

SULFOALUMINATES OF CALCIUM AS STABLE AND METASTABLE PHASES.

AND A STUDY OF A PORTION OF THE FIVE-COMPONENT SYSTEM

$\text{CaO-SO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-H}_2\text{O}$ AT 25°C .

GEORGE LAWRENCE KALOUSEK

Chem
LD
3231
.M70d
Kalousek,
G.L.
Folio

Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy

1941

CHEMISTRY LIBRARY
UNIVERSITY OF MARYLAND
UNIVERSITY OF MARYLAND
UNIVERSITY OF MARYLAND

UMI Number: DP70420

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI DP70420

Published by ProQuest LLC (2015). Copyright in the Dissertation held by the Author.

Microform Edition © ProQuest LLC.

All rights reserved. This work is protected against unauthorized copying under Title 17, United States Code



ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. M. S. Haring for his helpful interest and cooperation during the progress of this investigation. He is also indebted to Dr. L. S. Wells of the National Bureau of Standards for collaboration, and to Mr. P. M. Koburdie for X-ray determinations.

TABLE OF CONTENTS

- I. INTRODUCTION
- II. PROCEDURE
 - A. Starting materials and methods of chemical analysis
 - B. Experimental
- III. SULFOALUMINATES AS STABLE AND UNSTABLE PHASES
- IV. PORTION OF THE FIVE-COMPONENT SYSTEM $\text{CaO}-\text{Al}_2\text{O}_3-\text{SO}_3-\text{Na}_2\text{O}-\text{H}_2\text{O}$ at 25° C.
 - A. Method of study (theoretical)
 - B. Procedure
 - C. Solid solution series: $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 17\text{H}_2\text{O}\cdot 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$
 - D. Results and discussion of boundaries
 - 1. Boundary: $\text{Ca}(\text{OH})_2-\text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$ -trisulfate
 - 2. Boundary: $\text{Ca}(\text{OH})_2$ -trisulfate-monosulfate
 - 3. Boundary: $\text{Ca}(\text{OH})_2 \text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$ -monosulfate
 - E. Interpretation of data and application
- V. SUMMARY
- VI. BIBLIOGRAPHY

I. INTRODUCTION

The alumina bearing compounds in portland cements are generally believed to react under a variety of conditions with aqueous solutions of sulfates to form the sulfoaluminates of calcium. Two of these double salts having the compositions,



and



have been considered to be the products formed in hydrating portland cements. The double salt containing the equivalence of three moles of CaSO_4 , and known variously as "cement bacillus," "high form," Ektungite, and trisulfate was discovered by Candlot (1). The exact $\text{CaO}:\text{Al}_2\text{O}_3:\text{CaSO}_4$ molar ratio was later established by Michaelis (2), Klein and Phillips (3), and many others. The moles of hydrate water are variously given as 31 to 33. Lerch, Ashton and Bogne (4) prepared, and determined the composition and crystallographic properties of the double salt containing the equivalence of 1 mole of CaSO_4 . This double salt is known as the "low form" or monosulfate. Later Nylius (5) and Forsen (6) observed the same composition and crystallographic properties, but Forst (7) was unable to obtain the molar composition required for the monosulfate. A difficulty inherent in the preparation of this product has been its metastable nature. Thus, Nylius (5) was unable to prepare the compound from aqueous solutions of $\text{Al}_2(\text{SO}_4)_3$ and $\text{Ca}(\text{OH})_2$, however, no difficulty was experienced if the $\text{Al}_2\text{O}_3:\text{SO}_3$ molar ratio was maintained at unity in the starting mixture. Jones (8) and Forsen (6) observed that a high lime concentration was essential for the formation of the monosulfate.

Koyenagi (9), and Eogne and Leroh (10) expressed the view that the trisulfate was the product formed in hydrating cements. Forese (11), by shaking 0.3 g. of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ in one liter of a saturated $\text{Ca}(\text{OH})_2$ - CaSO_4 solution for 90 days, obtained a product which analyzed for CaO , Al_2O_3 and SO_3 in molar proportions approximating the composition of the monosulfate, and believed that for the stated conditions the monosulfate was formed. However, the product was not identified microscopically. cores of unreacted $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ being present. Further evidence by the same author, to substantiate this observation, was deduced from the amounts of CaSO_4 to combine with known amounts of alumina in cement pastes permitted to harden for 28 days in moist air. In these tests the excess of added CaSO_4 was extracted, and the $\text{Al}_2\text{O}_3/\text{SO}_3$ molar ratio which was computed from the data was found to be close to unity. F. Schlapfer (12) observed, microscopically, that the monosulfate was formed around grains of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ which had been mixed with 60 percent of water and 5 and 10 percent of gypsum; the trisulfate, however, was formed if the gypsum content was 20 or 40 percent. Jones (13), in a comprehensive study of the quaternary system: $\text{CaO}-\text{Al}_2\text{O}_3-\text{SO}_3-\text{H}_2\text{O}$ at 25°C ., concluded that the trisulfate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$, was the only quaternary compound formed.

Since the American cements contain, on the average, about 0.75 percent of $\text{K}_2\text{O} + \text{Na}_2\text{O}$ which dissolve more or less readily (14) (15), appreciable concentrations of NaOH and KOH may eventually be present in the aqueous phase of hydrating cements. The effects of NaOH on the stability of the sulfoaluminates has not been investigated. However, Leroh, Ashton and Eogne (4), by placing the double salts in a 3 percent NaOH solution, observed that both were apparently stable.

The sulfoaluminates are of interest with regards to theories of the early reactions of setting of cement pastes, and from the standpoint of the disintegration of concrete in sulfate bearing water. Also a consideration of the above findings of the different investigators suggests that the monosulfate may be formed as a metastable product which may persist as such for indefinite periods of time, finally however, converting to the trisulfate. It is interesting to note in this connection that various specifications limit the SO_3 in cements to above 2.0 percent. This limitation is predicated on observations by Bates (16) and others, that larger additions of the sulfates of calcium cause undue expansions in hydrating cements. The cause of this, although believed, (17) to be due to the formation of presumably the trisulfate, may equally as well be due to the early formation (about 24 hours (11)) of the monosulfate with a later conversion of this phase to the trisulfate. This conversion is theoretically accompanied by a positive volume change. From this standpoint the formation of the monosulfate with a later change to the trisulfate in hydrating cements may result in undesirable volume changes.

In order to understand more fully the behavior of these double salts as probable metastable and stable products in hydrating cements, an investigation concerned with their formation and the effects of $NaOH$ on their equilibria was carried out at the National Bureau of Standards.

II. PROCEDURE

A. Starting Materials and Methods of Chemical Analysis.

The starting materials used in this study were aqueous solutions of $\text{Ca}(\text{OH})_2$, NaAlO_2 , (or KAlO_2 only in portion of study, not alternately with NaAlO_2), $\text{Al}_2(\text{SO}_4)_3$, NaOH and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and solid $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$.

Since the chemical methods of analysis for the preparatory compounds were the same as those used for the aqueous and solid phases, they are outlined at this time. Calcium was precipitated as the oxalate and weighed as CaC_2O_4 (18). In the event that the solution for analysis contained more than traces of Na_2CO_3 or SO_3 , the presence of double precipitation was observed. Alumina was precipitated as $\text{Al}(\text{OH})_3$ (18), ignited at 1200°C ., and weighed as Al_2O_3 . When the hydrous alumina precipitate was large (0.02 g. or more) and the mother solution contained sulfate, the solid product was dissolved and reprecipitated. The sulfate was precipitated and weighed as BaSO_4 according to method B (given by Hillebrand and Lundell (18)), with the exception that the precipitate in contact with the aqueous phase was permitted to age overnight at room temperature. The OH^- concentration was determined by titration using gravimetrically (as AgCl) standardised HCl . Methyl red served as indicator (19) (20) in solutions containing $\text{Ca}(\text{OH})_2$ as the base alone, and in the presence of $\text{NaOH} + \text{Ca}(\text{OH})_2$ up to a total OH^- concentration of 0.10 equiv./l. Solutions above this OH^- concentration were titrated using phenolphthalein as indicator. Errors would be introduced by the use of either indicator for all solutions, but by the above somewhat arbitrary division the errors were minimized, and from the standpoint of this study are entirely negligible. Solutions containing SiO_2 (as

contaminant) were dehydrated in the presence of HCl. The precipitated residue was ignited, treated with H_2SO_4 and HF, re-ignited, and the loss in weight reported as SiO_2 .

Platinum crucibles were used for igniting CaO , Al_2O_3 and SiO_2 . Porcelain crucibles for $BaSO_4$ and ignition losses.

$Ca(OH)_2$ in aqueous solution was prepared from CaO , which was obtained by igniting $CaCO_3$ at $1000^\circ C.$ for 3 hours. The aqueous solution, after filtration to remove excess $Ca(OH)_2$, was analyzed gravimetrically and titrimetrically for CaO in the first preparation. Results by the two methods checked to 1 or 2 parts per 1000, and therefore, all subsequent determinations of CaO in the preparatory solutions were titrimetric.

Pure gypsum was prepared according to a method (21) used previously at this Bureau, namely, by mixing 10 percent solutions of o. p. $CaCl_2$ and H_2SO_4 . The water content of the properly washed and dried product was 21.12 percent, being slightly higher than the theoretical of 20.93 percent. However, the amount of the free water remained constant over a period of time, and therefore, was of no consequence. The product was free of chloride. The gypsum, aside from the water content, was analyzed primarily to check the accuracy of the procedures for CaO and SO_3 . Separate samples were used for CaO and SO_3 in the determinations, and the results in percentages are reported in the following table.

Theoretical*	Determination No.				
	1	2	3	4	5
CaO	32.49	32.46	32.43	-	-
SO_3	46.99	45.64	45.70	45.55	46.48
					46.52

*For gypsum containing 21.12% H_2O .

CaO was determinable with an accuracy of 1 part (or less) per 1000. However, the SO_3 in determinations 1, 2 and 3 was far too low.

In these, the BaCl_2 was added slowly during precipitation. Determinations 4 and 5 were identical to No. 1, 2 and 3, except that the BaCl_2 solution was added as rapidly as possible. The results for the latter determinations, although slightly high, 2 parts per 1000, were considered satisfactory, and accordingly the BaCl_2 solution was added rapidly in subsequent determinations. No difficulty was experienced during filtration.

A c. p. grade of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, containing 0.1 percent free H_2SO_4 according to the manufacturer's analysis, was dissolved in distilled water. Separate aliquots of the solution were analyzed, respectively, for Al_2O_3 and SO_3 . The results in moles SO_3 per mole Al_2O_3 are as follows:

Determination No.	1	2	3	4
$\text{SO}_3/\text{Al}_2\text{O}_3$	3.003	3.003	2.970	2.950

The Al_2O_3 was determinable on duplicate aliquots to 1 part per 1000.

