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STUDIES OF PORTIONS OF THE QUATERNARY SYSTEM SODA-LIME-SILICA-WATER AT 25° C

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ABSTRACT

A study has been made of portions of the system soda-lime-silica-water at 25° C. The only solid phases found were $\text{Ca}(\text{OH})_2$ and a four-component gel of variable composition. The boundary, $\text{Ca}(\text{OH})_2$ -soda-lime-silicate gels, was determined and the compositions of the gels along this boundary shown to vary from $0.003\text{Na}_2\text{O}:2.0\text{CaO}:1.0\text{SiO}_2:z\text{H}_2\text{O}$ (at 0.2 g of Na_2O per liter) to about $0.25\text{Na}_2\text{O}:1.0\text{CaO}:1.0\text{SiO}_2:z\text{H}_2\text{O}$ (at 20 g per liter and extending to 101 g per liter of Na_2O). In regions off the boundary, at selected constant concentrations of Na_2O but with increasing concentrations of SiO_2 in solution, the $\text{Na}_2\text{O}:\text{SiO}_2$ molar ratio of the gels varied only slightly from 0.2 in most cases; the $\text{CaO}:\text{SiO}_2$ molar ratio, however, decreased to values approaching 0.1 at the maximum concentrations of SiO_2 used. Interpretations pertaining to relations between the composition of the gels and solutions are given.

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I. INTRODUCTION

The role of the alkalis, soda and potash, in hydrating cements is not fully understood. Information on how these constituents alter the chemical composition of the lime silicate hydrates and of other products in hydrating cements should be highly useful in explaining the mechanism of the various hydration processes involved. Also, a knowledge of the compositions of the alkali solutions in which the hydrated cement compounds are stable should prove helpful in elucidating the effects of the alkalis on hydrating cements in the presence of "reactive" aggregates.

The present investigation was accordingly designed for obtaining a portion of such data and was concerned with the effects of Na_2O on the compositions of the lime silicate hydrates and of the aqueous phase in which they are stable. The investigation was essentially a study of portions of the quaternary system soda-lime-silica-water at 25°C .

II. MATERIALS

The starting materials were solutions of sodium silicate and sodium hydroxide of known compositions, crystals of $\text{Ca}(\text{OH})_2$ and distilled water.

The sodium silicate solution was a reagent-quality product containing not more than 0.2 percent of CO_2 and having a molar ratio of $1.00\text{Na}_2\text{O}:3.34\text{SiO}_2$. Sodium hydroxide was freed of carbonate by preparing a saturated solution. The clear supernatant liquid was drawn off and diluted as required.

Calcium hydroxide of reagent quality and having a particle size of less than 1 micron was used for most of the experiments. Also, $\text{Ca}(\text{OH})_2$ crystals of varying sizes, prepared by adding solutions of NaOH to saturated solutions of $\text{Ca}(\text{OH})_2$, were used in a number of exploratory preparations.

III. PROCEDURE

1. PREPARATION AND FILTRATION OF MIXTURES

A few tentative mixtures of the standard solutions and the $\text{Ca}(\text{OH})_2$ were made in order to establish the amounts required to produce the desired quantities (about 0.5 to 1.0 g) of the precipitates in mixtures having a volume of 200 ml. Most of the mixtures were made by adding a solution of sodium silicate to a well-agitated suspension of fine-grained $\text{Ca}(\text{OH})_2$ in a solution of NaOH . The resulting preparations in tightly stoppered ceresin-lined flasks were stored in an air bath maintained at $25 \pm 0.05^\circ\text{C}$ until filtered at ages ranging from 2 to 18 weeks. During the first 5 to 8 hours after mixing the preparations, they were shaken about once each hour, and then once daily after the first day. Although this was the general procedure followed, it will be necessary, as required in certain sections of this report, to give more specific details.

The time allowed the mixtures to "age" was selected arbitrarily. It may be mentioned, however, that neither the solid phase nor solution underwent any determinable changes in time periods of from several weeks to several months. It is recognized that this steady state may be displaced by eventual crystallization of the solid phase, a process which, however, appears to proceed exceedingly slowly at room temperature.

The mixtures were filtered through a medium-textured sintered glass crucible by application of suction. The residue on the filter during the last stages of filtration was firmly compacted with a rubber plunger, and as much of the solution was withdrawn as permitted by the retentivity of the gelatinous precipitate. The precipitate was next redispersed in a small amount of wash solution (ethyl alcohol and water or water if the filtrate contained more than 70 g of SiO_2 per liter) and the solution again filtered off. The most suitable ratio of alcohol to water for each wash solution was determined by testing a

few milliliters of the original filtrate and selecting the maximum alcohol content which just failed to produce a suspension. Four to five successive washings were made with solutions of progressively increasing alcohol content, then four to five washings with 95-percent ethyl alcohol, and finally four to five washings with ethyl ether. In the course of each washing, the precipitate was redispersed and during filtration, compacted on the filter. After being washed the precipitate was left in the laboratory air for 1 day and then stored in a tightly stoppered vial.

2. METHODS OF CHEMICAL ANALYSES

Standard procedures of chemical analyses were followed. All of the solutions and most of the precipitates were analyzed for soda, lime, and silica. The "hydrate" water of the precipitates was determined by difference.

The amounts of Na_2O in the filtrates containing relatively small amounts of SiO_2 (1 percent or less of the total solids) were determined by titrating the solutions with HCl , using methyl red as indicator. Allowance was made for the $\text{Ca}(\text{OH})_2$ present, which was determined gravimetrically. The errors in the results were not greater than 1 percent of the amount of Na_2O , as determined occasionally for check purposes by precipitation. In all the other determinations, the Na_2O , after removal of SiO_2 , was precipitated and weighed as sodium zinc uranyl acetate hydrate.

Calcium was precipitated as oxalate, ignited, and weighed as CaO . However, when the filtrates contained over 50 g of Na_2O per liter the CaO was precipitated as phosphate, converted to sulfate, and reprecipitated as oxalate according to the method described by Hillebrand Lundell [1].¹ In the analysis for SiO_2 the solutions were dehydrated twice with HCl . The combined residues were ignited to constant weight and treated with HF . The loss in weight was reported as SiO_2 .

IV. RESULTS AND DISCUSSION

1. PRELIMINARY OBSERVATIONS

Exploratory mixtures showed that only gelatinous precipitates were formed. Some of these, in mixtures of high concentrations of SiO_2 , were highly solvated gels and others, in mixtures of high concentrations of Na_2O and low concentrations of SiO_2 , appeared as grains of gel. Analyses indicated that the $\text{CaO}:\text{SiO}_2$ molar ratio of the gels decreased as the concentration of Na_2O in solution was increased and the $\text{Na}_2\text{O}:\text{SiO}_2$ molar ratios were found to increase up to a certain value. At constant concentrations of Na_2O in solution, but with increasing amounts of SiO_2 , the $\text{CaO}:\text{SiO}_2$ ratios were found to decrease. The four-component gelatinous products are referred to as soda-lime-silicate gels, or, more often, simply as gels.

The shifts in the compositions of the gels could not be followed microscopically as the changes in the indices were small and appeared to be affected by aging. The presence or absence of small amounts of fine-grained crystals of $\text{Ca}(\text{OH})_2$ could not be ascertained reliably by means of the microscope. Large crystals of $\text{Ca}(\text{OH})_2$ could not be

Figures in brackets indicate the literature references at the end of this paper.

used as they were converted but slowly to the siliceous products owing to the formation of gelatinous deposits around the crystals.

