

- Notes: (1) Numbers not followed by letters are for tests using $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ containing 2.04% free CaO . Other tests are with $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ containing no free CaO .
- (2) 15g sugar + 100ml water = 109.5ml of solution. Amounts of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ actually used have been reduced by the factor 100/109.5 to give the values shown in this column.
- (3) Column A for original extracts; column B for extracts after precipitation.
- (4) Materials shaken in a flask for about 5 minutes and then permitted to stand for precipitation.
- (5) Assumed, from the fact that the aluminate went into substantially complete solution at about 3 minutes, followed by start of secondary precipitation at about 5 minutes.
- (6) Impossible to determine because of secondary precipitation.
- (7) Could not determine because of broken glass electrode. See comments in text.

sum time that could be used for mixing and starting the tests, and the fact that larger quantities of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ caused secondary precipitation to start even sooner, it was not possible to test original extracts from larger quantities of the solid aluminate than 0.913 g per 100 ml of sugar solution. Therefore, tests with larger quantities of the compound than this were made only to observe the nature of the extracts obtained after the secondary precipitation reaction had reached completion.

With reference to the two tests with 1.37 g and 2.28 g of pure $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ per 100 ml of solution, the first showed almost complete solution within about 3 minutes, followed by initiation of precipitation at approximately 5 minutes, and the second started precipitation within approximately 2 minutes. It was not possible to determine whether or not the initial process of solution continued to completion in this latter test at the same time that the secondary process of precipitation was underway.

Use of amounts of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ in excess of 0.229 g per 100 ml of solution resulted in metastable extracts containing increasing amounts of dissolved lime and alumina, from which solid gelatinous material separated on standing. The amounts of precipitate formed from starting amounts of the aluminate of 0.229 g and 0.458 g were only slight. It is of interest to note that this "threshold" amount of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ necessary for the formation of metastable extracts is approximately the same as that for $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. The precipitation reaction for this aluminate was considerably more rapid than for either $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ or $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, one week being sufficient in all cases for complete precipitation.

The mol ratio, CaO to Al_2O_3 , of the original $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is 3.00. As indica-

ted in column 9 of Table V, the values of this ratio for the original extracts from $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ did not change within the range of amounts possible to study, due to the complete solution of the material.

With reference to column 14 of Table V, varying amounts of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ had distinct effects on the optical rotatory powers of the extracts. This is more clearly illustrated in figure 5, wherein both the rotatory power and the pH of the extracts are plotted against the corresponding amounts of total dissolved calcium oxide per 100 ml of solution. The reduction in rotatory power of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ extracts is evidence of the occurrence of hydrolysis of the compound to liberate calcium hydroxide which, in turn combines with the sugar in the solution. However, as indicated in figure 5, the reduction in rotatory power with increasing amounts of total dissolved calcium oxide is not as great for the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ extracts as for the CaO -sugar solutions, thus indicating that the aluminate was not entirely hydrolyzed within the 20-minute period that it was in contact with the sugar solution prior to measuring the rotatory power. It is probable that longer contact periods would have resulted in more complete hydrolysis (see the discussion of the secondary precipitation reaction below) but the early occurrence of the secondary precipitation reaction precluded a study of this possibility.

The pH of the original extracts, as indicated in column 12 of Table V and in figure 5, increased with increasing amounts of total dissolved calcium oxide but not to the extent noted with CaO -sugar solutions. This is again at least partially due to the limited extent of hydrolysis within the 20-minute contact period. It was not possible to determine the pH of original