In determinations 1 and 2 the BaCl_2 solution was added slowly, and in 3 and 4, rapidly to the $\text{Al}_2(\text{SO}_4)_3$ solution. Results from determinations 1 and 2 were considered to be closer to the true value, and are used in all computations being, respectively, 4.156 g. Al_2O_3 and 9.300 g. SO_3 per liter.

Potassium aluminate was prepared by slowly adding pure metallic aluminum in excess to a 10 percent aqueous solution of KOH which had been freed of K_2CO_3 . The system was cooled and protected against CO_2 of the air. The solution after reaction was filtered, diluted with distilled water, and stabilized with a slight excess of KOH . Analysis in triplicate of 10.00 ml. aliquots showed, respectively, 0.0340, 0.0339, 0.0340 g. Al_2O_3 .

Sodium aluminate was prepared by the above method, the solution showing, on duplicate samples, 0.1053 and 0.1055 g. Al_2O_3 per 10.00 ml. aliquot.

A saturated solution of e. p. NaOH was placed in a ceresin lined flask, and at the end of 10 days was decanted through a G 3 Jena glass crucible. No perceptible loss in weight of the glass crucible occurred. Analysis of various lots of solutions for silica showed 0.10 to 0.14 percent SiO_2 of the anhydrous product. The aqueous solution, diluted to 2.5 N with CO_2 -free water, was stored in a ceresin lined flask.

B. Experimental.

Mixtures to yield the expected solid phases were prepared by carefully aliquoting the aqueous solutions, or weighing the solids, in desired proportions. CO_2 -free water was used for dilution purposes. In all preparations the aqueous solution of alumina was introduced as the last component, the final volume of the mixtures being 1000 ml. The preparations in well-stoppered pyrex flasks were stored in an air-bath thermostat maintained at $25 \pm .1^\circ \text{C}$. To facilitate the attainment of equilibrium the mixtures were frequently shaken (generally once a day).

The course of reaction was followed by microscopic examination of small portions of the solid phases, which were withdrawn from the flasks from time to time. These precipitates were separated from the aqueous phase by filtration through a G 3 Jena glass crucible, then washed successively with alcohol and ether, and finally dried over anhydrous CaCl_2 for about 18 hours. The crystallographic properties best suited for the identification of the solid phases were the indices of refraction and the character of elongation. Since other phases in addition to the sulfoaluminates had to be considered, their crystallographic properties, as compiled by Mylius (5), and others as designated in the following table, are presented at this time.

		Character of Elongation
Trisulfate	$\omega = 1.469, \quad \epsilon = 1.459$	Negative
Monosulfate	$\omega = 1.504, \quad \epsilon = 1.485$	Positive
$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$	$\omega = 1.577, \quad \epsilon = 1.500$	Positive
$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$	$\omega = 1.528, \quad \epsilon = 1.503$	Positive
$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	1.604 (isotropic)	-
$\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ (17)	1.47-1.49 (isotropic)	-
$\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ (18)	1.525 (isotropic)	-
$\text{Ca}(\text{OH})_2$ (22)	$\omega = 1.574 \quad \epsilon = 1.545$	-

An interesting observation with regard to the sulfoaluminates was the crystallization of the monosulfate on the walls of the flask, whereas the trisulfate showed no tendency to adhere to the glass. Since a quantitative transfer of the trisulfate was possible under such circumstances, advantage was taken of this for identification purposes as discussed later.

The mixtures were filtered after 4 to 12 weeks, except in a few instances as noted in the text. Because the attainment of equilibrium is often very slow, the ages at which the various mixtures were filtered are reported in the tables along with other pertinent data.

A filtering apparatus, to provide protection against the CO_2 of the atmosphere and to facilitate the transfer of the precipitate from the reaction flask to the glass crucible, was set up as shown in figure 1. The supernatant solution, when swirled by imparting a slight rotary motion (in the horizontal plane) to the flask, served as the wash liquid. The connection to the vacuum pump was provided with a pet-cock so that the suction flask after partial evacuation could be closed, thus preventing serious evaporational losses in the numerous instances when

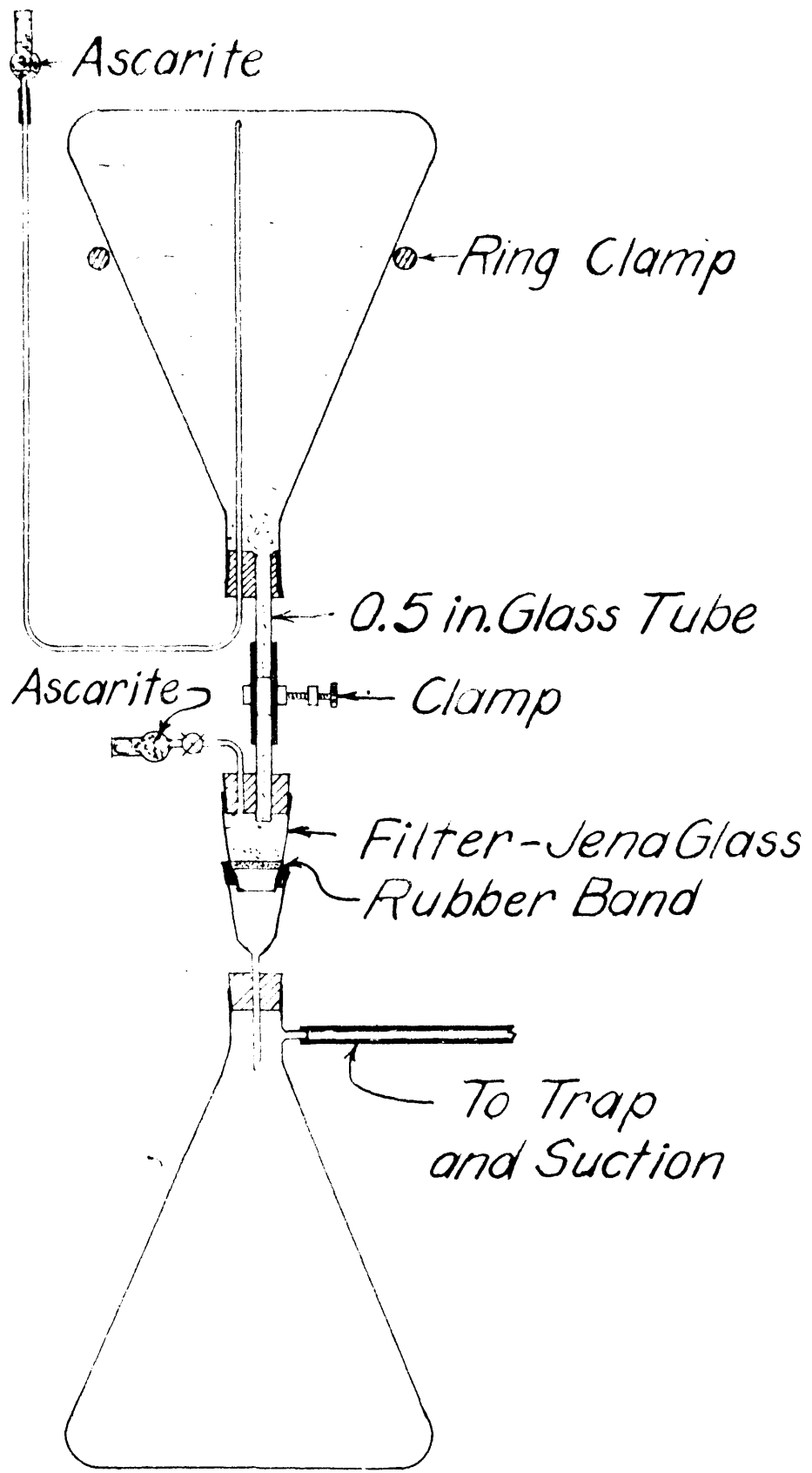


Fig. 1. Filtration Apparatus.

filtration was slow. The maximum time to filter one liter of the mixture was six hours. After filtration was completed, the precipitate was thoroughly washed four times with alcohol, then four to six times with ethyl ether, and finally dried over anhydrous CaCl_2 to constant weight. Since the theoretical mass, assuming one solid phase, could be computed from the amounts of Al_2O_3 to react, the observed mass of the precipitate was used for identification purposes in a number of instances when the crystals were sub-microscopic in size.

The aqueous phase was aliquoted as follows for chemical analysis: 500 ml. for Al_2O_3 , the filtrate of which (after the Al_2O_3 determination) was used, totally or in part, for CaO ; and 250 ml. or less for CO_2 . The solutions, after acidification, were evaporated down to 100 ml. in preparation for the analysis. The OH^- concentration was determined immediately after filtration.

III. SUBPOLYMERIZES AS STABLE AND METASTABLE PRODUCTS.

The experiments in this portion of the investigation were concerned primarily with (1) the persistence of the monosulfate as a metastable phase and its solubility, (2) the solubility of the trisulfate, (3) the coexistence of the trisulfate and a calcium aluminates, and (4) the precipitation of the monosulfate as a metastable phase from solutions containing excess sulfate.

The data are reported in Table I. The compositions of the starting mixtures, as grams per liter of CaO , Al_2O_3 and SO_3 , are given in columns 2, 3, and 4 respectively. In column 5 is reported the ages at which the mixtures were filtered. Columns 6, 7, 8, and 9 give the composition of the aqueous phase as OH^- (equiv./l.), CaO , Al_2O_3 , and SO_3 (g./l.) respectively. The molar composition, $\text{CaO}:\text{Al}_2\text{O}_3:\text{SO}_3$, of the precipitates is reported in column 10. The solid phases and the amounts of these estimated microscopically are listed in column 11. In these mixtures the total of $\text{Ca}(\text{OH})_2$ and CaSO_4 . The Al_2O_3 was introduced as KAlO_2 and the final aqueous phase, therefore, contains some KOH . This amounts to about 0.0029 equl. of OH^-/l .

The composition of the solid phases were generally computed from the known amounts of the constituents in the preparatory and final solutions. The results of analysis of the solid phases as required to supplement the computed ratios are given in the text.

Mixtures of series A were prepared so that the $\text{Al}_2\text{O}_3:\text{SO}_3$ molar ratio in the preparatory solutions was nearly equal to unity, and the $\text{Ca}(\text{OH})_2$ was decreased from near saturation to 0.2 g. CaO/l . As regards the concentration of SO_3 , the solutions after reaction simulate those of the aqueous phase of hydrating cements, except for the absence of

Table 1. Sulfoaluminates as stable and metastable phases.