2. BOUNDARY, $\text{Ca}(\text{OH})_2$ —SODA-LIME-SILICATE GELS

Considerations based on the preliminary results indicated that the best initial procedure to follow in studying the system would be to ascertain the compositions of the aqueous phase in contact with $\text{Ca}(\text{OH})_2$ and the soda-lime-silicate gels. Accordingly, the mixtures for establishing this boundary were prepared, only a moderate excess of crystalline $\text{Ca}(\text{OH})_2$ being used. The concentration of Na_2O was varied from 0.2 to 152 g per liter. After 2 to 7 weeks, the mixtures were filtered and the filtrates and precipitates analyzed.

All the data pertaining to the mixtures, filtrates, and precipitates are reported in table 1, the compositions of the solutions being given in grams per liter of Na_2O , CaO , and SiO_2 . The table shows that the amount of CaO in solution decreased from 0.92 to about 0.02 g per liter as the concentration of Na_2O was increased from 0.2 to about 20 g per liter. Simultaneously, the concentrations of SiO_2 increased from 0.002 to about 0.020 g per liter. In the range of concentrations of Na_2O from 20 to 152 g per liter, the amounts of CaO in solution remained nearly constant at a value of about 0.010 g per liter, but those of SiO_2 increased from 0.02 to over 1.1 g per liter.

Figure 1 shows the g per liter of CaO and SiO_2 found in solution at the different concentrations of Na_2O .

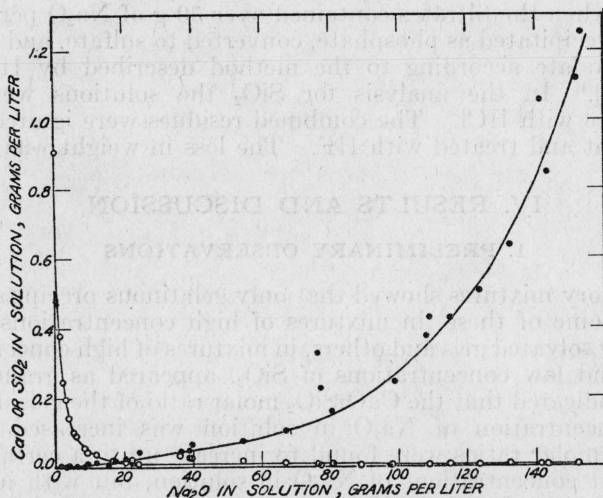


FIGURE 1.—Amounts of Na_2O , CaO , and SiO_2 in filtrates from mixtures containing solid $\text{Ca}(\text{OH})_2$ and soda-lime-silicate gels.

○ = CaO

● = SiO_2

TABLE 1.—Compositions of solutions in contact with crystalline $\text{Ca}(\text{OH})_2$ and soda-lime-silicate gels and the compositions of the mixed solids

No.	Composition of Mixtures in grams per liter			Age in weeks	Composition of solutions in grams per liter			Molar compositions of mixed solids				
	Na_2O^a	CaO	SiO_2		Na_2O	CaO	SiO_2	Computed $\text{CaO}:\text{SiO}_2$	From direct analyses			
									Na_2O	CaO	SiO_2	H_2O
1	2.0	1.864	0.655	4	1.69	0.380	0.001	2.43	0.03	2.42	1.00	-----
2	3.5	1.490	.655	4	3.16	.195	.001	2.12	.05	2.09	1.00	-----
3	4.5	1.248	.655	7	4.00	.140	.006	^b 1.83	.05	1.69	1.00	-----
4	6.5	1.116	.655	4	6.17	.090	.002	1.89	.12	1.60	1.00	-----
5	9	0.932	.655	4	8.74	.055	.002	1.43	.13	1.38	1.00	3.3
6	13	.745	.655	4	12.00	.037	.011	1.18	.18	1.18	1.00	3.0
7	16	.947	.655	7	15.30	.029	.008	1.52	.18	1.49	1.00	-----
8	18	.655	.640	4	17.8	.019	.015	1.09	.22	1.09	1.00	3.3
9	21	.618	.640	4	20.6	.013	.026	1.06	.22	1.03	1.00	2.9
10	25	.596	.655	4	24.3	.009	.043	1.03	.23	1.02	1.00	3.1
11	37	1.490	1.310	6	36.5	.038	.046	1.23	.23	1.25	1.00	2.9
12	40	0.945	0.655	2	39.0	.028	.048	^b 1.63	.29	1.31	1.00	3.6
13	40	.851	.655	5	39.6	.025	.065	1.40	-----	-----	-----	-----
14	55	1.490	1.310	6	54.5	.018	.071	1.24	.26	1.26	1.00	3.2
15	68	1.490	1.310	6	67.0	.011	.106	1.32	.25	1.34	1.00	3.0
16	77	0.605	0.655	2	76.2	.008	.325	^b 1.93	.23	1.08	1.00	3.6
17	78	.606	.655	5	77.4	.004	.227	1.51	-----	-----	-----	-----
18	82	1.490	1.310	6	80.8	.010	.157	1.38	.25	1.37	1.00	3.0
19	100	1.490	1.310	6	99.0	.004	.241	^b 1.49	.24	1.36	1.00	2.9
20	110	0.932	1.310	7	108.1	.006	.377	1.07	.27	1.02	1.00	2.7
21	110	.756	1.192	2	109	.004	.428	1.05	.24	1.06	1.00	3.0
22	116	.932	1.310	6	115.0	.008	.424	1.09	-----	1.12	1.00	2.7
23	125	.932	1.310	6	123.5	.010	.501	1.22	.29	1.26	1.00	3.2
24	135	.932	1.310	6	132.5	.006	.633	1.46	.25	1.43	1.00	3.2
25	144	.380	1.310	3	141.6	.005	1.058	1.60	.19	1.55	1.00	-----
26	145	.932	1.638	5	143.5	.006	0.845	1.27	.26	1.26	1.00	2.9
27	155	.932	1.965	5	152.0	.007	1.131	1.18	.26	1.16	1.00	2.6
28	155	.530	1.310	5	153.1	.00	1.250	-----	-----	-----	-----	-----

^a The amount of Na_2O added is approximate in these preparations.

^b $\text{Ca}(\text{OH})_2$ separated partly from mixture of solids.

(a) COMPOSITIONS OF SODA-LIME-SILICATE GELS

The precipitates obtained in the mixtures used for locating the boundary, although containing $\text{Ca}(\text{OH})_2$, were suitable for ascertaining the $\text{Na}_2\text{O}:\text{SiO}_2$ molar ratios of the soda-lime-silicate gels.

The compositions of the precipitates, assigning a value of unity to the mols of SiO_2 , are given in table 1 (last four columns) as the molar ratios of $\text{Na}_2\text{O}:\text{CaO}:\text{SiO}_2:\text{H}_2\text{O}$. Thus, the column under Na_2O gives the molar ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ of the gels.

The molar ratios of CaO to SiO_2 of gels along the boundary could not be determined reliably by preparing mixtures, computed to be removed just slightly off the boundary so as to avoid the presence of $\text{Ca}(\text{OH})_2$, and analyzing the precipitates. Because of this difficulty, the following procedure for determining the composition of the gel coexisting with crystalline $\text{Ca}(\text{OH})_2$ at constant concentration of Na_2O was selected as the most expedient and the one likely to give reliable results.