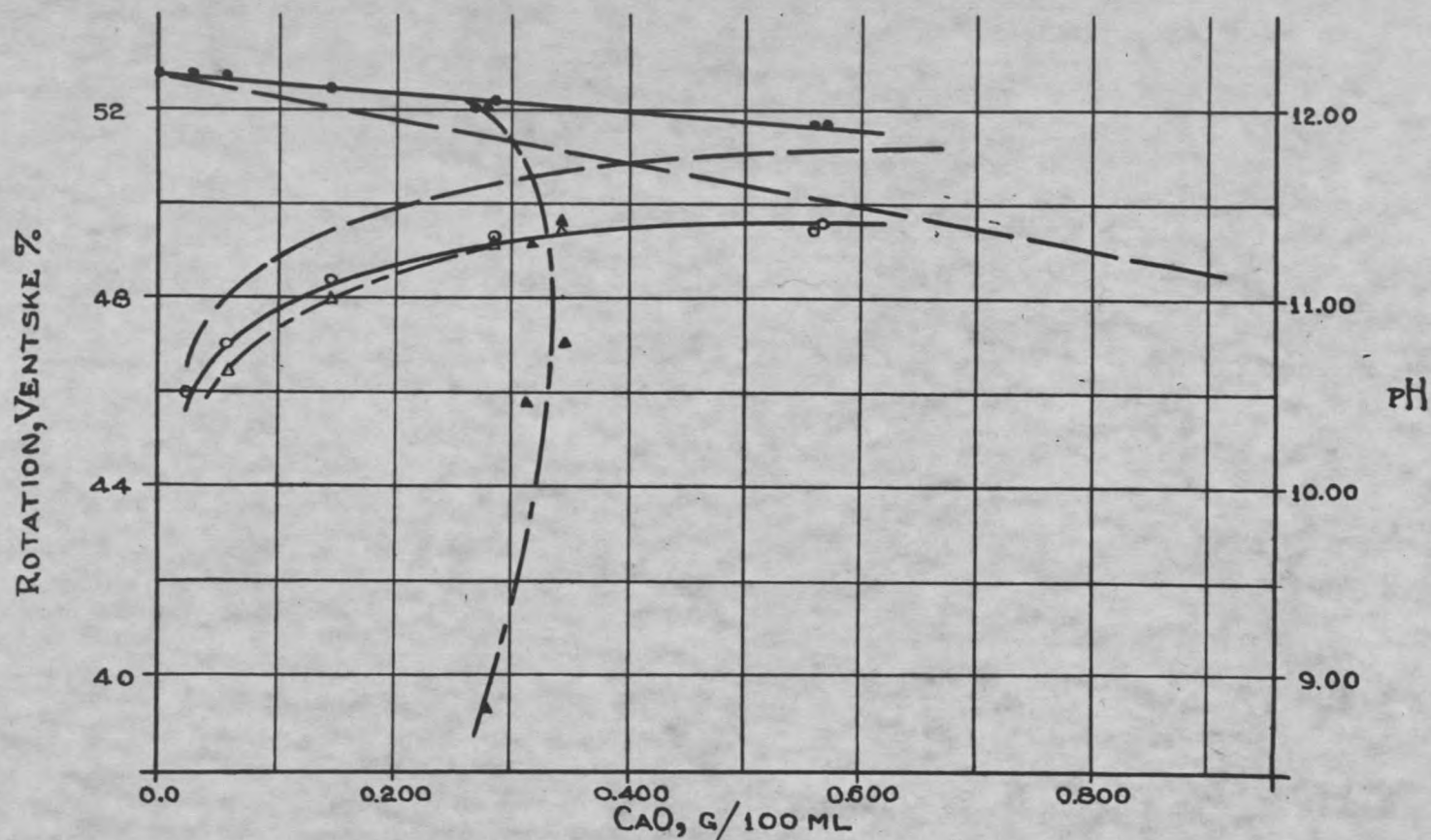


FIGURE 5

SUGAR CONTENT AND pH VS. CaO CONTENT OF EXTRACT FROM $3\text{CaO} \cdot \text{Al}_2\text{O}_3$

LEGEND: —●— ROTATION OF ORIGINAL EXTRACTS
 -■- ROTATION OF EXTRACTS AFTER PRECIPITATION
 —○— pH OF ORIGINAL EXTRACTS
 -△- pH OF EXTRACTS AFTER PRECIPITATION
 — CAO-SUGAR SOLUTION

extracts containing more than 0.913 g of total dissolved aluminate or of extracts which had reacted more than approximately 20 minutes, because of the early occurrence of secondary precipitation.

Further discussion of the significance of the pH values of the extracts will be given in Section IX-A, below.

Unlike the results obtained with extracts from $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, the extracts from $3\text{CaO}\cdot \text{Al}_2\text{O}_3$ from which solid phase separated on standing did not all approach the same composition after equilibrium was attained. As indicated in columns 6 and 8 of Table V, both the dissolved alumina and dissolved calcium oxide, in the extracts after precipitation, reach a maximum and then decrease with further increases in amounts of original $3\text{CaO}\cdot \text{Al}_2\text{O}_3$. Further, as indicated in column 10 of Table V and as illustrated in figure 6, wherein the mol ratios of the extracts before and after precipitation are plotted against the corresponding total amounts of dissolved alumina and calcium oxide, the mol ratios (CaO to Al_2O_3) of the extracts after precipitation markedly increase with increasing amounts of original $3\text{CaO}\cdot \text{Al}_2\text{O}_3$. In connection with these results, the seemingly unusual optical rotatory powers of the extracts after precipitation must also be considered. As shown in figure 5, the extracts after precipitation, upon standing for one week, showed very decided decreases in rotatory power. In fact, these decreases are much greater than can be accounted for from the amounts of dissolved calcium oxide in the solutions.