1	2	3	4	5	6	7	8	9	10	11	Phases in precipitate	
											Precipitate	Molar Ratio
Starting composition in g./l.		Weeks		Reacted Composition of Aqueous Phase		Gross per liter		Precipitate		Molar Ratio		
CaO	Al ₂ O ₃	SO ₃	CH ⁻ equiv./l.	CaO	Al ₂ O ₃	SO ₃	CaO	Al ₂ O ₃	SO ₃	CaO	Al ₂ O ₃	SO ₃
A1	1.180	0.0840	0.0667	6	0.0372	0.986	0.0006	0.0025	4.24	1.00	.98	Monosulfate + 1-5% Trisulfate
2	1.010	"	"	6	0.0312	.871	0.0004	0.0034	4.11	"	.96	" + 1%
3	.899	"	"	6	0.0253	.639	0.0003	0.0044	4.48	"	.95	" + 5-15%
4	.669	"	"	6	0.0195	.493	0.0022	0.0089	3.91	"	.86	" + 1%
5	.556	"	"	6	0.0161	.388	0.0042	0.0136	3.83	"	.85	" (only phase)
6	.486	"	"	6	0.011	.246	0.0274	0.0175	4.14	"	1.00	" + trisulfate
7	.272	0.0892	0.0656	6	0.009	.188	0.0580	0.0174	6.2	"	2.5	Trisulfate (only phase)
8	.159	"	"	6	-	.159	0.0892	0.0656	-	"	-	No precipitate
B1	1.411	0.0840	0.0959	4	0.0776	1.120	0.0006	0.200	6.32	1.00	2.99	Trisulfate
2	1.241	"	"	4	0.0315	.96	0.0004	.20	"	"	"	"
3	1.071	"	"	4	0.0256	.79	0.0002	.20	"	"	"	"
4	.901	"	"	4	0.0196	.62	0.0002	.20	"	"	"	"
5	.731	"	"	4	0.0137	.44	0.0002	.20	"	"	"	"
6	.617	"	"	4	0.0080	.24	0.0004	.20	"	"	"	"
7	.502	0.0892	0.0919	3	0.0604	.233	0.0008	0.202	5.96	1.00	2.96	Trisulfate
8	.445	"	"	3	0.0403	.131	0.0018	0.205	5.94	1.00	2.90	"
C1	1.296	0.0840	0.232	7	0.0372	1.02	0.0004	0.09	"	"	"	Trisulfate
2	1.361	"	.325	7	0.0372	1.09	0.0002	.12	"	"	"	"
3	1.459	"	.464	7	0.0371	1.18	0.0006	.26	"	"	"	"
4	1.588	"	.650	7	0.0369	1.31	0.0006	.45	"	"	"	"
5	1.751	"	.832	7	0.0368	1.47	0.0004	.63	"	"	"	"
6	1.881	"	1.067	7	0.0368	1.60	0.0002	.87	"	"	"	"
7	1.195	"	1.248	7	0.0377	.851	0.0002	1.152	"	"	"	"
SO ₃ as H ₂ SO ₄												
D1	1.134	0.0840	0.0800	7	0.0374	"	"	"	"	"	"	(a) 70-90%
2	1.226	0.0840	.1220	12	0.0370	.995	0.0020	0.0008	5.11	1.00	2.04	Trisulfate + unidentified phase
3	1.305	.1680	.2440	12	0.0349	.805	0.0030	0.0010	5.55	1.00	2.05	"
4	1.386	.2520	.3960	12	0.0330	.663	0.0043	0.0011	5.23	"	2.02	"
5	1.466	.3360	.5280	12	0.0311	.524	0.0084	0.0012	5.22	"	2.04	"
6	1.548	.4200	.6600	12	0.0291	.386	0.0116	0.0015	5.15	"	2.04	"

(a) 3CaO·Al₂O₃·6H₂O + (a calcium aluminate)

large amounts of alkali hydroxides after the gypsum had been more or less completely removed (11) as the sulfoaluminate.

Examinations of these solid phases at various times after separation showed that the monosulfate formed in all mixtures, and persisted as such in A1 to A5 for about 4 weeks before conversion to the trisulfate had started. The precipitate in A5 showed no indication of conversion even at 6 weeks, whereas, the monosulfate in A6 and A7 began converting to the trisulfate and monosulfate of mean index of 1.51-1.52 at, respectively, 2 weeks and 2 days. The conversion in A7 was completed in about a day, but in A6 the rate of conversion of the monosulfate was very slow.

The computed compositions of the solid phases reflect the presence of two phases, the estimated amounts of which are given in column 10. The fact that no second solid phase appeared in mixture A5 and the mean index of the solid phase present in this mixture and other mixtures of series A was 1.51-1.52, somewhat higher than that of the monosulfate, necessitated a careful check of the results. Direct analysis of the precipitate gave the composition, 3.90 CaO:1.00 Al_2O_3 :0.82 SO_3 :11.5 H_2O , which is in good agreement with the computed results. In an attempt to account for the fractional molar ratio, a duplicate mixture was prepared, but filtered 5 minutes after preparation. Direct analysis of this solid phase gave the following composition: 3.90 CaO:1.00 Al_2O_3 :0.85 SO_3 :11.5 H_2O which agrees, within limit of error, with the above. The monosulfate (4) was prepared simultaneously with the latter preparation, showing the correct molar ratio (3.96 CaO:1.00 Al_2O_3 :0.99 SO_3), and also having the refractive indices reported in literature. Apparently the product formed in series A is not the monosulfate. Since

similar discrepancies in the molar ratios were observed later, precipitate A5 will be considered at that time.

The results of this series show that a product of a slightly different composition than the monosulfate is formed and persists, as presumably a metastable phase, for relatively long periods of time.

The Al_2O_3 found in solution may be considered as approximating the solubility of the new product, which is referred to as the monosulfate. The g. of Al_2O_3 /l. are plotted against corresponding amounts of CaO in g./l. in figure 2. The solubilities of the sulfoaluminates are compared in the following section.

Mixtures of series B were prepared for the purpose of determining the solubility of the trisulfate in contact with solutions containing 0.20 g. SO_3 as $CaSO_4$ and decreasing amounts of $Ca(OH)_2$. The trisulfate was the only solid phase found microscopically.

All filtrates were analyzed carefully for Al_2O_3 , complete analysis being made of filtrates B1, B7 and B8. Computation of the composition of precipitate B1 showed that an excess of CaO was removed from solution. Also it was observed that the mass of precipitates B1 to B6 was about 1 to 2 percent higher than the theoretical. The presence of a second solid phase was indicated, and analysis of precipitates B7 and B6, which showed molar ratios of, respectively, 5.90 CaO:1.00 Al_2O_3 (2.80 SO_3 and 5.30 CaO:1.00 Al_2O_3 :2.78 SO_3 , suggested SiO_2 from the pyrex glass as a contaminant. This constituent during analysis would be counted largely as Al_2O_3 , which is the reference component in the computation of the molar ratios. In order to ascertain the extent of this contaminant and its manner of combination, precipitates B1, B7, and C5 (the latter, although discussed later, was included because its

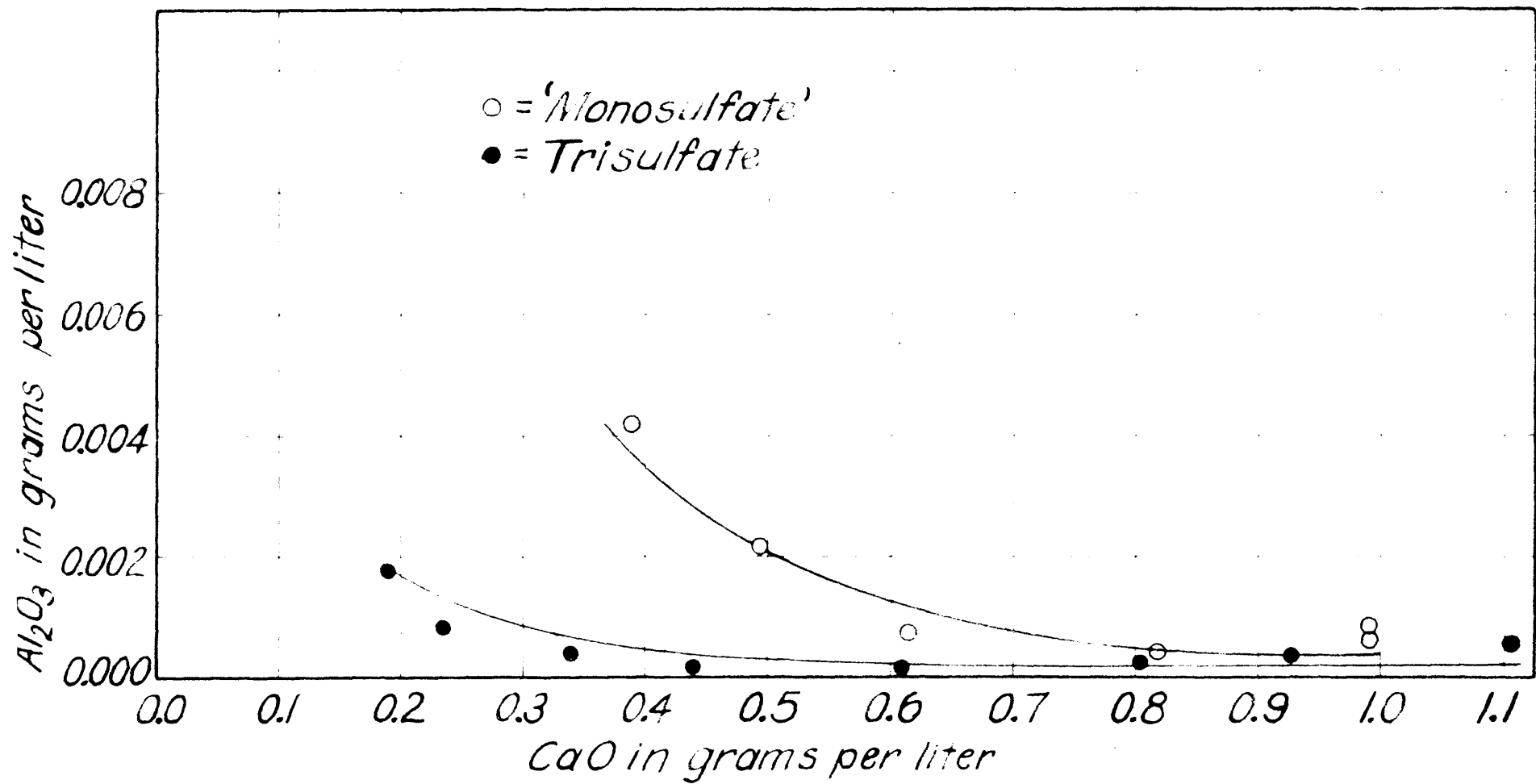


Fig. 2. Solubility of the sulfoaluminates of calcium.

mass was about 4 percent higher than the theoretical) were carefully analyzed. Appreciable amounts of SiO_2 were found in B1 and C5, but the molar composition of these precipitates was still not correct as an excess of CaO was present. It was assumed that $2\text{CaO} \cdot \text{SiO}_2 \cdot 4\text{H}_2\text{O}$ (11) precipitated as an independent phase, and the molar composition of the trisulfate was computed from the analytical results corrected for the amount of CaO and H_2O required for the assumed compound. The results, respectively, in percentages and molar compositions are as follows:

	Percentage			Molar Composition		
	B1	B7	C5	B1	B7	C5
SiO_2	0.98	0.10	0.76	-	-	-
Al_2O_3	8.71	8.20	7.93	1.00	1.00	1.00
CaO	27.60	27.00	27.67	5.96	5.95	6.02
SO_3	19.10	19.44	19.19	2.96	3.02	3.07
H_2O^*	44.71	45.26	44.45	20.7	21.2	21.3

* H_2O taken by difference.