Series of 5 to 10 mixtures each were prepared at Na_2O concentrations (or levels) of 0.2, 2.4, 5.5, 9.2, 11.6, 22.3, 51, 75, and 101 g per liter. (See table 2.) The total quantities of $\text{Ca}(\text{OH})_2$ and SiO_2 , added as sodium silicate, were estimated from the amounts needed for the solutions as shown in figure 1, plus the approximate amounts required for the precipitates as indicated by results on exploratory

TABLE 2.—Data pertaining to the CaO:SiO₂ molar ratios of soda-lime-silicate gels coexisting with Ca(OH)₂ and solutions containing between 0.19 and 101 g of Na₂O per liter

No.	Composition of mixtures in grams per liter			Age, in weeks	Composition of solutions in grams per liter			Composition of precipitates molar ratios				
	Na ₂ O	CaO	SiO ₂		Na ₂ O	CaO	SiO ₂	Computed CaO:SiO ₂	Direct analyses			
									Na ₂ O	CaO	SiO ₂	H ₂ O
1	0.205	1.891	0.655	6	0.195	0.862	0.002	1.69				
2	.200	1.968	.655	18	.190	.888	.002	1.90				
3	.205	1.968	.655	6	.195	.858	.002	1.82				
4	.205	2.042	.655	6	.195	.886	.002	1.90				
5	.205	2.119	.655	6	.195	.912	.003	1.98	0.003	1.94	1.00	3.2
6	.205	2.192	.655	6	.190	.894	.002	2.13				
7	.200	2.270	.655	18	.186	.915	.002	2.23				
8	.200	2.420	.655	18	.188	.911	.002	2.48				
9	*2.5	1.058	.655	5	2.37	.193	.003	1.42				
10	2.5	1.135	.655	5	2.38	.237	.003	1.47	.04	1.41	1.00	3.3
11	2.5	1.210	.655	5	2.36	.240	.003	1.59				
12	2.5	1.285	.655	5	2.38	.243	.003	1.71				
13	2.5	1.361	.655	5	2.38	.245	.002	1.83				
14	5.8	0.525	.655	5	5.40	.002	.039	0.92	.18	0.90	1.00	2.60
15	5.8	.600	.655	5	5.42	.010	.015	.99	.15	.98	1.00	2.68
16	5.8	.675	.655	5	5.42	.022	.009	1.08	.13	1.07	1.00	2.80
17	5.8	.750	.655	5	5.42	.041	.005	1.17	.12	1.15	1.00	3.00
18	5.8	.826	.655	5	5.46	.063	.005	1.24	.11	1.21	1.00	3.06
19	5.8	.900	.655	5	5.46	.100	.005	1.32	.07	1.30	1.00	2.98
20	5.8	.975	.655	5	5.46	.099	.003	1.44	.08	1.41	1.00	(3.10)
21	5.8	1.050	.655	5	5.46	.101	.002	1.55	.08	1.52	1.00	(3.35)
22	5.8	1.125	.655	5	5.46	.097	.003	1.69				
23	5.8	1.200	.655	5	5.52	.103	.003	1.80				
24	9.5	0.522	.655	6	9.14	.011	.060	0.92				
25	9.5	.596	.655	6	9.15	.015	.038	1.01				
26	9.5	.671	.655	6	9.17	.025	.017	1.08				
27	9.5	.745	.655	6	9.15	.039	.012	1.18	.14	1.13	1.00	2.9
28	9.5	.820	.655	6	9.14	.046	.007	1.27				
29	9.5	.894	.655	6	9.14	.044	.006	1.40				
30	12.0	.530	.655	5	11.55	.003	.060	0.95				
31	12.0	.606	.655	5	11.53	.007	.025	1.02				
32	12.0	.682	.655	5	11.56	.023	.014	1.05	.19	1.05	1.00	2.7
33	12.0	.757	.655	5	11.56	.036	.008	1.19				
34	12.0	.833	.655	5	11.60	.036	.008	1.315				
35	22.0	.373	.655	5	22.11	.002	.236	0.95				
36	22.0	.466	.655	5	22.11	.003	.149	.98				
37	22.0	.559	.655	5	22.30	.016	.071	1.00	.21	0.94	1.00	2.6
38	22.0	.652	.655	5	22.28	.024	.033	1.08				
39	22.0	.746	.655	5	22.28	.027	.019	1.20				
40	51.0	1.092	1.705	8	50.8	.01	.488	0.95				
41	51.0	1.390	1.705	8	50.9	.01	.178	.97	.22	.95	1.00	2.7
42	51.0	1.688	1.705	8	50.7	.01	.105	1.13				
43	51.0	1.985	1.705	8	50.5	.01	.074	1.30				
44	51.0	2.273	1.705	8	50.5	.01	.070	1.48				
45	75.2	0.993	1.772	4	75.4	.01	.752	1.03				
46	75.2	1.242	1.772	4	75.2	.01	.420	0.98				
47	75.2	1.490	1.772	4	75.2	.01	.220	1.03	.24	.95	1.00	2.9
48	75.2	1.737	1.772	4	75.3	.01	.121	1.12				
49	75.2	1.985	1.772	4	75.5	.01	.106	1.28				
50	101.5	0.993	1.772	4	101.2	.01	.721	1.00				
51	101.5	1.242	1.772	4	100.6	.01	.498	1.04	.25	.99	1.00	2.6
52	101.5	1.490	1.772	4	100.8	.01	.320	1.10				
53	101.5	1.737	1.772	4	101.0	.01	.289	1.25				
54	101.5	1.985	1.772	4	100.8	.01	.350	1.49				

* The amount of Na₂O added is approximate in preparations 9 to 54.

mixtures. The CaO:SiO₂ ratio was varied systematically in each series so that, after reaction, about half of the mixtures contained Ca(OH)₂ and the remainder none. After 4 to 18 weeks the mixtures were filtered and the filtrates analyzed. The computed CaO:SiO₂

molar ratios,² representing the differences between the amounts of CaO and SiO₂ in the mixtures and the amounts found in solution, are used for the graphical presentation of the data. Most of the precipitates in the series containing 5.4 to 5.5 g of Na₂O per liter were analyzed for check purposes, and in each series those having compositions nearest to the boundary curve were also analyzed. The results are given in table 2.

The CaO:SiO₂ molar ratios of the precipitates at the different Na₂O levels are plotted in figure 2 against the amounts of CaO or SiO₂

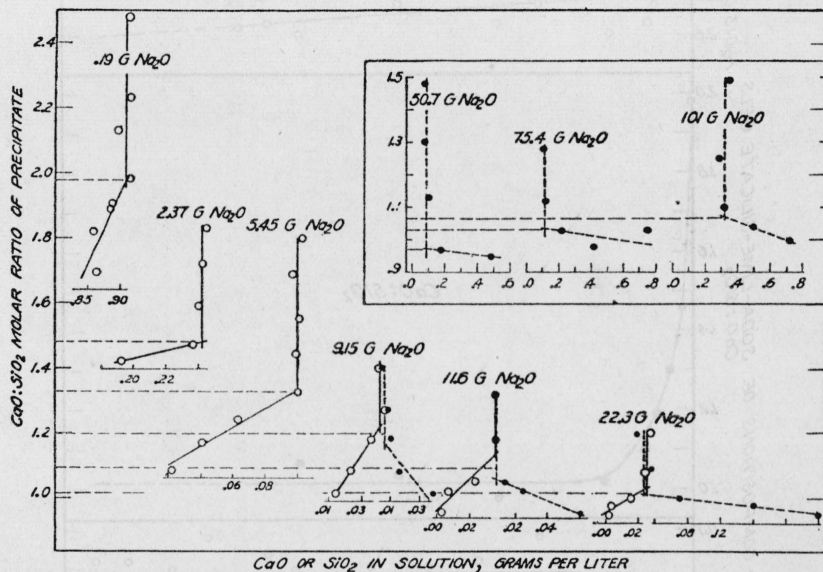


FIGURE 2.—Plots of the CaO:SiO₂ molar ratios of precipitates against the amounts of CaO or SiO₂ in solution for each of nine series of mixtures of varying CaO and SiO₂ contents but of constant Na₂O concentrations.