Explanation of the secondary precipitation reaction of $3\text{CaO}\cdot \text{Al}_2\text{O}_3$ extracts entails an explanation of the above-mentioned unusual reduction in rotatory power of the extracts. Referring to the rotatory powers of CaO -sugar solu-

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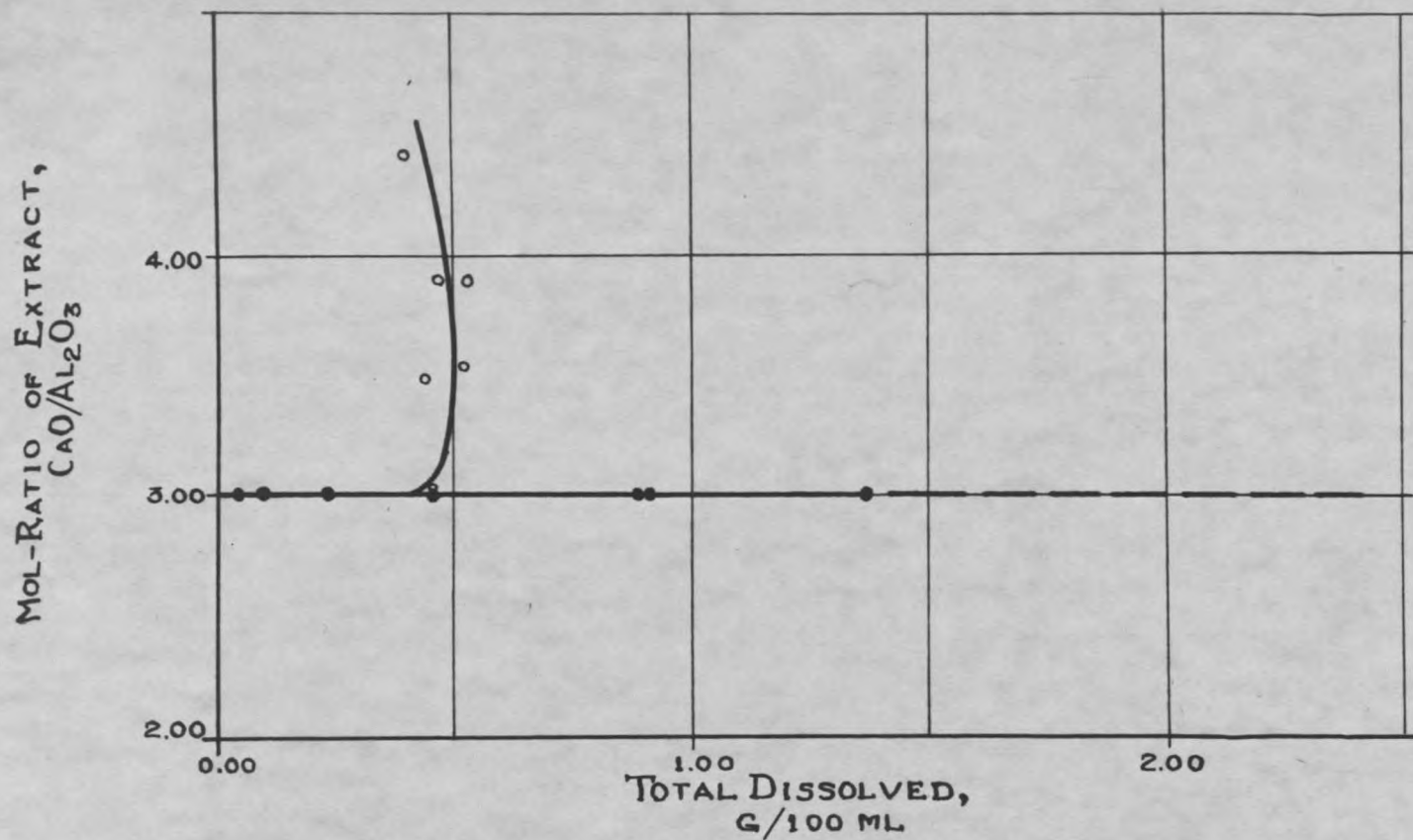


FIGURE 6

THE RATIO OF CaO TO Al_2O_3 VS. TOTAL GRAMS OF $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ DISSOLVED.