The computed compositions, on the assumption that $2\text{CaO} \cdot \text{SiO}_2 \cdot 4\text{H}_2\text{O}$ is formed, are within reasonable limits. It is interesting to note that CaO- Al_2O_3 - SiO_2 combinations (29) are precluded because the withdrawal of $\text{Al}_2\text{O}_3 + \text{SiO}_2$ from the reported amounts of Al_2O_3 would badly distort the molar ratio for the trisulfate. It appears, therefore, that the trisulfate is stable against solutions containing SiO_2 in equilibrium with $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$. This is reflected by the very low solubility of the trisulfate.

The solubility of this compound, as grams Al_2O_3 per liter, are plotted against corresponding amounts of total CaO in g./l. in figure 2. Although the solutions contained 0.20 g. of SO_3 as CaSO_4 per liter, the common ion does not have a detectable effect on altering the solubility.

as the present writer (24) had observed previously that in the absence of excess SO_3 in solution, 200 ml. aliquots of lime solution, in contact with the trisulfate, analyzed for 0.0000 g. Al_2O_3 over a range of $Ca(OH)_2$ concentration extending from 0.4 to 0.9 g. CaO/l. Lerch, Ashton and Eogne (4) reported "none" for Al_2O_3 originating from the trisulfate placed in saturated $Ca(OH)_2$ solution; and Forsen (11) reported values of 0.0005, 0.0000 and 0.0000 g. Al_2O_3 /l. for the solubility of this compound in a saturated $Ca(OH)_2$ - $CaSO_4$ solution. As can be seen from figure 2 and Table 1, the trisulfate is highly insoluble in solutions of varying $Ca(OH)_2$ concentrations.

The solubilities of the two sulfoaluminates are given in figure 2. It is seen that these two double salts approach the same solubility in solutions nearly saturated (1.1 g. CaO/l.) with respect to $Ca(OH)_2$. Although the values for the "monosulfate" represent only an approximation of the solubility of this compound because of the presence of the trisulfate, the trend manifested, nevertheless, indicates that the solubilities of the two forms at the higher CaO concentrations are of the same order. This may account in part for the slow conversion of the monosulfate to the trisulfate.

Mixtures of series C were prepared so that the CaO concentration, as $Ca(OH)_2$, would be near saturation after reaction. The $CaSO_4$ concentration was progressively increased up to near saturation. Because the solutions containing the high SO_3 concentrations approximate, in composition, the aqueous phase of hydrating cement pastes, the products formed in this region are of interest to theories of early setting. Thus, Poller (15) claimed that $4CaO \cdot Al_2O_3 \cdot 13H_2O$ was formed when early setting of cement pastes was successfully retarded. Forsen (11) believed that the formation of the monosulfate accounted for retardation of early

setting. The crystals formed in solutions containing the higher lime and gypsum concentrations are extremely small.

The mixtures in series C were filtered at 7 weeks after preparation in order to permit the crystals to develop in size. The masses of the precipitates exceeded by 2 to 4 percent the theoretical mass, and this is ascribed to the formation of a dicalcium silicate as a second solid phase. This latter phase is known to exist in submicroscopic crystals or as an amorphous mass, and this may account for the failure to find it in the finely crystalline mass of the trisulfate.

The filtrates were analyzed only for Al_2O_3 . The amounts of CaO and SO_3 in the aqueous phases were computed and are inserted in Table 1 for purposes of discussion.

Up to a concentration of 0.45 g. CaO per liter the trisulfate precipitated immediately from solution as spherulites of needles. It was noted, not only in this series, but in all precipitates examined, that the trisulfate originating as a conversion product was always present as individual needles relatively much thicker than those of the spherulites, except as noted below.

The solid phase appearing at first in the mixtures C5, C6 and C7 was very fine grained, and its mean index coincided with the mean index of the monosulfate. After a few days the precipitate began to convert to a gel-like phase having a bluish tinge and generally appearing like hydrous alumina. Attempts to filter off a portion for microscopic examination resulted in a partial passage of the solid phase through a G3 Jena glass filter. Microscopic analyses were inconclusive as to whether this new phase was the trisulfate. Since this occurred in mixtures whose aqueous phase simulates those of cement pastes, a number of

additional mixtures were prepared to observe the changes more closely.

To 1 liter lots of solutions saturated with respect to $\text{Ca}(\text{OH})_2$ and CaSO_4 were added 0.0840 g. Al_2O_3 as KAlO_2 , and the mixtures treated as follows:

	Solid Phases
1. Filtered immediately	Monosulfate
2. Seeded with 2 mg. of trisulfate (C5) and filtered immediately	About 50-50 mixture of 2 sulfocaluminates
3. Al_2O_3 solution added simultaneously with "seeding" solution of trisulfate (trisulfate prepared as in C5)	Only trisulfate
4. Filtered at 4 weeks (not seeded)	Only trisulfate
5. 20 g. H_2SO_4 added (not seeded), and filtered at 1 week	Only trisulfate

In experiment 1 the mixture filtered readily, 5 minutes being required to filter 1 liter; the filtrate was clear and analyzed 0.0008 g. Al_2O_3 /l. The solid phase was identified as the monosulfate, microscopically, chemically (13.1% SO_3 to theoretical of 17.9%), and by mass of the precipitate. In experiment 2, two mg. of dried trisulfate were dispersed throughout the solution and the Al_2O_3 was added rapidly. The precipitate had a bluish tinge, required 5 hours for filtration, passing partially at first through the G3 Jenn glass filter, and after washing and proper drying had a mass indicating a 50-50 mixture of the two sulfocaluminates. In experiment 3 a suspension of trisulfate originating from a mixture identical to C5, and containing about 3 mg. of the solid phase, was simultaneously added with the aluminate solution, the flask with contents being shaken after addition of each drop. Filtration and the appearance of the solid phase were the same as in No. 2, but the precipitate consisted essentially of the trisulfate as indicated by the

observed mass of 1.01 g. to the theoretical of 1.02 g. Experiment 4 was the same as No. 1 except that the mixture was filtered at 4 weeks. As indicated by the swelling of the precipitate, about 3 weeks were required for the conversion which started at about 2 days. Filtration was slow, but the filtrate was clear indicating that the crystals had grown in size although the solid phase appeared gelatinous. The mass of the product agreed with the theoretical for the trisulfate. In experiment 5, 20 grams of K_2SO_4 were dissolved in a liter of saturated $Ca(OH)_2$ - $CaSO_4$ solution, the mixture filtered, and the aluminate solution added. Conversion of the monosulfate began in about 20 hours, and appeared to be complete in 3 to 4 days as indicated by the mass of the flocculent precipitate. The mixture was filtered at 7 days, a small portion of the solid phase passing through the glass filter. As shown by the observed mass, conversion of the monosulfate was complete.

On the basis of the above observations, it is concluded that the monosulfate is formed in solutions nearly saturated with respect to $CaSO_4$ and $Ca(OH)_2$. The phase, although metastable, may persist as such in the presence of excess sulfate and the conversion is relatively slow. Since the $CaSO_4$ in cement pastes is combined in about 24 hours (11) as the sulfoaluminate, the possibility of the monosulfate persisting in hardening cements is greatly enhanced as shown by the results of series A. The seeding* of the aqueous phase with the trisulfate to relieve supersaturation with respect to this compound results in the immediate formation of the stable phase. To what extent this might occur in hydrating cements is a matter for conjecture, depending on the relative rates of solution of the participating constituents. Thus, in mixtures C1 to C4, at lower $CaSO_4$ concentrations, the trisulfate precipi-

tated immediately. Therefore, excluding the immediate formation of the trisulfate, the monosulfate is formed in the presence of excess sulfate in hydrating cements regardless of the presence of K_2O and MgO . These two latter constituents, although dissolving in part as KOH , are immediately converted to corresponding sulfates by the excess gypsum present (15).

The above results are in accord with Forssen's (11) observation. However, in the case of his alkali-free cement, the monosulfate was present as a metastable phase. There exists the possibility, therefore, that the expansion of cements made of cements rich in gypsum is due to the formation of the monosulfate as a metastable phase with a later conversion to the trisulfate.

Forssen (11) has advanced the theory that "false" setting occurs if the trisulfate is formed, the preferential formation of which he ascribed to the presence of $CaSO_4 \cdot 1/2H_2O$ in the cement. False setting is a "solidification" of the cement-water paste which may occur a few seconds, or few minutes, after mixing, but which can be worked out by a further mixing for a minute or two. A given cement may exhibit this phenomena day after day, while another will show it one day and not the next; another will show it after long storage, although originally not manifesting it. In view of the experimental evidence that the trisulfate appears immediately when the $CaSO_4$ concentration is low (mixtures C1 to C4) or when the lime concentration is low (series B), there exists the possibility that in certain instances precipitation nuclei of the trisulfate are formed with the consequence that the trisulfate is the only sulfate bearing compound formed during the setting of the cement-water mixture.

In series D an excess of alumina over that required for the formation of the trisulfate was added, the molar ratio of $Al_2O_3:SO_3$ was maintained at 1:2, and the quantity of Al_2O_3 as $KAlO_2$ was progressively increased in mixtures D1 to D5 inclusive. The original $Ca(OH)_2$ concentration was near saturation (1.174 to 1.086 g. $CaO/l.$). Sufficient CaO was present to combine with the excess Al_2O_3 to form a calcium aluminate. Thus, the compounds $2CaO.Al_2O_3.8H_2O$, $3CaO.Al_2O_3.13H_2O$, and $4CaO.Al_2O_3.13H_2O$, have been reported (25) as metastable phases which, depending on the composition of the solution, may persist as such for various periods of time. The stable form of these, known as the isotropic or isometric or hexahydrate aluminate, is the compound, $3CaO.Al_2O_3.6H_2O$. It belongs to the cubic system, whereas the others belong to the hexagonal system. The end products expected in this series were, therefore, respectively $3CaO.Al_2O_3.6H_2O$ and trisulfate. In order to expedite the microscopic identification of the aluminates, mixture D1, which had no added sulfate, was prepared.