○—○ = CaO.
●—● = SiO₂.

(or both) in grams per liter of solution. The CaO:SiO₂ molar ratios of the gels coexisting with Ca(OH)₂ at different Na₂O levels are those corresponding to the "breaks" in the curves shown in figure 2. These breaks were quite sharp except for the series of mixtures containing small amounts of CaO or SiO₂ in solution. This may be due to the experimental errors in the determination of these small quantities and therefore, to obtain as nearly a representative value as possible, the respective concentrations of both constituents were plotted. The average CaO:SiO₂ ratio of the two was selected as being more accurate than either one.

The approximate water content of the gels, as moles of H₂O per mole of SiO₂, is given in table 2. However, in table 1 the water content

² Both the computed and observed CaO:SiO₂ molar ratios were determined, and are given in table 1 for the purpose of indicating the reliability of the former. With a few notable exceptions, in which the observed ratios were markedly lower than the computed ratios, the two agreed within a few hundredths of a mole. Such small differences are not serious, and knowing the cause for the exceptions, the computed ratios only were used in some of the following parts of the study. The marked exceptions, which occurred in the earlier experiments, were due to a partial separation of the solid phases, the Ca(OH)₂ adhering firmly to the ceresin lining of the flasks. In subsequent mixtures such separation was prevented by using a finely crystalline Ca(OH)₂ and vigorously shaking the mixture during preparation and also at frequent intervals during the first day. The resulting suspensions did not cake in the bottom of the flasks.

of the precipitates showing a $\text{CaO}:\text{SiO}_2$ molar close to 1 (the precipitates being mostly gel) also indicates approximately the water content of the gels.

The molar ratios of $\text{Na}_2\text{O}:\text{SiO}_2$, $\text{CaO}:\text{SiO}_2$, and $\text{H}_2\text{O}:\text{SiO}_2$, representing the compositions of the gels along the boundary, $\text{Ca}(\text{OH})_2$ —soda-lime-silicate gels, are presented graphically in figure 3. This

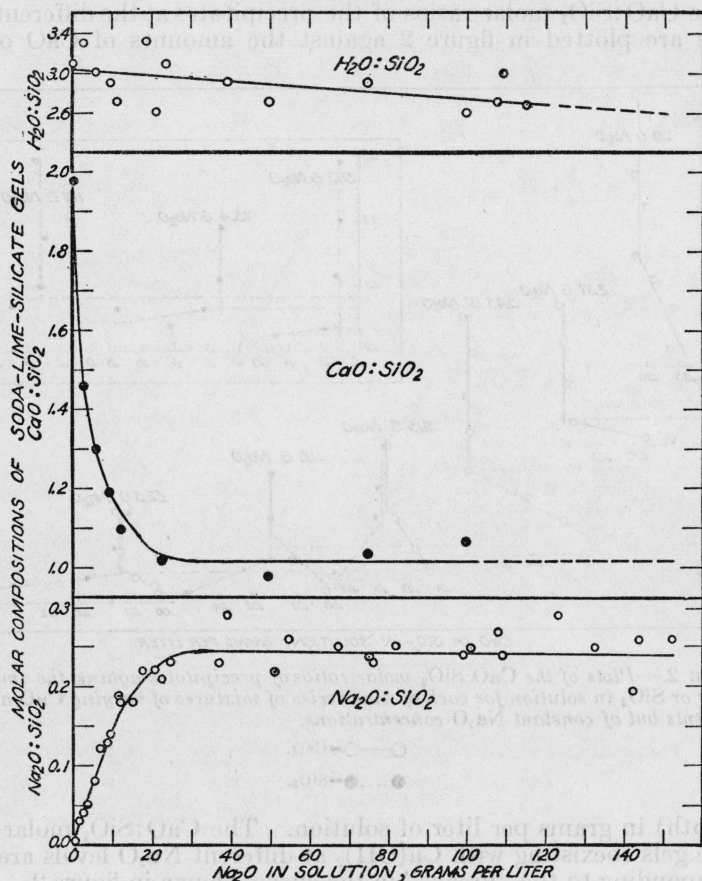


FIGURE 3.—Relations between the concentrations of Na_2O in solution and the compositions of corresponding soda-lime-silicate gels expressed in molar ratios of $\text{H}_2\text{O}:\text{SiO}_2$, $\text{CaO}:\text{SiO}_2$, and $\text{Na}_2\text{O}:\text{SiO}_2$.

figure, based on data from tables 1 and 2, and figure 2, shows that the $\text{Na}_2\text{O}:\text{SiO}_2$ molar ratio increased from a value of 0.003 to a value of about 0.23 as the concentrations of Na_2O in solution were increased from 0.2 to about 20 g per liter and then remained nearly constant at this value for all higher concentrations of Na_2O , up to 152 g per liter.

The $\text{CaO}:\text{SiO}_2$ molar ratios of the gels, as shown by figure 2, decreased from 1.98 to 1.00 as the concentration of Na_2O was increased

from 0.2 to 22.3 g per liter. At the higher concentrations of Na_2O used the ratio remained nearly constant at a value of about 1.0.

The $\text{H}_2\text{O}:\text{SiO}_2$ molar ratios varied between 2.5 and 3.3. This spread in the results is rather large, but not surprising, considering the nature of the materials.

(b) RELATION BETWEEN COMPOSITIONS OF GELS AND SOLUTIONS ALONG BOUNDARY

In order to show the relation between the compositions of the gels and solutions along the boundary, the data for mixtures 5, 10, 19, 27, 32, and 37 in table 2 were computed as mole percent of Na_2O , CaO , and SiO_2 , the water being disregarded. These results are plotted in

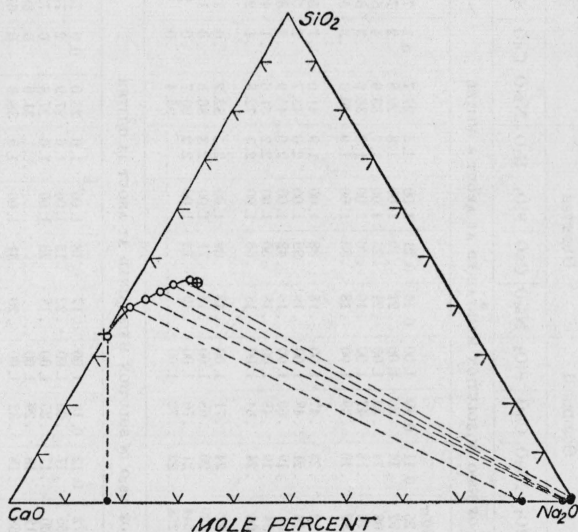


FIGURE 4.—Compositions of gels coexisting with $\text{Ca}(\text{OH})_2$ and of the contact solutions.

The results are expressed in mole percent of Na_2O , CaO , and SiO_2 (anhydrous basis).

○=Gel.
●=Solution.