LEGEND: ● - BEFORE PRECIPITATION
○ - AFTER PRECIPITATION

tions illustrated in figure 1, attention is invited to the fact that the period of standing prior to testing was 2 hours for all CaO-sugar solutions containing less than 2.5 g. of calcium oxide. Although amounts of calcium oxide of less than 2.5 g were completely dissolved within 2 hours, it might be that a precipitate of tricalcium sucrate would have formed from them, had they been permitted to stand for a sufficiently long time. In any event, the decidedly greater reduction in optical rotatory power of the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ extracts after precipitation, as compared to that of CaO-sugar solutions, can be explained on the basis that, in the case of the extracts, sugar not only combined in solution with calcium hydroxide but also precipitated from solution as insoluble tricalcium sucrate during the 1-week period of standing. A further explanation, involving the combination of hydrated alumina and sugar at the relatively high hydroxyl-ion concentrations existing in these solutions, has some merit but lacks any experimental confirmation.

It appears evident that the calcium oxide and alumina remaining in solution after precipitation was complete were not combined with each other but that, rather, the calcium oxide was combined with sugar and the alumina was present as free dissolved aluminum hydroxide because of the relatively high hydroxyl-ion concentration. Although, as previously noted, it was not possible to determine the pH values for several of the extracts after precipitation because of the only available glass electrode being broken, it might well be that the marked reduction in amount of dissolved alumina in the case of test No. 7-a is associated with a reduction in the pH of the extract. The reduction in amount of dissolved calcium oxide in the case of the same test is probably due to an increase in the amount of lime precipitated as sucrate.

Although the precipitates from the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ extracts have approximately the same composition, even though varying considerably in amounts, this condition may be due to the limited range of concentrations of original aluminate studied. As indicated in column 11 of Table V, there is a slight increase in the mol ratio, CaO to Al_2O_3 , in the precipitates, going from original amounts of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ of 0.90 g to 1.37 g. In this connection, reference is made to figure 7, wherein the mols of dissolved calcium oxide and alumina per 100 ml after precipitation are plotted against the corresponding original amounts of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$. In this plot, one logical assumption is made; that is, in the cases of greater amounts of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ where secondary precipitation starts prior to completion of the initial solution process, it is assumed that the initial solution continues to completion while the precipitation reaction is underway. In this way, the mol ratios of precipitates have been estimated beyond the range covered by the present investigation and are shown in Table VI. It is evident from these data that the mol ratio increases to a maximum of at least approximately 2.80. However, because of the extensive hydrolysis that has been found to take place, the alumina and calcium oxide must be present in the precipitate mostly as free hydrated alumina and calcium sucrate rather than as combined calcium aluminate. A similar condition is probably associated with the well-known very deleterious action of sugar on the setting of Portland cement. A final summarization of the reactions involved between $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and sugar solution will be given in Section IX-C, below.