In this mixture very small hexagonal crystals were first formed, whose mean refractive index of 1.53-1.54 suggested that $4CaO.Al_2O_3.13H_2O$ was the product precipitated. In 3 to 4 weeks the stable aluminate began to form, and at 7 weeks the conversion to this product was estimated to be about 70-90 percent completed. To preserve a portion of the metastable product as an aid in identifying the aluminates in the other mixtures, the mixture was filtered at 7 weeks.

The trisulfate and a second phase in submicroscopic crystals, of positive character of elongation and mean index of 1.52-1.54, indicating a calcium aluminate, were present in mixtures D2 to D5, inclusive, from the time of preparation until filtered at 12 weeks. The high mean refractive index excluded the presence of the monosulfate. Analysis

of the filtrates precluded the presence of metastable calcium aluminates. Bessey (25) has shown that their solubility is in the order of tenths of grams of Al_2O_3 /liter instead of the few thousandths observed here.

The complete chemical analysis of the filtrates and the computed compound compositions are given in Table 1. The average SO_3 concentration of 0.0017 g./l. in this series, and the average Al_2O_3 concentration of 0.0009 g./l. in series E, compute to an $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio of 5. This value, within limit of experimental errors, agrees with the theoretical of 3 required for the congruent solubility of the trisulfate. On this basis it appears that the trisulfate is congruently soluble in the two series of mixtures. Since the solid phase in addition to the trisulfate is neither a metastable aluminate, nor the monosulfate, nor the expected stable aluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$, it probably is another species of the sulfoaluminates. This compound is either incongruently soluble, or if congruently soluble, it must have a low $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio. Evidence given later shows that sulfoaluminates other than the monosulfate and trisulfate are formed.

The results on the reaction of solid $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O}$ with CaSO_4 in contact with a saturated lime solution is of interest from the standpoint of the monosulfate as a metastable phase. Two grams of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O}$ were placed in liter lots of saturated lime solution, and increasing amounts of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ were added. The preparations and results after 6 weeks are presented in the following table.

Preparatory Mixture				Results	
	g. 4CaO- Al ₂ O ₃ - 13H ₂ O	g. CaSO ₄	Moles SO ₃ /Al ₂ O ₃	SO ₃ in Soln.	Crystalline Phase
E 1	2.00	.29	0.6	None	Monosulfate
E 2	2.00	.48	1.0	None	Monosulfate
E 3	2.00	.77	1.6	Trace	Monosulfate + trisulfate
E 4	2.00	1.44	3.0	Trace	Monosulfate + trisulfate
E 5	2.00	1.67	3.5	Large	Trisulfate + Ca(OH) ₂

The hexagonal plates of the calcium aluminate hydrates remained unchanged in mixtures 1, 2, and 3 at 1 week, except for a lowering of the refractive index; this was also true for the original solid phase in 4 and 5, but in these two mixtures needles of the trisulfate were present. 50 ml. aliquots withdrawn from the five mixtures showed that all sulfate has combined in No. 1 and 2, but increasing amounts were found in, respectively, No. 3, 4 and 5.

The mixtures were filtered at 6 weeks, the results of microscopic examinations on the solid phases were surprising insofar as Ca(OH)₂ was absent from No. 1, 2, and 3. Apparently the CaSO₄ molecule enters the 4CaO·Al₂O₃·13H₂O lattice, the compositions of precipitates No. 1 and 2 being, respectively, 4.2CaO·Al₂O₃·6SO₃ and 4.3CaO·Al₂O₃·9SO₃. The refractive index was 1.52-1.53. Jones (13) obtained approximately the same compounds from the reaction of 2CaO·Al₂O₃·3H₂O with Ca(OH)₂ and CaSO₄. These compounds will be considered later with other members of the solid solution series.

IV. PORTION OF THE FIVE-COMPONENT SYSTEM $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-H}_2\text{O}$ at 25° C.

A. Method of Study (Theoretical).

The second portion of this study was concerned with the effects of NaOH on the equilibria of the sulfoaluminates. A systematic study was made of a portion of the five-component system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-H}_2\text{O}$ at 25° C. The boundary of importance to cement chemistry is that defining the solubility of $\text{Ca}(\text{OH})_2$ in the ternary system $\text{CaO-Na}_2\text{O-H}_2\text{O}$; d'Anselme (26), Lea and Desch (17), and Porsen (11) have reported values defining the boundary. The presence of $\text{Ca}(\text{OH})_2$ as one solid phase in the five-component system is mandatory from the standpoint of applying the findings to the system cement- H_2O , and therefore, it is included as one of the solid phases in the preparations studied. In addition to the sulfoaluminates, the calcium aluminates and hydrous alumina have to be considered as other solid phases.

In a condensed, isothermal five-component system, three solid phases and the liquid phase define a univariant system. The selected variable was the NaOH concentration. Since a five-component system cannot be represented in space, with a projection of the space model boundaries on a horizontal plane, an alternate method (a hybrid one) was selected to expedite the study and presentation. The H_2O is arbitrarily set as that amount required for one liter of solution, and the composition of the aqueous phase in mole percent of CaO , Al_2O_3 and SiO_2 is projected on the base of a triangular prism. The OH^- concentration in equiv./l., as $\text{NaOH} + \text{Ca}(\text{OH})_2$, represents the vertical dimension, similarly as temperature represents the isothermal levels in the presentation of a three-component system. In order to define the boundary for three solid phases, for example $\text{Ca}(\text{OH})_2$ -trisulfate-monosulfate, the NaOH

concentration is fixed as a constant (a given vertical distance as equiv. $\text{OH}^-/\text{I.}$), and the invariant point in the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 25°C. is located. Location of these points at various CH^- concentrations defines the given boundary in the five-component system. The disappearance of one of the three phases, specifically either the trisulfate or monosulfate, as the composition of the aqueous phase is varied, indicates the regions of stability of the remaining double salt.

B. Procedure.

The procedure in preparing the mixtures and following the reactions was that used previously, namely, mixing required amounts of $\text{Ca}(\text{OH})_2$, $\text{Al}_2(\text{SO}_4)_3$, (or $\text{NaAlO}_2 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$) and $\text{Na}(\text{OH})$, so that the desired phases would appear. For a part of the study $\text{Al}_2(\text{SO}_4)_3$, (0.1093 g. $\text{Al}_2\text{O}_3/\text{l.}$ and .2450 g. $\text{SO}_3/\text{l.}$) in the presence of excess CaO , yielded the two sulfosaluminates. NaAlO_2 plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were used alternately with the $\text{Al}_2(\text{SO}_4)_3$. A o. p. grade of Na_2SO_4 was used for increasing the sulfate concentration in a few preparations.

All mixtures were stored in oersein lined flasks to provide protection against contamination from the glass. This material gave good service when certain precautions* were observed.

* At least 100 ml. of molten oersein ($100-110^\circ \text{C.}$) were placed in a 1 liter flask preheated to $100-110^\circ \text{C.}$ The flask and contents were permitted to cool spontaneously in the laboratory air, while being gently rotated during the solidification of the oersein, care being taken to obtain a fairly heavy coating on the neck of the flask with the remainder of the surface having no thin spots. The coated flasks upon reaching room temperature were placed in the colorimeter to prevent cracking caused by sudden temperature changes.

C. Solid Solution Series: $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O} - 4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 5\text{SO}_3\cdot 12\text{H}_2\text{O}$.

A number of exploratory mixtures having such amounts of Al_2O_3 and SO_3 to form 1.2 g. of the trisulfate, but containing various amounts of NaOH , yielded no trisulfate above a concentration of 0.25 equiv. of OH^-/l . A new phase having a mean refractive index of about 1.53 was formed which analysis showed to have a variable $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio of less than unity. Since solid $\text{Ca}(\text{OH})_2$ was present, the total composition of the phase could not be determined.

In order to ascertain the composition of this solid phase, and to determine what effect NaOH had on the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio, a number of mixtures were prepared which yielded this product in a pure form. The initial composition, except for the NaOH , of each mixture was 0.1054 g. Al_2O_3 as NaAlO_2 , 0.1738 g. of CaSO_4 as $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, and 0.3 g. CaO as $\text{Ca}(\text{OH})_2$ per liter. The mixtures were shaken for 10-20 minutes and then filtered. Although the amounts of $\text{Ca}(\text{OH})_2$ were in excess of those required for saturation, some supersaturation was permissible, as $\text{Ca}(\text{OH})_2$ precipitates very slowly (27) from supersaturated solutions. The compositions of the solid and liquid phases are given in Table 2; precipitates No. 3 to No. 8, inclusive, were obtained by the above procedure. Since the $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio varied from 0.68 to 0.77 for the solid phases, whose $\text{CaO}/\text{Al}_2\text{O}_3$ ratio was close to 4, and thus suggesting a solid solution series, additional solid phases were prepared to complete the series. Number 1 is the monosulfate prepared according to the method of Lerch, Ashton and Bogne (4), No. 2 is the No. A5 mentioned previously, No. 9 was obtained by the decomposition of 1.2 g. of freshly precipitated trisulfate (C5), in an 0.5 N NaOH solution, over a period of 4 weeks. Number 10 was prepared from a mixture which was the same as No. 3 to No. 8, except that $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ was not added, and the NaOH concentration was .5 N.

Table 2. Members of solid solution series: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH})_2 \cdot 12\text{H}_2\text{O} - 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$

Run No.	Molar Composition of Solid Phase				Composition of Aqueous Phase				n
	CaO	Al ₂ O ₃	SO ₃	H ₂ O	OH ⁻ equiv./l.	CaO g./l.	Al ₂ O ₃ g./l.	SO ₃ g./l.	
1	3.96	1.00	0.99	12.0					1.50
2	3.90	1.00	.85	12.1	0.016	0.783	0.0047	0.0136	1.51
3	3.90	1.00	.67	12.0	.172	.154	.0108	.0243	1.52
4	3.96	1.00	.65	11.7	.209	.148	.0092	.0210	1.52
5	3.98	1.00	.65	12.4	.266	.143	.0080	.0246	1.52
6	4.03	1.00	.48	12.5	.295	.143	.0086	.0461	1.53
7	3.96	1.00	.33	12.3	.500	.154	.0114	.0582	1.53
8	(4.0) ^(a)	1.00	.22	-	.622	.124	.0120	.0666	1.53
9	(4.0) ^(a)	1.00	.07	-	.780	.030	.0220	.2078	1.54
10	4.03 ^(b)	1.00	.00	13.0	.522	.111	.0222	.000	1.54

(a) Ca(OH)₂ present, 4.0 moles CaO assumed.

(b) Sulfate not added in No. 10.

Attempts to prepare a solid phase having a molar ratio of SiO_2/Al_2O_3 greater than 0.7 were unsuccessful when NaOH was present.