THEORETICAL

⊕= $0.25\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{SiO}_2$
+= $2\text{CaO} \cdot \text{SiO}_2$.

figure 4. It should be noted that gels and solutions obtained at Na_2O concentrations above 22 g per liter had an average composition, in mole percent, almost identical with that of mixture 37 table 2, and therefore would fall nearly on the same point.

Figure 4 shows that the amounts of SiO_2 in solution along the boundary were relatively small throughout the entire range. It is seen, however, that the decreases in the amounts of CaO in solution caused large changes in the compositions of the gels. But, once the CaO concentrations attained an approximately constant value, the compositions of the gels remained nearly constant.

TABLE 3.—Data showing the effects of varying concentrations of SiO₂ on the compositions of the soda-lime-silicate gels formed at constant concentrations of Na₂O

No.	Composition of mixtures			Age	Composition of solutions			Molar composition of precipitates						Composition of solutions (in mole percent)			Composition of precipitates (in mole percent)						
								Computed			Observed						Computed			Observed			
	Na ₂ O	CaO	SiO ₂		Na ₂ O	CaO	SiO ₂	Na ₂ O	CaO	SiO ₂	Na ₂ O	CaO	SiO ₂	H ₂ O	Na ₂ O	CaO	SiO ₂	Na ₂ O	CaO	SiO ₂	Na ₂ O	CaO	SiO ₂
CONCENTRATION OF Na ₂ O IN SOLUTION MAINTAINED AT ABOUT 6 G/LITER																							
1	g/liter	g/liter	g/liter	Weeks	g/liter	g/liter	g/liter	0.11	0.19	1.00	0.15	0.21	1.00	1.5	27.7	0.1	72.3	8.5	14.5	77.0	11.0	15.5	73.5
2	7.29	1.117	23.43	11	6.61	0.02	17.25	.14	.25	1.00	.21	.19	1.00	1.8	29.8	.2	70.0	10.0	18.0	72.0	14.5	13.5	71.0
3	7.02	1.117	19.52	11	6.37	.04	14.92	.14	.32	1.00	.21	.25	1.00	1.7	33.9	.4	65.6	9.5	22.0	68.5	14.5	17.0	68.5
4	6.74	1.117	15.62	11	6.25	.08	12.08	.18	.47	1.00	.16	.36	1.00	1.8	36.6	.3	63.1	11.0	28.5	60.5	10.5	23.5	66.0
5	6.14	1.117	12.16	5	5.66	.05	9.76	.16	.39	1.00	.18	.35	1.00	1.9	40.3	.3	59.4	10.5	25.0	64.5	12.0	23.0	65.0
6	6.47	1.117	11.72	7	6.00	.05	8.82	.23	.47	1.00	.18	.38	1.00	1.9	41.0	.7	58.3	11.5	24.5	64.0	11.5	24.5	64.0
7	6.11	1.117	10.25	5	5.56	.10	7.92	.21	.48	1.00	.19	.39	1.00	2.0	43.7	.2	56.1	12.5	28.5	59.0	12.0	24.5	63.5
8	6.11	1.117	9.62	5	5.59	.03	7.18	.19	.50	1.00	.16	.42	1.00	2.0	45.9	.2	53.9	11.5	29.5	59.0	10.0	26.5	63.5
9	6.10	1.117	8.98	5	5.63	.02	6.61	.19	.48	1.00	.18	.50	1.00	2.2	51.6	.1	48.3	11.5	28.5	60.0	10.5	30.0	59.5
10	6.19	1.117	7.81	11	5.71	.01	5.34	.24	.64	1.00	.18	.65	1.00	2.3	72.8	.1	27.0	13.0	34.0	53.0	10.0	35.5	54.5
11	5.92	1.117	3.91	11	5.66	.01	2.06	.24	.71	1.00	.18	.69	1.00	2.5	82.2	.0	17.7	12.5	36.5	51.0	9.5	37.0	53.5
12	6.03	1.117	2.89	5	5.62	.002	1.21	.20	.68	1.00	.18	.71	1.00	2.3	86.5	.0	13.5	10.5	36.0	53.0	9.5	37.5	53.0
13	5.53	0.746	1.92	5	5.30	.003	0.829	.21	.70	1.00	.19	.73	1.00	2.2	90.7	.0	9.3	11.0	36.5	52.5	10.0	38.0	52.0
14	5.53	.746	1.60	5	5.30	.003	.544	.22	.72	1.00	-----	-----	-----	-----	95.4	.0	4.6	11.5	37.0	51.5	-----	-----	-----
CONCENTRATION OF Na ₂ O IN SOLUTION MAINTAINED AT ABOUT 13 G/LITER																							
15	14.58	1.117	48.86	8	13.57	0.005	40.72	0.12	0.18	1.00	0.17	0.18	1.00	1.6	25.0	0.0	75.0	9.0	14.0	77.0	12.5	13.5	74.0
16	15.85	1.117	43.78	6	14.95	.12	38.56	.17	.20	1.00	.22	.15	1.00	1.6	27.9	.2	71.8	12.5	14.5	73.0	16.0	11.0	73.0
17	14.03	1.117	39.05	8	13.20	.005	34.30	.17	.25	1.00	.18	.23	1.00	1.6	27.8	.0	72.2	12.0	17.5	70.5	13.0	16.0	71.0
18	13.48	1.117	31.23	8	12.72	.005	27.12	.18	.29	1.00	-----	-----	-----	-----	31.9	.0	68.1	-----	-----	-----	-----	-----	-----
19	12.94	1.117	23.43	8	12.23	.005	19.68	.18	.32	1.00	.20	.31	1.00	1.9	38.3	.0	61.7	12.0	22.0	68.0	13.0	20.5	66.5
20	15.84	1.117	19.45	8	14.95	.06	17.01	.35	.47	1.00	.22	.39	1.00	1.8	46.7	.2	53.2	19.0	25.5	55.0	14.0	24.0	62.0
21	15.83	1.117	17.02	8	15.05	.02	14.44	.29	.46	1.00	.21	.41	1.00	1.9	51.0	.1	48.9	16.5	26.5	57.0	13.0	25.0	62.0
22	12.38	1.117	15.62	8	11.75	.01	12.72	.21	.41	1.00	.20	.42	1.00	1.9	48.0	.0	52.0	13.0	25.5	61.5	12.5	26.0	62.0
23	15.85	1.117	14.59	8	15.35	.02	12.48	.23	.56	1.00	.21	.46	1.00	1.9	55.1	.1	44.8	13.0	31.0	56.0	12.5	27.5	60.0
24	15.84	1.117	12.16	8	15.40	.02	10.00	.20	.54	1.00	.22	.52	1.00	2.2	60.6	.1	39.3	11.5	31.0	57.5	12.5	30.0	57.5

25	11.83	1.117	7.81	8	11.30	.01	5.52	.23	.52	1.00	.19	.59	1.00	2.1	67.2	.0	32.8	13.0	30.0	57.0	10.5	33.0	56.5
26	11.64	1.117	3.85	5	11.16	.01	2.17	.28	.72	1.00	.21	.65	1.00	2.4	83.8	.0	16.3	14.0	36.0	50.0	11.0	35.0	54.0
27	11.64	0.746	1.92	5	11.25	.01	0.871	.37	.70	1.00	.19	.71	1.00	2.2	92.8	.0	7.2	18.0	34.0	48.0	10.0	37.5	52.5
28	11.64	.746	1.28	5	11.32	.01	.300	.29	.76	1.00	.21	.77	1.00	2.5	97.5	.0	2.5	14.0	37.0	49.0	10.5	39.0	50.5