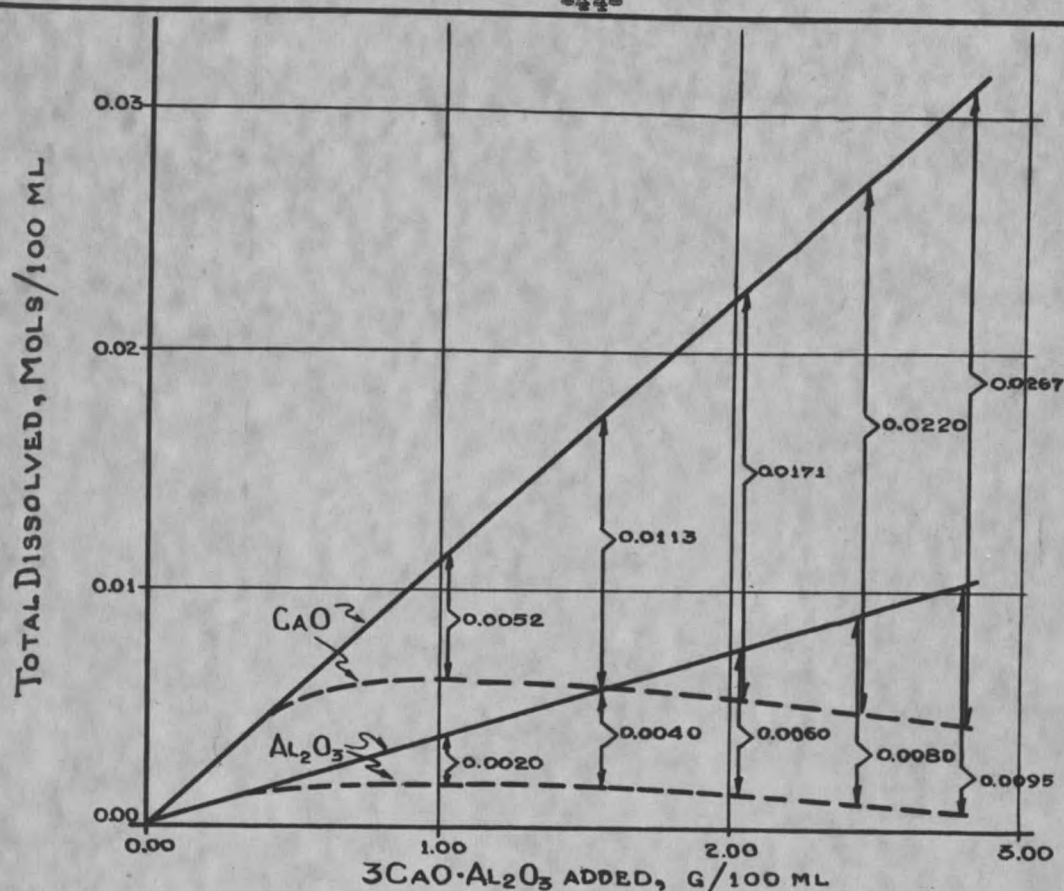


FIGURE 7
COMPARISON OF TOTAL MOLS. (CaO AND Al_2O_3) VS. GRAMS $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ added.
LEGEND: — BEFORE PRECIPITATION; --- AFTER PRECIPITATION

TABLE VI
INTERPOLATED MOL RATIOS
OF PRECIPITATES FROM $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ EXTRACTS
(From Figure 7, Above)

Total $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ added, g/100ml	Mol ratio of precipitate, $\text{CaO}/\text{Al}_2\text{O}_3$
1.93	2.60
1.57	2.83
2.02	2.85
2.45	2.75
2.80	2.81

IX. DISCUSSION OF RESULTS

A. Significance of Hydroxyl-Ion Concentration

Lersch and Bogue (5), in studies on the hydrolysis of compounds which may occur in Portland cement, considered the hydroxyl-ion concentrations of solutions obtained from treating the compounds with water as measures of the degree to which the compounds had been hydrolyzed to liberate dissolved calcium hydroxide. The fact that the anhydrous calcium aluminates, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, are formed from the relatively strong base, CaO , and the weak acid, Al_2O_3 , is considered by them to be indicative that hydrolysis of these aluminates should take place by ionization into a relatively strongly basic constituent and a weakly acidic constituent. They found that solid $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, when extracted with water over a period of several months and when the solutions were replaced by fresh water at frequent intervals, yielded solid residues consisting only of hydrous alumina, from which they deduced the complete hydrolysis of the aluminates under these conditions. However, they did not report whether the amount of alumina remaining in each case was the same as the amount of alumina in the original sample of aluminate. It is therefore impossible to determine from their published data whether the original calcium aluminates were completely hydrolyzed to calcium hydroxide and hydrous alumina or whether they were only partially hydrolyzed to more basic soluble aluminates with the excess alumina remaining behind as residue.

As previously mentioned in this paper, Wells (15) found that $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ reacted with water to form a metastable solution of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $\text{Ca}(\text{OH})_2$, from which hydrated tricalcium aluminate and hydrated alumina precipitated

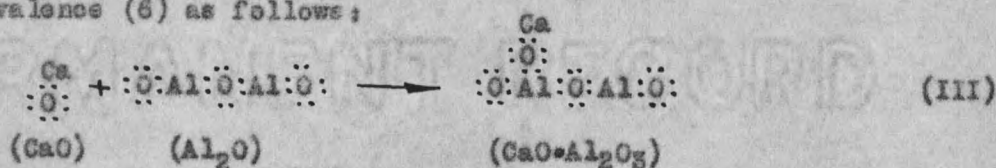
on standing. It is significant that, during the course of the secondary precipitation reaction, the hydroxyl-ion concentration of the solution phase substantially increased, even though the concentration of total dissolved lime was markedly reduced. During the secondary reaction, it was necessary that part of the lime, which originally existed in the solution in an uncombined state, combined with $\text{CaO} \cdot \text{Al}_2\text{O}_3$ to form the precipitated $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. These results indicate that the formation of relatively highly ionized calcium hydroxide and a weakly ionized acid or acid salt by hydrolysis is not the only possible explanation for the high pH values observed in such solutions.