An examination of the data in Table 2 shows that the SiO_2/Al_2O_3 molar ratio of the solid phase decreased from .68 as the NaOH was increased above 0.27 equiv./l. It is to be noted that this ratio remained nearly constant in preparations No. 3, 4 and 5. Although the reason for this remained unknown, it is interesting to note that a compound of the composition $4CaO \cdot Al_2O_3 \cdot 2SiO_2$ (12-13) H_2O is indicated.

The solid phases appeared homogeneous and precipitated out in agglomerates which, assuming the hexagonal form by analogy to the monosulfate, were submicroscopic hexagonal plates aligned parallelwise. The mean index of refraction could only be estimated roughly, and the values reported in the last column of Table 2 are only approximations.

The molar compositions of the precipitates were computed from the known compositions of the preparatory solution and the filtrate after reaction. Direct analyses were also made of seven of the ten precipitates reported; these checked the computed compositions within the equivalence of 0.06 or less moles of the values reported in Table 2. The hydrate water by ignition was slightly lower than that obtained by difference. Thus, ignition loss for precipitate No. 10 gave 12.98 moles of hydrate water, whereas the value calculated by difference was 13.4 moles. This indicates an impurity in the solid phase, probably Na_2CO_3 , as previously reported (11). H_2O contaminations amounted to about 1.0 percent. No attempt was made to account for the discrepancy (or impurity) because the exact moles of hydrate H_2O in these precipitates is difficult to reproduce, being dependant on the extent and type of drying. The moles of hydrate water reported in Table 2 are those obtained by ignition

at 900° C. Ignition at 1100° C. resulted in a loss of SO_2 .

The chemical compositions of the solid phases and the gradual change in the refractive index suggests a solid solution series, having as end members $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$. In order to have more substantial proof of such a series, X-ray diffraction patterns were obtained on precipitates 1, 2, 5, 6, 7, 8 and 10. Some difficulty was experienced in obtaining well developed lines in the spectrum pattern. An exposure of 48 hours was required and even then the lines were somewhat blurred. An objectionable habit of these minute crystals is their pronounced tendency to agglomerate parallel-wise making random distribution very difficult to obtain. This may account in part for apparently small shifts in the cell sizes between some of the samples. The interplanar spacings between 001 planes were computed and are plotted in figure 3 against corresponding moles of SO_4 found in the solid phase. It is seen that the cell size decreases with decreasing number of SO_4^{--} ions in the molecule. Also it was observed that spectrum lines of both end members were missing in the pattern obtained on the intermediate members. The X-ray evidence, therefore, indicates that a solid solution series best explains the observed data. The end members formulated as follows. $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH})_2 \cdot 12\text{H}_2\text{O}$, show that one SO_4^{--} is replaced by 2 OH^- in the monosulfate molecule. The amount of this replacement increases as the OH^- concentration is increased in the aqueous phase above 0.27 N for the given conditions.

The apparently homogeneous solid phases just discussed, those mentioned previously (A5, B1 and B2), and those reported in literature are schematically compiled in Table 3 as members of possible solid solution series. It is quite probable that the unidentified new phase found in series D belongs in this schematic outline.

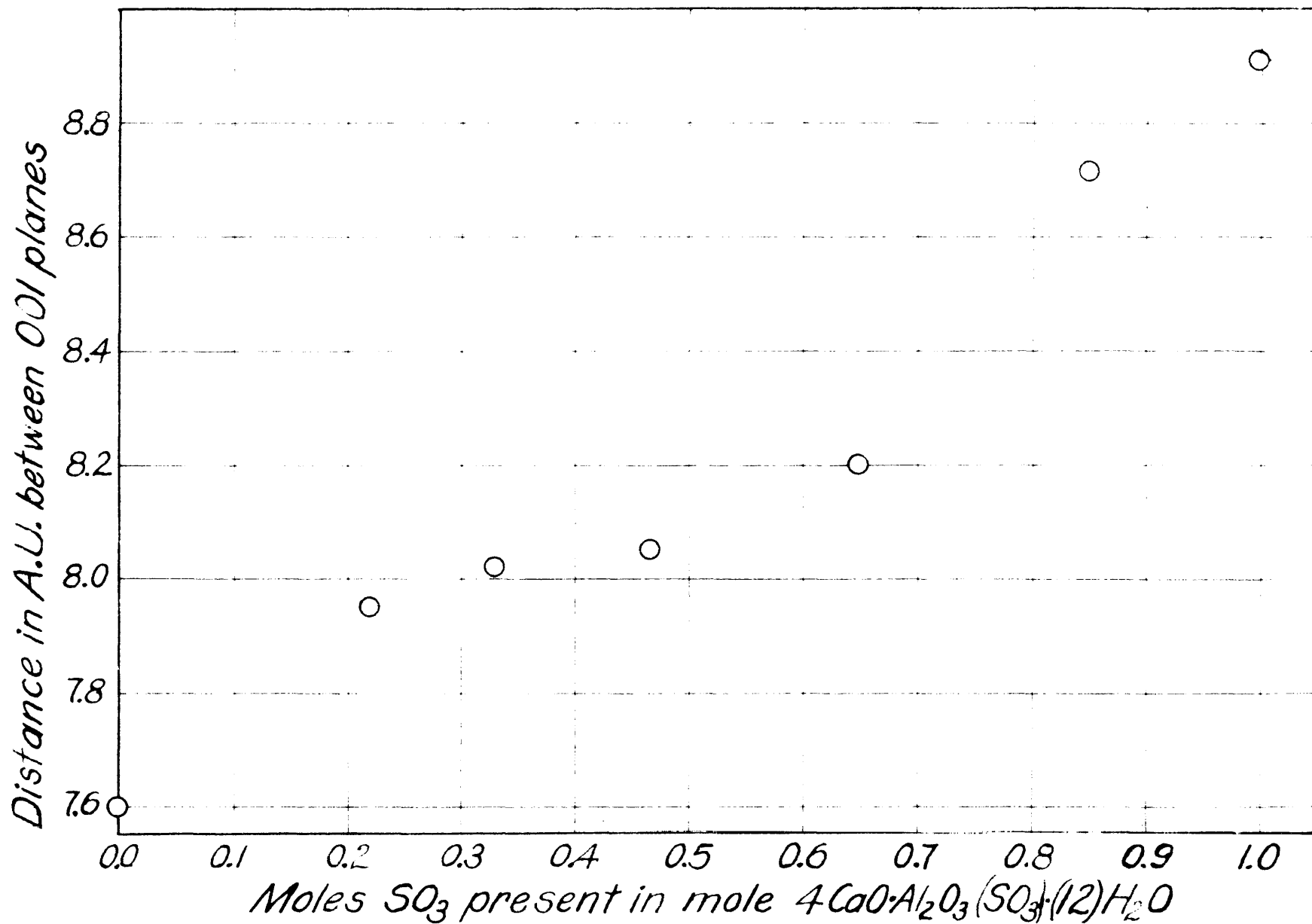
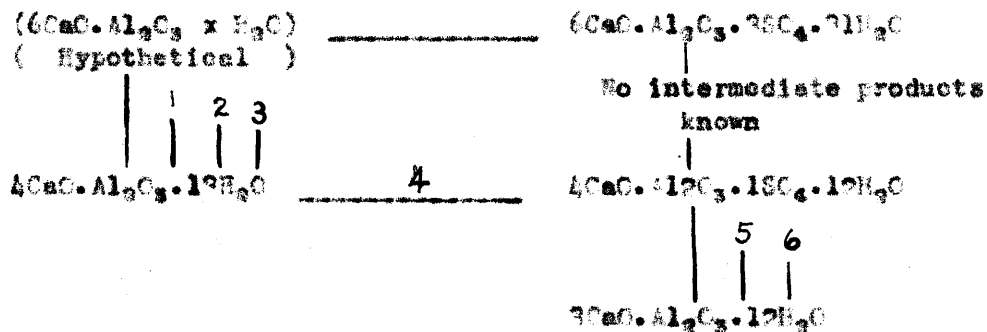


Fig. 3. Variation of interplanar (001) distances with composition.

Table 3. Probable solid solution series between the calcium aluminate hydrates and the sulfoaluminates of calcium.



Reported compounds and relative place in diagram.

	CaO	Al ₂ O ₃	SO ₃
1. Assarson	5.0	1.00	trace
2. Jones	4.4	1.00	.54
Jones	4.2	1.00	.62
3. This Study (E1-a?)	4.2	1.00	.6
This Study (A1-b?)	4.4	1.00	.9
4. This Study	(See table 3 and text)		
5. This Study table 3 No. 3	3.90	1.00	.67
This Study A5	3.90	1.00	.85
6. Jones	3.90	1.00	.41
	3.6	1.00	.45
	3.2	1.00	.27
	3.2	1.00	.20

Jones (13) in attempting to locate the boundary $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ -trisulfate by shaking solid $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ with aqueous solutions of various CaSO_4 concentrations observed that up to a certain initial concentration of CaSO_4 , the trisulfate did not appear, but the CaSO_4 was removed from solution. The crystals of $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ showed no apparent changes except for a lowering of the refractive index. The solid product showed a composition of $\text{CaO}:\text{Al}_2\text{O}_3:\text{SO}_3 = 3.9:1.0:0.4^2$ to $3.2:1.0:0.37$. By increasing the $\text{Ca}(\text{OH})_2$ in the starting mixtures, Jones obtained solid phases having more than the equivalence of 4 moles of CaO , e. g., $4.2 \text{ CaO}:\text{Al}_2\text{O}_3:0.62 \text{ SO}_3$. The latter phases apparently are members of the same series as No. E1 and E2 obtained in this study. Jones expressed the view that these phases were probably members of a solid solution series. Assarson (26) prepared a pentacalcium aluminate of the formula $5\text{CaO} \cdot \text{Al}_2\text{O}_3 (\text{tr } \text{SO}_3) \cdot 32\text{H}_2\text{O}$. The compound $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$ is a hypothetical one and is merely inserted as an analogue to the trisulfate in Table 3.

In the following sections of the paper the formation of apparently stable products having $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratios of less than unity are considered as possible compounds in hydrating cements.

D. Results and Discussion of Boundaries.

The data concerned with the boundaries are reported in Table 4. In columns 2, 3 and 4 are given the composition of the starting mixtures in g./l., in column 5 are listed the ages at which the mixtures were filtered, column 6 gives the OH^- concentration obtained by titrating the filtrate. In columns 7, 8 and 9 are reported, respectively, the g./l. of CaO , Al_2O_3 and SO_3 in the aqueous phase. Column 10 gives the computed molar composition of the solid phases.