CONCENTRATION OF Na₂O IN SOLUTION MAINTAINED AT ABOUT 50 G/LITER

29	50.0	1.117	158.7	7	48.7	0.00	152.2	(*)	0.18	1.00	0.22	0.09	1.00	1.6	24.2	0.0	75.8				17.0	7.0	76.0
30	50.0	1.117	134.5	7	49.2	.00	126.1	(*)	.14	1.00	.22	.15	1.00	1.8	28.1	.0	71.9				16.0	11.0	73.0
31	50.0	1.117	115.4	7	49.3	.00	106.3	(*)	.13	1.00	.21	.19	1.00	1.9	31.7	.0	68.3				15.0	13.5	71.5
32	50.0	1.117	96.2	7	49.4	.00	91.0	(*)	.22	1.00	.22	.27	1.00	1.8	35.2	.0	64.8				15.0	18.0	67.0
33	50.0	1.117	76.9	7	49.6	.00	70.3	(*)	.18	1.00	.20	.35	1.00	1.9	41.4	.0	58.6				13.0	22.5	64.5
34	50.0	1.117	48.05	7	49.5	.00	42.60	(*)	.21	1.00	.17	.52	1.00	2.2	53.8	.0	46.2				10.0	31.0	59.0
35	50.0	1.117	34.00	5	49.1	.00	31.28	(*)	.43	1.00	.16	.57	1.00	2.0	61.2	.0	38.8				9.0	33.0	58.0
36	50.0	1.117	29.13	5	49.9	.00	25.58	(*)	.34	1.00	.17	.59	1.00	2.3	66.1	.0	33.9				9.5	33.5	57.0
37	50.0	1.117	24.28	5	49.9	.00	22.90	(*)	.86	1.00	.17	.61	1.00	2.2	68.5	.0	31.5				9.5	34.0	56.0
38	50.0	1.117	19.42	5	49.9	.00	17.83	(*)	.74	1.00	.16	.64	1.00	2.2	73.6	.0	26.4				9.0	35.5	55.5
39	50.0	1.117	14.56	5	49.8	.00	13.03	(*)	.77	1.00	.17	.67	1.00	2.4	79.3	.0	20.7				9.0	36.5	54.5
40	50.0	1.117	9.71	5	49.7	.00	8.50	(*)	.98	1.00	.15	.71	1.00	2.2	85.4	.0	14.6				8.0	38.0	54.0
41	50.0	1.117	4.86	5	49.2	.00	3.58	(*)	.93	1.00	.16	.77	1.00	2.3	93.3	.0	6.7				8.5	40.0	52.0
42	50.0	1.117	3.85	5	49.9	.00	2.43	(*)	.97	1.00	.19	.77	1.00	2.7	95.4	.0	4.6				9.5	39.5	51.0
43	50.0	1.117	2.56	5	49.4	.00	1.34	(*)	.97	1.00	.22	.82	1.00	2.8	97.5	.0	2.5				11.0	40.0	49.0
44	50.0	1.117	1.28	5	49.8	.00	0.21	(*)	1.01	1.00	.19	.93	1.00	2.7	99.6	.0	0.4				9.0	44.0	47.0

CONCENTRATION OF Na₂O IN SOLUTION MAINTAINED AT ABOUT 96 G/LITER

45	97.0	1.117	76.9	6				(*)	(*)	(*)	0.26	0.49	1.00	2.0							15.0	18.0	57.0
46	97.0	1.117	38.5	6	96.0	0.00	37.17	(*)	(*)	(*)	.23	.63	1.00	2.0	71.0	0.0	29.0				12.0	34.0	54.0
47	97.0	1.117	19.23	6	95.9	.00	18.85	(*)	(*)	(*)	.11	.64	1.00	2.0	83.0	.0	17.0				6.0	37.0	57.0
48	97.0	1.117	9.78	6	95.8	.00	8.76	(*)	(*)	(*)	.17	.82	1.00	1.7	91.0	.0	9.0				8.5	41.0	50.5
49	97.0	1.117	3.92	6	96.1	.00	2.88	(*)	(*)	(*)	.28	.92	1.00	2.7	97.0	.0	3.0				13.0	42.0	45.0

* Not computed because of small differences between the amounts in mixtures and those found in solution.

3. REGIONS OF HIGHER SILICA CONCENTRATIONS

The effect of the SiO_2 contents of the solutions on the compositions of the gels was studied by maintaining the concentrations of Na_2O at approximately 6, 13, 50, and 96 g per liter, and increasing the concentrations of SiO_2 in each series to a value of 3.3 moles of SiO_2 per mole of Na_2O . These mixtures contained insufficient $\text{Ca}(\text{OH})_2$ to saturate the solutions.

Both the solutions and solids were analyzed and the results are given in table 3. The compositions of the gels were computed only for the 6- and 13-g Na_2O levels, since the computations for the 50- and 96-g Na_2O levels would be subject to large errors due to the relatively small amounts of constituents that precipitated compared to the amounts that remained in solution. The occasional large difference between computed and observed compositions at the 6- and 13-gram Na_2O levels may be due to the same cause.

The last nine columns of table 3 give the compositions of the gels and solutions in mole percentages of Na_2O , CaO , and SiO_2 . It may be mentioned that the compositions of the gels computed to mole percent of the four constituents showed that the H_2O content was nearly constant at a value of 55 ± 3 mole percent for all but two of the gels at the different Na_2O levels. It is evident, therefore, that presenting the data for the gels as a ternary system is in reality showing the 55 mole percent H_2O -level of the quaternary system.

The results for the 6-g and 13-g Na_2O levels are plotted in figure 5, and those for the 50- and 96-g Na_2O levels in figure 6. The effect of Na_2O on the compositions of the solids is readily ascertained by comparing the diagrams in the two figures. In order to facilitate the comparison, the amounts of SiO_2 in solution, in grams per liter, are given in the diagrams to the right of the points representing the compositions of the solutions.

Both the computed and observed compositions of the solids are plotted in figure 5. Considering the highly solvated nature of the gels, which made filtration and washing difficult, and that small analytical errors caused large errors in the computed results, the differences between the two sets of values are not to be regarded as significant. The trends of both, however, are about the same, and the averages may be taken as representative of the true compositions of the gels. Figure 5 shows that as the SiO_2 in solution was increased, the mole percent of Na_2O in the gel did not vary greatly, but that of CaO decreased markedly. A comparison of the two diagrams in figure 5 indicates that the gels in contact with solutions of the same mole percent composition have about the same compositions. Noting that a given mole percent of SiO_2 at the two Na_2O levels does not represent the same concentration of SiO_2 in solution, it follows, therefore, that the ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ (or $\text{Na}_2\text{O}:\text{SiO}_2$), in solution governs greatly the compositions of the gels.

About the same remarks apply to figure 6 as were made for figure 5 except that the curve for the 50-g level, above 65 mole percent of SiO_2 in solution, is displaced slightly further to the right than those at the 6- and 13-g Na_2O levels. Whether this is an actual shift in compositions or is due to an incomplete washing out of the Na_2O and SiO_2 in the solution associated with the gel is not known. The mixtures at the 96-g Na_2O level, having SiO_2 concentrations in excess

of 90 g per liter, contained exceedingly fine-grained precipitates which passed readily through the filter even after 7 weeks of aging and, therefore, only a few filtrates were available for analysis. The few results available at this level do not show as smooth a relation as those at the other levels.