It is believed that the above discussion lends credence to an assumption by the writer that, in those cases where both free lime and lime combined with alumina exist in solution, the free lime may well be the chief contributor to the high pH values of such solutions, but that ionization of a hydrated dissolved calcium aluminate may also be a contributing factor. In those cases where only combined lime exists in solution, as was found with sugar extracts of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ in the present investigation and as was found in the case of sugar extracts of the calcium silicates in previous unpublished work by the writer, the entire hydroxyl-ion concentration must come from ionization rather than hydrolysis of the hydrated dissolved compounds.

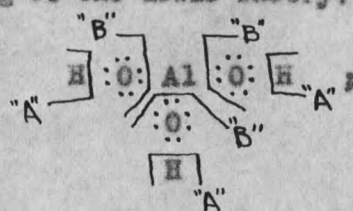
It is believed that the formation of hydroxyl ions by ionization of dissolved hydrated aluminate can be illustrated in the following manner:

Monocalcium aluminate, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, as found by Wells (15) to exist in water solutions from $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and other calcium aluminates,

is a complex molecule with the Al-atoms undoubtedly playing the coordinating roll. The formation and structure of the unit $\text{CaO} \cdot \text{Al}_2\text{O}_3$ group can be depicted according to the Lewis theory of valence (6) as follows:

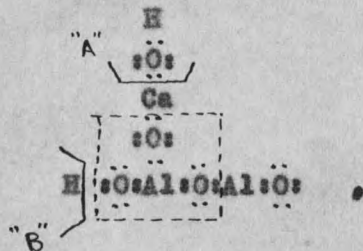


By further additions of CaO, aluminates of increasing basicity could be illustrated. However, the monocalcium aluminate structure adequately serves the present purpose if it is borne in mind that this represents only the basic structure of the compound and that each Al-atom is probably surrounded by six O-atoms in the crystal lattice. Aluminate molecules containing more than one Al_2O_3 group in the basic structure cannot be satisfactorily illustrated on paper by means of the Lewis picture. The above structure for Al_2O_3 is believed to be a reasonable representation of that compound, by reason of the amphoteric nature of its hydrate. Thus, hydrated alumina can be pictured as follows, according to the Lewis Theory:



From which H-ions and (AlO₃)-ions or (OH)-ions and Al-ions may result, depending on whether ionization takes place at "A" or "B".

The simplest hydrate of monocalcium aluminate, that is, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, can reasonably be pictured as follows:



where the hydroxyl ion from the water is attached to the Ca-atom and the hydrogen ion from the water is attached to one of the Al-atoms through an oxygen linkage.

The groups surrounded by dotted lines in the formula immediately above is the basic aluminate group and it is believed that this group must be considered as a weakly acidic constituent in such a compound. On the other hand, the $-\text{Ca} : \text{O} : \text{H}$ group immediately above it must be considered relatively strongly basic, from which it follows that ionization of this latter group at "A" to give a hydroxyl-ion must be stronger than ionization of the aluminate group at "B" to give a hydrogen ion. Therefore, if the above is a reasonable representation of actual conditions, it is to be expected that considerable hydroxyl-ion concentration can arise in such solutions simply by ionization of the hydrated aluminate.

B - Nature of Solutions of Cement Compounds.

Phillips (11) has studied the nature of solutions of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ in water and reports that a small amount of the aluminate goes into true solution but that most of the aluminate goes into colloidal solution. The results he obtained with $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ can be reasonably expected to apply in general also for other calcium aluminate solutions.