Table 4. Data pertaining to boundaries in the 5-component system: $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaSO}_4-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$ at -75°

1	Starting Mixture (grams per liter)		Weeks	Reported Composition of Aqueous Phase (grams per liter)						Precipitate Molar Ratio			Aqueous Phase Mole Percent		
	CaO	CaSO ₄		CaO	Al ₂ O ₃	CaSO ₄	SO ₃	CaO	Al ₂ O ₃	SO ₃	CaO	Al ₂ O ₃	SO ₃	(CaO+Al ₂ O ₃ +SO ₃)	SO ₃
1	0.964	0.1093	0.2450	7	0.673	0.614	0.0003	0.0090	0.0090	0.91	93.6	0.1	1.9		
2	0.704	"	"	7	0.675	0.457	0.0017	0.0193	0.0193	0.91	93.0	0.1	2.9		
3	0.609	"	"	8	0.480	0.767	0.0014	0.0080	0.0080	0.70	92.0	0.3	7.1		
4	0.955	0.0415	0.0990	9	0.066	0.800	0.0000	0.0102	0.0102	0.70	93.8	0.1	1.1		
5	0.657	"	"	9	0.526	0.521	0.0000	0.0152	0.0152	0.57	97.3	0.1	2.1		
6	0.440	"	"	9	0.173	0.774	0.0003	0.0003	0.0003	0.17	92.0	0.5	6.5		
7(a)	0.794	"	"	9	0.1519	0.711	0.0000	0.0376	0.0376	0.33	81.5	0.6	17.9		
Boundary: $\text{Ca}(\text{OH})_2$ -trisulfate- $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$															
8	0.544	0.1008	0.2450	3	0.160	0.147	0.0022	0.0500	0.0500	0.00	79.2	0.6	20.2		
9	0.544	"	"	3	0.179	0.129	0.0003	0.0697	0.0697	0.77	71.9	1.3	26.3		
10	0.489	"	"	8	0.078	0.115	0.0006	0.1104	0.1104	1.69	53.2	0.7	40.0		
11	0.572	0.1054	0.2450	9	0.046	0.167	0.0026	0.1660	0.1660	1.0	53.0	0.6	41.4		
12	0.424	0.1028	0.2450	8	0.013	0.165	0.0043	0.1793	0.1793	1.3	51.0	1.3	47.7		
13	0.424	"	"	8	0.010	0.093	0.0090	0.1910	0.1910	0.69	41.5	2.0	56.5		
14	0.572	0.1054	0.2450	9	0.5100	0.056	0.0004	0.759	0.759	1.1	1.6	0.1	98.7		
Boundary: $\text{Ca}(\text{OH})_2$ -monosulfate)- $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$															
15	0.376	0.0415	0.0990	8	0.047	0.166	0.0044	0.0899	0.0899	0.28	71.7	1.0	27.3		
16	0.344	0.1054	0.0997	8	0.090	0.126	0.0090	0.0440	0.0440	0.51	73.1	3.2	13.3		
17	0.356	"	"	8	0.120	0.113	0.0140	0.0513	0.0513	0.44	71.9	5.0	23.1		
18	0.444	"	"	8	0.0890	0.083	0.0176	0.0572	0.0572	0.37	62.7	7.2	30.1		
19	0.944	"	"	8	0.5260	0.057	0.0080	0.0050	0.0050	0.26	43.4	19.3	38.3		
20	0.424	0.1093	0.2450	8	0.010	0.037	0.0100	0.140	0.140	0.43	34.4	2.3	62.3		
21	0.424	"	"	8	0.5000	0.073	0.0136	0.130	0.130	0.33	32.7	2.3	64.0		
Miscellaneous															
22	0.297	0.1054	0.0997	15 min.	0.273	0.097	0.0165	0.0743	0.0743	4.00	0.0	0.0	0.0		
23	0.297	"	"	6	0.273	0.097	0.0190	0.0757	0.0757	4.00	0.0	0.0	0.0		
24	0.299	"	"	6	0.261	0.071	0.0203	0.0700	0.0700	3.95	1.0	0.0	0.0		

(a) Invariant point: $\text{Ca}(\text{OH})_2 \cdot 30\text{Ca} \cdot \text{Al}_2\text{O}_3 \cdot 20\text{CaSO}_4 \cdot 21\text{H}_2\text{O} - \text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ -monosulfate

In view of the fact that a member of a solid solution series had to be considered as a third solid phase, which has a variable index, and further is submicroscopic in size, other mixtures in addition to those containing $\text{Ca}(\text{OH})_2$, trisulfate, and monosulfate were prepared. It was hoped that the precipitate free of the trisulfate would yield an $\text{SO}_4/\text{Al}_2\text{O}_3$ ratio which would serve as a supplement to the meager information obtained by microscopic observations on the monosulfate. Although this was realized in part, hydrous Al_2O_3 in very small amounts appeared as a third solid phase. The amount of this phase was barely observed microscopically, but was indicated during analysis by a faint turbidity imparted to the solution when the precipitate was dissolved in dilute HCl (1:20). The monosulfate was not present as a stable phase in the reported mixtures which contained less than 0.15 equiv. of $\text{OH}^-/1$. Hydrous Al_2O_3 , trisulfate, and $\text{Ca}(\text{OH})_2$ were found in mixtures containing 0.05 and 0.12 equiv. of $\text{OH}^-/1$. The hydrous Al_2O_3 was not found in mixtures when the OH^- concentration was lower than 0.05 equiv./1.; however, the analytical results gave a lower $\text{SO}_4/\text{Al}_2\text{O}_3$ molar ratio indicating the possibility that this phase or some other phase was present. The $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ had a variable index, being, generally, between 1.50 and 1.55. Jones (19) reported a mean index of 1.525 for $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ precipitated in the presence of sulfate.

The stable tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, was not found in any of the precipitates.

The members of the solid solution series are referred to as "monosulfate" for lack of a better name. Although the indices of this product could not be determined with any degree of certainty, the mean index was estimated to be about 1.52 to 1.54. The monosulfate appeared as a metastable product with respect to the trisulfate in a number of

preparations. However, by "seeding" the solutions with fine grained trisulfate, simultaneously with the addition of the aluminate solution, the trisulfate precipitated immediately. A few of the mixtures were not seeded in order that the development of the trisulfate could be observed. These are mentioned in the text.

1. Boundary $\text{Ca}(\text{OH})_2\text{-Al}_2\text{O}_3 \times \text{H}_2\text{O-trisulfate}$.

The data for this boundary are given in Table 4 by mixtures 4, 5 and 6. Mixtures 1, 2 and 9 are included although 1 and 2 are slightly unsaturated with respect to $\text{Ca}(\text{OH})_2$. Mixture 7 contained four solid phases, namely, $\text{Ca}(\text{OH})_2$, trisulfate, monosulfate and hydrous Al_2O_3 , and therefore, represents an invariant point. This boundary may extend further with increasing OH^- concentration. Also, attention is called to the fact that, although the boundary $\text{Ca}(\text{OH})_2\text{-trisulfate-monosulfate}$ had not been determined in the region from lime saturation (0.04 equiv. $\text{OH}^-/1.$) to a OH^- concentration of 0.15 equiv./1., its presence is not precluded. It is very probable that if the $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio of the starting compositions is decreased below three, the monosulfate will be formed.

2. Boundary: $\text{Ca}(\text{OH})_2\text{-trisulfate-monosulfate}$.

This boundary is given by mixtures 8, 9, 10, 11, 12 and 14. No. 10 and 11 represent attempted checks on one of the boundary points. No. 11 was prepared from NaAlO_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and was not seeded. The first crystals of the trisulfate appeared in about 4 weeks in this mixture. Mixture 13 is metastable with respect to mixture 12 and therefore does not represent a point on the boundary. Precipitate 14, as shown by the composition of the starting mixture, was formed in a solution rich in sulfate. Precipitation nuclei of the trisulfate were not introduced. The solid phase first formed had a mean index of 1.50 indicating that the

compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ had formed. However, at 4 weeks, the refractive index had increased to about 1.53, and a few crystals of the trisulfate were present. During the next 4 weeks the amount of the trisulfate, estimated microscopically at 1 to 5 percent, did not increase in amount. Analysis of the precipitate gave an $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio of 1.1. Considering the small amount of trisulfate present, this ratio decreased to about .9, may be considered to approximate the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio of the monosulfate present in the precipitate. This indicates that increasing the SO_3 in the aqueous phase increases the relative amount present in the crystal lattice. Thus, at an OH^- concentration of 0.5 equiv./l. precipitates 14, 21, and 19 represent a series of monosulfates showing $\text{SO}_3/\text{Al}_2\text{O}_3$ ratios of, respectively, .9, 0.4, 0.3. Because mixture 14 was not seeded originally, and the sulfate concentration of the aqueous phase appears high, it is submitted only tentatively as a point on the curve.

3. Boundary: $\text{Ca}(\text{OH})_2 - \text{Al}_2\text{O}_3 \times \text{H}_2\text{O} - \text{monosulfate}$.

This is not a boundary in the true sense of the word because the monosulfate is a compound of a variable composition. Thus, the aqueous phases of mixtures 15, 20 and 21 are richer in sulfate than the others. The amount of $\text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$ was small in all these preparations. Mixtures 20 and 21 were originally nearly the same as 18 and 19, respectively, except that more SO_3 was present. This is reflected in the higher $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio of precipitates No. 18 and 19 compared to respectively, No. 20 and 21.

Mixtures 22, 23 and 24.

Attempts to ascertain shifts in the molar ratio of $\text{CaO}:\text{Al}_2\text{O}_3:\text{SO}_3$ with time are represented by mixtures 22, 23, and 24, the latter of which contained no sulfate. No. 22 and 23 were identical, except that the

former was filtered after 15 minutes and the latter after six weeks.

Precipitate 23 and 24 were dissolved in dilute HCl, filtered immediately to obtain a separation from the hydrous Al_2O_3 , and then analyzed.

Precipitate 22 was free of $\text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$. The results indicate that the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio remains close to 4.0, but the decrease in the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio may indicate a change in the solid phase. The difference, however, is almost within the limits of experimental error, and pending further study a conclusion that the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio of the precipitate changes with time cannot be made.

E. Interpretation of data and application of findings to system cement-water.

The compositions of the aqueous phase as mole percent of CaO , Al_2O_3 and SO_3 , neglecting the Na_2O and H_2O , were computed and are presented in column 11 of Table 4. The data for the boundaries $\text{Ca}(\text{OH})_2$ -trisulfate- $\text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$, and $\text{Ca}(\text{OH})_2$ -trisulfate-monosulfate are plotted in figure 4. In this figure the data are presented in one plane, the mole percent of CaO , Al_2O_3 and SO_3 are projected on the base of the prism. The value for the OH^- concentration, as equivalents per liter of $\text{NaOH} + \text{Ca}(\text{OH})_2$, corresponding to each point in space was projected on the wall of the prism, which as presented in figure 4, was rotated through 90° into the horizontal plane. No differentiation is made between the two boundaries presented in figure 4, as it is probable that the extension of the boundary $\text{Ca}(\text{OH})_2$ -trisulfate-monosulfate will be close to that of the boundary $\text{Ca}(\text{OH})_2$ - $\text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$ -trisulfate.