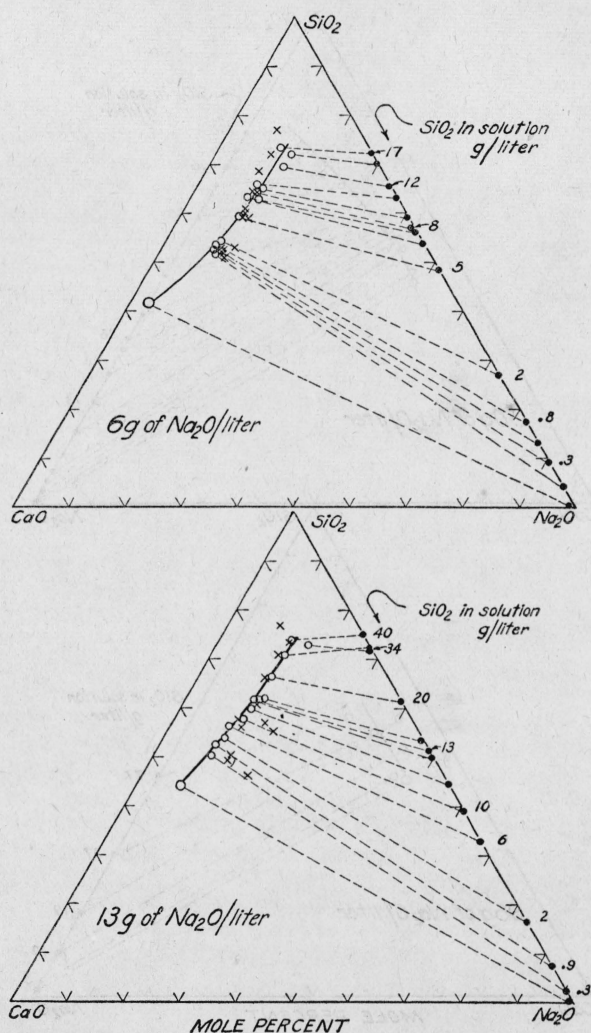


FIGURE 5.—Compositions of two series of solutions containing 6 and 13 g of Na₂O per liter, respectively and of the corresponding gels in mole percent of Na₂O, CaO and SiO₂ (anhydrous basis).

- = Gel, analyzed.
- × = Gel, computed.
- = Solution, analyzed.

V. APPLICATIONS OF THE RESULTS OF THE STUDY TO CONCRETE

This investigation has shown that gels coexisting with crystalline $\text{Ca}(\text{OH})_2$ and with solutions containing between 0.0 and 100 g of

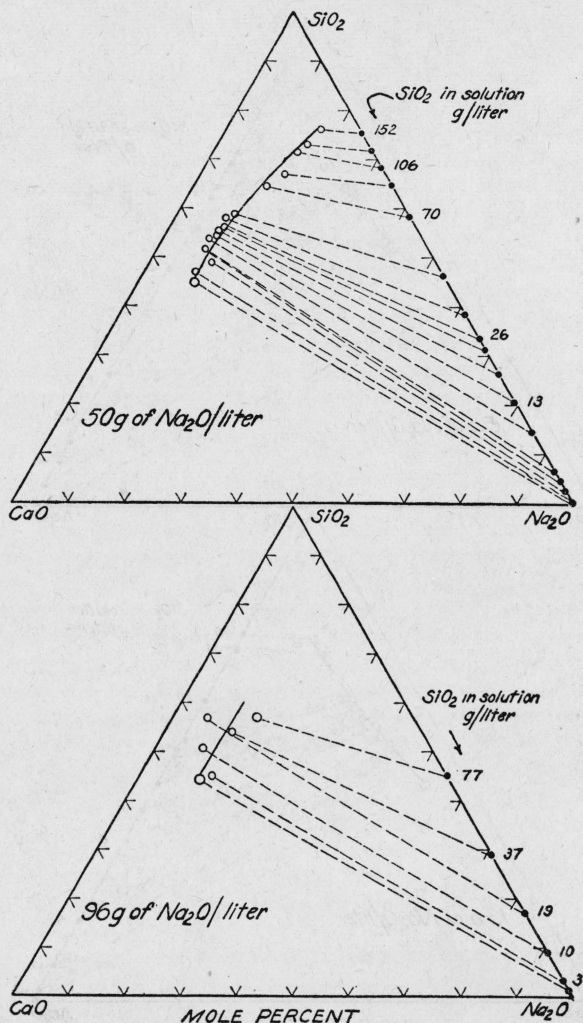


FIGURE 6.—Compositions of two series of solutions containing 50 and 96 g of Na_2O per liter, respectively, and of the corresponding gels in mole percent of Na_2O , CaO , and SiO_2 (anhydrous basis).

○ = Gel.
● = Solution.

Na_2O per liter have compositions that range between about $2\text{CaO} \cdot 1\text{SiO}_2 \cdot x\text{H}_2\text{O}$ and $0.25\text{Na}_2\text{O} \cdot 1\text{CaO} \cdot 1\text{SiO}_2 \cdot x\text{H}_2\text{O}$. If similar relations prevail in a completely hydrated cement, the approximate compositions of the gel and solution may be deduced as follows:

For purposes of illustration, a cement containing 20 percent of SiO_2 and 1 percent of Na_2O is used. The extent of combination of Na_2O and SiO_2 as a soda-lime-silicate gel will depend on the extent to which the Na_2O -bearing compounds and the two lime silicates have hydrolyzed. Because of this the simplest deductions, as follows, are those for a completely hydrated cement. If all of the Na_2O combined with SiO_2 as soda-lime-silicate gel, the $\text{Na}_2\text{O}:\text{SiO}_2$ molar ratio of the gel would be 0.05. As shown in figure 3, a gel of this $\text{Na}_2\text{O}:\text{SiO}_2$ ratio is stable in contact with a solution containing 3 g of Na_2O per liter. Since this amount³ of Na_2O in solution is only 2 percent of the total, it may be disregarded in calculating the composition of the gel. Figure 3 also shows that a soda-lime-silicate gel coexisting with a solution containing 3 g of Na_2O per liter has a $\text{CaO}:\text{SiO}_2$ molar ratio of 1.4. A combination of the two ratios gives the following composition for the gel, $0.05\text{Na}_2\text{O}:1.4\text{CaO}:1\text{SiO}_2:x\text{H}_2\text{O}$. The solution in contact with this gel would contain about 3 g of Na_2O , 0.1 g of CaO , and 0.005 g of SiO_2 per liter.

It is recognized that the above calculations are not entirely valid. For example, it is probable that a portion of the silica in a completely hydrated cement is present in combinations other than soda-lime-silicate gel. Also the composition of the gel may be altered by the prolonged aging required to bring about complete hydration of the cement.

In a partially hydrated cement, the compositions of the gel and solution will differ from those given above. It is known that the dicalcium silicate in a cement paste is only slightly hydrated at 28 days, but the tricalcium silicate in the same time may approach a state of complete conversion to its hydration products. Since, on the average, about one-third of the SiO_2 in a cement is combined as dicalcium silicate, it would follow that the gels formed during the earlier periods would contain more Na_2O than those prevailing at complete hydration, providing the Na_2O -bearing compounds react with water at rates comparable to that of tricalcium silicate. Also the solution would be richer in soda. Making allowance for the average value of SiO_2 combined as dicalcium silicate, calculations indicate that the gels formed during the earlier periods may have $\text{Na}_2\text{O}:\text{SiO}_2$ molar ratios as high as 0.1, and the contact solution may contain as much as 10 g of Na_2O per liter.