The phenomenon of the formation of gelatinous precipitates from extracts from the cement compounds studied in the present investigation, and as noted by others in the case of water solutions of the compounds, is probably associated with the at least partially colloidal nature of the extracts. The pronounced "super-saturated" condition of these extracts, can hardly be expected of entirely true solutions. Further, the speed with which the precipitates form indicates more a process of gelation or coagulation than of precipitation from true solutions. Further, the slow rate of hydrolysis noted in the original extracts from $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, which continued to take place even after clear extracts were obtained, indicated that the initial solution process was probably fundamentally colloidal in nature. Finally, the very gelatinous nature of the precipitates is indicative of colloidal processes. However, time and suitable equipment were not available during the present investigation for an adequate study of colloidal phases that might be present in the various extracts and solutions studied.

The discussions throughout this paper have been concerned chiefly with two types of reactions, first, the initial reaction of solution of the particular compound in the sugar solution and, next, the secondary reaction of

precipitation of solid phase from these extracts which were metastable. In the case of the initial reaction, there was no evidence except for the calcium oxide-sugar solutions that an equilibrium point was ever reached between solution and solid phase. This is indicative that the initial reaction of solution is primarily colloidal in nature, being more a process of colloidal dispersion or peptization than of true solution. On the other hand, in the secondary reaction of precipitation, definite equilibrium points were attained or indicated between solution and solid phase, as evidenced by the tendency of each metastable extract to go to a point of constant composition. The secondary reaction therefore appears to involve a true solution in equilibrium with a gelatinous solid phase, which would necessitate that part of the material that originally entered the extracts in the colloidal state be converted to the molecular state.

A further point which must be borne in mind while considering the possible natures of the solutions studied in the present investigation is that of calcium aluminates and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ are highly complex compounds and that their individual molecules are not limited in dimension to the sizes represented by the hypothetical formulae used in this paper. In dealing with such compounds, the matter of differentiating between true molecules and colloidal particles is purely a matter of selecting an arbitrary dimension above or below which a particular aggregation falls into one or the other class. Certainly it is to be expected that one class will exhibit to a considerable degree the same chemical properties as the other.

Based on these considerations, it is the opinion of the writer that a sharp differentiation between true solutions and colloidal solutions in the pre-

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sent investigation is neither possible nor necessary to adequately interpret the results.

C. Summarization of Reactions.

Series 1. The results obtained from tests of Series 1 with calcium oxide are of value in the present investigation primarily for comparison with results obtained in the other series. The fact that lime-sugar solutions show decreased optical rotatory power with increased concentration of dissolved lime is considered useful in determining whether or not calcium hydroxide has been liberated by hydrolysis from cement compounds in sugar solution. The phenomenon of increase in the apparent solubility of calcium hydroxide in sugar solution in the presence of increasing amounts of the solid phase should be an interesting subject for future investigation.

Series 2. Aluminum hydroxide is too weak a base to form sucrate compounds, at least at the low hydroxyl-ion concentration existing in water solutions containing only dissolved sugar and hydrated alumina.

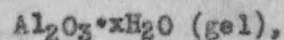
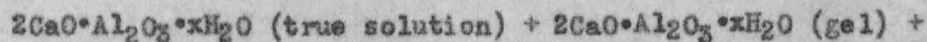
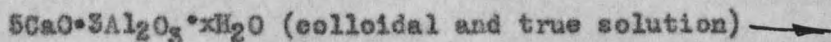
Series 3. The results obtained from tests of Series 3 with $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ indicate that the reactions involved may be represented as follows:

1. Below concentrations where secondary precipitation starts before initial solution is complete, the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ goes completely into solution without formation of calcium hydroxide by hydrolysis. The form of the initial solute can be either hydrated $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ or a more basic hydrated aluminate plus dissolves hydrated alumina, the mol ratio of which mixture is the same as that of $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$.
2. Extracts containing more than approximately 0.228 g of total dissolved calcium oxide and alumina per 100 ml are metastable or "super-saturated". Secondary precipitation takes place from such extracts without formation of calcium hydroxide by

hydrolysis. The solution phase approaches a constant composition with the final solute probably having the formula, $2\text{CaO} \cdot \text{Al}_2\text{O}_3$, or some multiple thereof.

3. The precipitate from the extracts, with a mol ratio (CaO to Al_2O_3) of approximately 4:3, is assumed to consist of a hydrated aluminate, other than $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ or $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, which is stable in the presence of sugar solution, plus possibly hydrated alumina. $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ are eliminated as possibilities because of their demonstrated instabilities. No other aluminates known to exist in the anhydrous system, $\text{CaO}-\text{Al}_2\text{O}_3$, comply with the requirements of a mol ratio of 4:3 in the precipitates without free calcium hydroxide. However, numerous other calcium aluminates, meeting the requirements of the composition of the precipitates obtained in the present case, can exist in the system, $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$. In view of the fact that the basic formula of the solute in the extracts at final equilibrium in probably $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, a similar basic formula for the calcium aluminate in the precipitates is logical. In this case, the precipitate also contains hydrated alumina.