The absence of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ is rather surprising, and since some of the mixtures, now 4 1/2 months old, do not show this phase when CO_2 is also present, there exists the possibility that it may not appear as a phase in the presence of NaOH and sulfate. Therefore, in applying

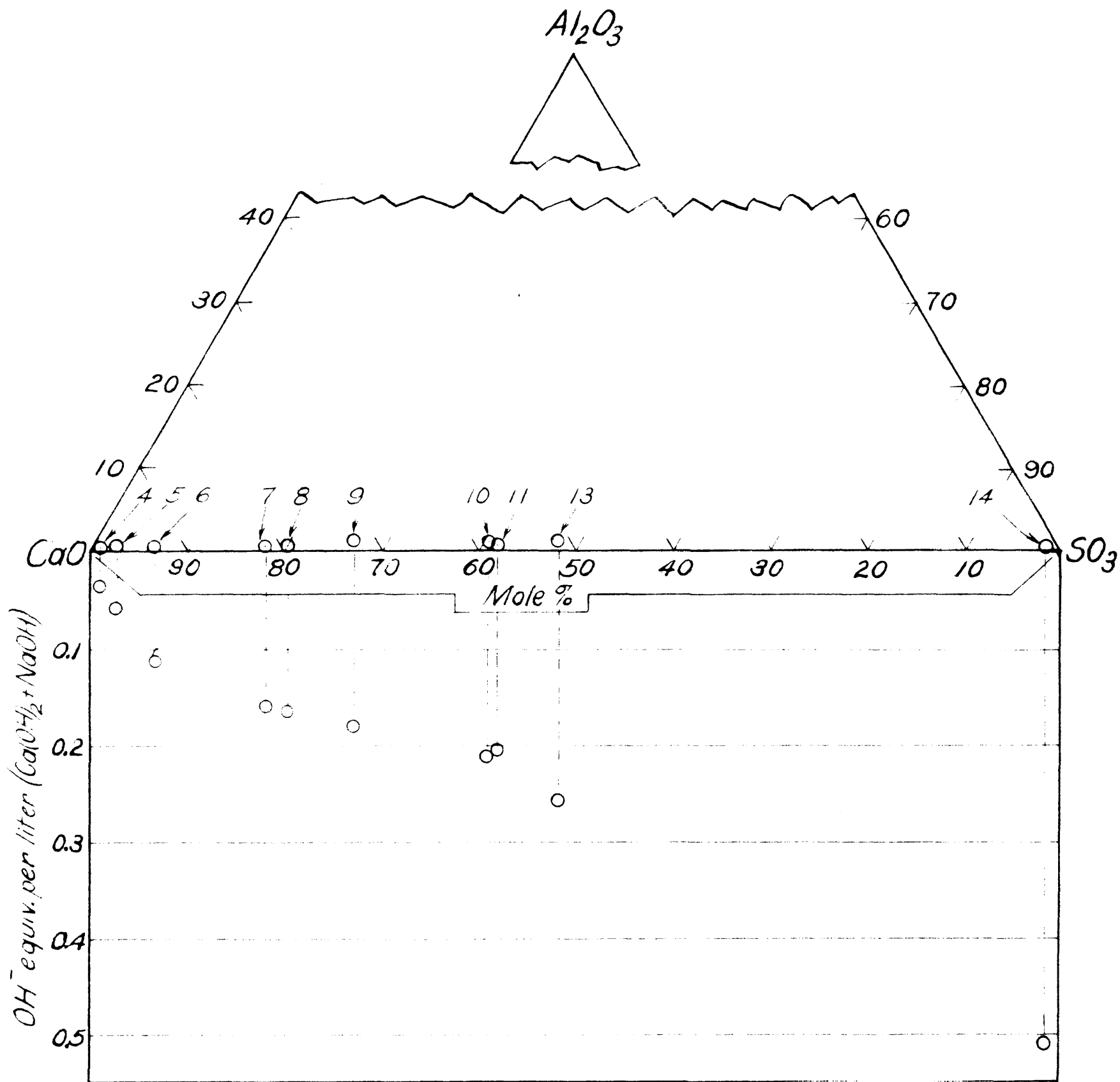


Fig. 4. Portion 5 component system. Projections on base and vertical plane, the latter rotated thru 90° into horizontal plane.

the findings of this system to the system cement- H_2O consideration is only given to the phases found in the precipitates.

When cement and water react the calcium aluminate of the cement combines, in about 24 hours (11), with the available CaSO_4 which is insufficient in quantity to combine with all the alumina as a sulfoaluminate. When the excess sulfate has disappeared from the aqueous phase, the balance of the aluminate will continue to react, and on the assumption that no other constituent combines with it, the amounts in solution will increase over those defined by the boundary. Aqueous phases containing up to 0.5 equiv. OH^-/A . will have compositions above the boundary $\text{Ca}(\text{OH})_2$ -trisulfate-monosulfate, and the trisulfate, if it had formed, will disappear. An SO_3 -poor monosulfate will be precipitated. The $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio of the latter will depend upon the composition of the aqueous phase. On the basis of this study the amount of hydrous alumina coexisting with the SO_3 -poor monosulfate will be small.

V. SUMMARY

1. The compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ forms as a metastable phase in contact with solutions of varying $\text{Ca}(\text{OH})_2$ concentrations, and in contact with solutions nearly saturated with respect to $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. In the absence of excess sulfate it persists for weeks as a compound of a variable composition before converting to the stable trisulfate. If precipitation nuclei of the trisulfate are present, the monosulfate will not form.

2. A solid solution series is formed between $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH})_2 \cdot 12\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ in the presence of FeCl_3 . The amount of sulfate in the crystal lattice decreases with increasing OH^- concentration in the aqueous phase from which the product is precipitated.

3. The boundary: $\text{Ca}(\text{OH})_2$ -trisulfate- $-\text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$ was partially defined, and the boundary: $\text{Ca}(\text{OH})_2$ -trisulfate-monosulfate ($-\text{Al}_2\text{O}_3 - 1$) was defined between OH^- concentration of 0.15 to 0.5 equiv./l.

VI. BIBLIOGRAPHY

1. Candlot: Bull. soc. encour. ind. nat., 39, 687 (1890).
2. Michaelis: Tonind. Ztg., 105 (1897).
3. Klein and Phillips: Techn. pap. Bur. of Stds., No. 47, (1914).
4. Lerch, Ashton and Bogue: Jour. of Res. Bur. of Stds., 2, 715. (1929).
5. Mylins: Acta Acad. Abcensis VII, 2, (1923).
6. Forsen: Zement, 12, 1130 (1930).
7. Foret: Hermann et Cie, Paris (1935), p. 60.
8. Jones: Symp. Chem. Cements, Stockholm 1930, p. 231.
9. Foyanagi: Zement, 21, 1016 (1931).
10. Bogue and Lerch: Ind. and Eng. Chem., 26, 837 (1934).
11. Forsen: Symp. Chem. Cements, Stockholm 1930, p. 298.
12. P. Schlapfer: *ibid*, p. 270.
13. Jones: Ware. Soc. Trans. 25 (2), 1434, (1939).
14. Kalousek, Jumper, and Tregoning: Pock Products, April, 1941.
15. Toller: Ind. and Eng. Chem., 26, 669, (1934).
16. Bates: Proc. A. S. T. W. 15 (II), 123 (1915); 22 (II), 243 (1923).
17. Lee and Besoh: Chemistry of Cement and Concrete (1935). Edward Arnold and Company (London), Publ.
18. Fillebrand and Lundell: Applied Inorganic Analysis (1929). John Wiley and Sons, publ.
19. Johnstone and Grove: J. Am. Chem. Soc. 53, 3976 (1931).
20. Flint and Ellis: Jour. of Res. Bur. of Stds. 11, 103 (1933).
21. Newman and Ellis: *ibid*, 12, 751 (1934).
22. Ashton and Wilson: Amer. Jour. Sci. 13, 209 (1907).
23. Flint, McMurdie and Ellis: Jour of Res. Bur. of Stds. 26, 1355 (1941).

24. Valousek: Master of Science Thesis, June 1936, University of Maryland, College Park, Md.
25. Kessey; Symp. Chem. Events, Stockholm, 1933, p. 173.
26. d'Anselle: Bull. soc. chim. 22, 996 (1922).
27. Bassett: J. Chem. Soc. 1271 (1921).
28. Andersson: Symp. Chem. Events, Stockholm, 1933, p. 200.

ABSTRACT

The sulfoaluminates of calcium, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$, named, respectively, trisulfate and monosulfate, are generally believed to be formed in hydrating cements. The sulfate bearing compounds are of interest to theories of early setting of cement pastes, and also are believed to be the cause of the disintegration of concrete in sulfate bearing water.

An investigation concerned with the metastability of the monosulfate, and the effect of NaOH on the equilibria of these double salts was carried out. A product simulating the monosulfate was formed and was found to persist for several weeks as presumably a metastable phase in contact with solutions poor in sulfate. In a solution, nearly saturated with respect to CaSO_4 and $\text{Ca}(\text{OH})_2$, the monosulfate formed as a metastable phase which converted rather slowly to the trisulfate. The monosulfate does not form if precipitation nuclei of the trisulfate are present. The chemical composition of the monosulfate is variable, the compound being probably a member of a solid solution series.

In the presence of NaOH a solid solution series, with $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH})_2 \cdot 12\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ as end members, was found. The amount of SO_4^{--} in the crystal lattice decreases with increasing amounts of OH^- in the contact solution. The boundaries, $\text{Ca}(\text{OH})_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ -trisulfate, and $\text{Ca}(\text{OH})_2$ -trisulfate-(members of solid solution series) were located, in part, in the five-component system $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot \text{Na}_2\text{O} \cdot \text{H}_2\text{O}$ at 25°C . Application of the findings of this system to the system cement-water, indicates that members of the above solid solution series are the sulfate bearing compounds in hydrating cements.

BIOGRAPHY

Born May 16, 1906 in Fayette, North Dakota.

Attended public grade schools in Funn and Stark Counties, N. D., finishing eighth grade in 1919. Attended Buhl High School graduating in 1923. Matriculated in Chemical Engineering at the University of Idaho in 1925, after working the previous two years on father's farm.

While in attendance at the University, worked part time for Chemistry Department and engaged in various other part time work. Spent summers and two semester terms working in the lead and zinc mines of northern Idaho, and doing concrete construction of different types. Graduated with B. S. in Chemical Engineering in June 1930.

Obtained position in July 1930 as junior chemical engineer at National Bureau of Standards. Worked on research problems concerned with engineering and chemical properties of cements and concretes.

Matriculated in 1934 in the Graduate School at the University of Maryland as part time student. Graduated with M. S. degree in chemistry in June 1936.

Married in 1936, and has one child, a boy, three years old.