4. The following equation is believed to schematically represent the reactions involved:



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where "x" denotes any undetermined number of molecules of water of hydration.

5. In the case of extracts from $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ alone, hydroxyl-ion concentrations are not reached which are sufficiently high to cause hydrolysis of the compound to the extent of liberation of calcium hydroxide. The maximum pH values reached in the present investigation accomplished only the hydrolysis of the compound to a more basic aluminate plus hydrated alumina. However, this does not preclude the possible hydrolysis of this compound to the extent of liberation of free calcium hydroxide in cases where higher pH values than 11.05 obtain. Such cases as mixtures of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, alkalis, or large amounts of free calcium oxide, or the case of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ in Portland cement, might result in complete hydrolysis of the $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ by sugar solution; however, these possibilities were not investigated.

Series 4. Results obtained from investigations of the reactions between sugar solution and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ are not sufficiently conclusive, because of uncertainties as to the true composition of the material used, to permit of summarization. Under these conditions, the results are of value only in connection with possible future studies of these reactions.

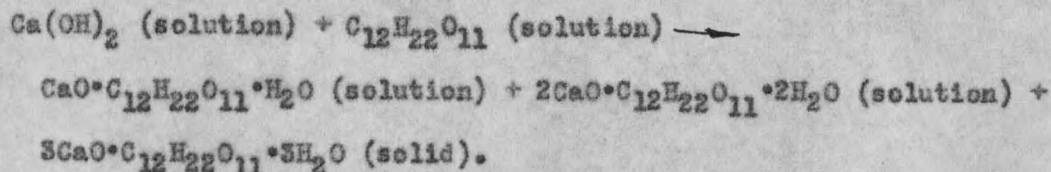
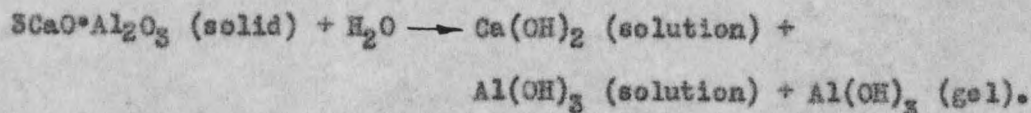
Series 5. The results obtained from tests of Series 5 with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ indicate that the reactions involved may be represented as follows:

1. Amounts of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ up to 2.28 g per 100 ml went complete-

ly into solution prior to initiation of secondary precipitation (within two minutes) and it is logically assumed that initial solution of larger amounts of the compound would go to completion at the same time that secondary precipitation is underway.

2. Hydrolysis of the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ to the extent of liberation of calcium hydroxide starts immediately upon entry of the compound into solution, the calcium hydroxide then combining with dissolved sugar to form sucrares.
3. Extracts containing 0.229 g or more of total dissolved calcium oxide and alumina per 100 ml are metastable or "super-saturated". Secondary precipitation progresses more rapidly than in the case of extracts from $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$. The composition of the solution phase at equilibrium is dependent on the amount of starting material, the amounts of dissolved alumina and calcium oxide in the extracts at equilibrium going to a maximum and then decreasing with increasing starting amounts of the compound. The final solutes in the extracts probably consist of free aluminum hydroxide plus calcium hydroxide combined with sugar as sucrares.
4. The precipitates from the extracts are assumed to consist chiefly of hydrated alumina plus tricalcium sucrares. However, the possibility of the existence of a solid calcium aluminate more stable with respect to the final extracts than calcium sucrares was not investigated.

5. The following equations are believed to schematically represent the reactions involved:



6. The high reactivity of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ with sugar solution is considered to be due to the high hydroxyl-ion concentrations resulting in the extracts. The reverse of this is not the case, because the secondary precipitation reactions in those tests where the pH values were measured caused no change in hydroxyl-ion concentration. In those tests where the pH values of the final extracts could not be measured because of the broken glass electrode, there was evidence to indicate that the hydroxyl-ion concentrations decreased rather than increased.

X. ACKNOWLEDGEMENTS

The writer wishes to acknowledge the valuable assistance and advice given throughout the course of this investigation by Dr. Ray Woodruff of the Staff of the Chemistry Department at Montana State College.

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