The different values reported in the literature for the compositions of the silicate gels in hydrated cements may be related to the alkali contents of the cements as indicated by the following considerations. Bogue and Lerch [2], in a study of the alkali-free lime silicates, came to the conclusion, from results of free-lime determinations, that the hydrated products had compositions approaching a value of $2\text{CaO}:\text{SiO}_2:x\text{H}_2\text{O}$. This result is in accord with that obtained in studies of the system lime-silica-water reported by Flint and Wells [3] and Bessey [4]. Using cements that contained between 0.6 and 1.5 percent of total alkalis, Bessey [5] concluded from calorimetric results and free-lime determinations that the hydrous silicates formed in the pastes had a composition of about $3\text{CaO}:2\text{SiO}_2:x\text{H}_2\text{O}$. This value of the $\text{CaO}:\text{SiO}_2$ ratio is in fair agreement with that computed

³ In making these computations, the C/W ratio was selected as 2.86 by weight, and it was assumed that the "fixed" water amounted to 30 percent by weight of the cement. No allowance was made for water gained or lost by the paste.

in this study for hydrated cements containing about 1 percent of Na_2O .

Concretes made from high-alkali cements and aggregates containing opal or certain other active siliceous materials have been shown by numerous investigations to be unsound. A gelatinous product formed in such concrete is generally associated with this unsound state. Analyses of some of these gels show them (see table 4) to consist largely of silica, alkalis, and water (ignition loss), together with

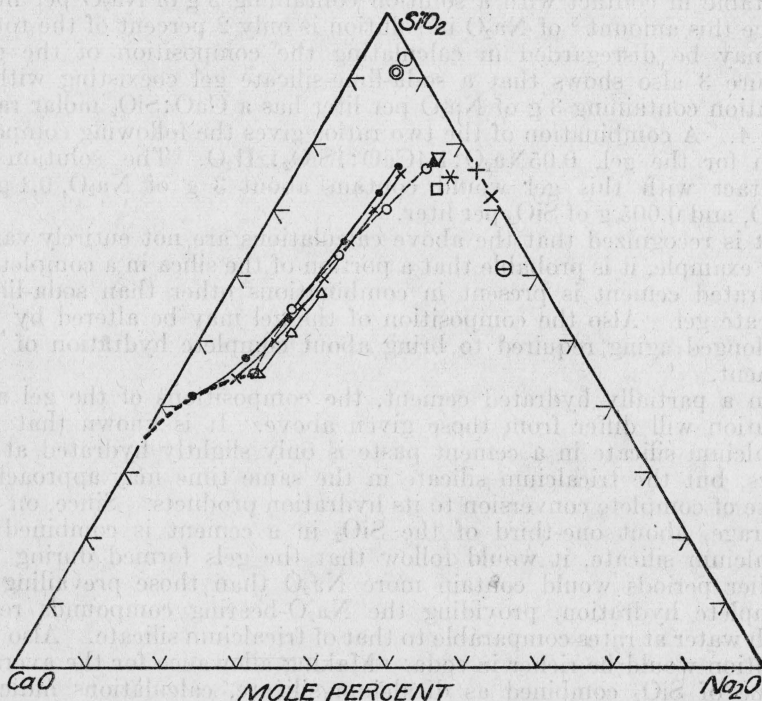


FIGURE 7.—Compositions of synthetic gels and of gels found in concretes showing expansion and cracking

The results are expressed in mole percent of Na_2O , CaO , and SiO_2 (anhydrous basis).

- Composition of gels, solution containing 6 g of Na_2O /liter.
- ×—× Composition of gels, solution containing 13 g of Na_2O /liter.
- Composition of gels, solution containing 50 g of Na_2O /liter.
- △—△ Composition of gels, solution containing 96 g of Na_2O /liter.
- Composition of gels coexisting with $\text{Ca}(\text{OH})_2$

COMPOSITION OF GELS FROM CONCRETE

- | | |
|-------------|--------------|
| ○=Meissner. | □=Meissner. |
| ⊙=Coombs. | ×=Blanks. |
| ▲=Stanton. | + =Meissner. |
| ▽=Stanton. | ⊖=Hanna. |

*=Average of above.

smaller quantities of CaO , R_2O_3 , MgO , and SO_3 . The data computed to mole percent of Na_2O (the K_2O being counted as Na_2O), CaO , and SiO_2 are presented in figure 7. Since some of the constituents were disregarded in these computations, the results are to be considered as only approximating the true ratio of Na_2O to CaO to SiO_2 of the gels. Giving consideration to this and the fact that the gels were

obtained from different sources under different circumstances, the spread in the data is not surprising. The average of these compositions is given in figure 7 for facilitating comparisons between the synthetic gels and those found in concrete. The compositions of the gels shown in figure 7 are those previously given in figures 4, 5, and 6.

TABLE 4.—Percentage oxide compositions of gels found in or on concretes containing "reactive" aggregates

Number	SiO ₂	R ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Loss	Reported by—
1.....	81.9	0.7	1.1	-----	-----	4.0	2.0	10.5	Meissner [6]
2 ^a	85.0	2.2	2.0	-----	-----	4.4	1.9	16.1	Coombs [7]
3.....	53.4	7.8	2.6	0.8	-----	12.8	^b	16.7	Stanton [8]
4 ^d	53.9	6.8	2.9	.6	-----	12.9	^b	22.4	Do.
5.....	53.4	1.5	4.7	.0	0	12.7	4.5	20.5	Meissner [6]
6.....	58.7	.5	0	.0	0	19.9	6.5	13.8	Blanks [9]
7.....	51.2	-----	-----	-----	0	16.8	^b	-----	Meissner [6]
8.....	50.0	.5	2.8	.2	2.6	24.7	8.2	11.0	Hanna [9]

^a Analysis of water soluble portion of gel amounting to 90.9 percent of total (ignited basis)—loss on ignition determined on gel as found.

^b K₂O counted with Na₂O.

^c Sum of "Moisture" and "Combined H₂O and organic matter."

^d Analyses also show 3.9 percent of CO₂ and 0.5 percent of Cl.

Because large amounts of Ca(OH)₂ are present in concrete, it might seem that the compositions given in table 4 should approximate those of the gels which coexist with Ca(OH)₂, as determined in this study. An examination of figure 7, however, shows that the reported compositions of the gels in concrete are notably and consistently lower in CaO and either higher or lower in Na₂O than those along the boundary.

A theory advanced recently by Hansen [10] to account for expansion of concretes containing "reactive" aggregates and alkalis also appears to explain why such low-lime alkali silicates may be present in concrete. This theory postulates that a membrane, permeable to sodium and hydroxyl ions and water but impermeable to silicate ions, is formed around the "reactive" aggregate particles. As a result of the transfer of the alkali hydroxide solution, an osmotic pressure great enough to cause expansion is produced. Also there occurs a reaction between the alkali hydroxide and the siliceous aggregate forming alkali silicates.

VI. SUMMARY

The only solids found, in the foregoing study of portions of the system soda-lime-silica water at 25° C, were Ca(OH)₂ and a four-component gelatinous product of variable composition. In contact with crystalline Ca(OH)₂ and solutions of increasing Na₂O contents, this gel showed a composition varying between 0.003 Na₂O:2.0 CaO:1.0SiO₂:xH₂O (at 0.2 g of Na₂O per liter) and 0.25Na₂O:1.0 CaO:1.0SiO₂:xH₂O (at 20 to 101 g of Na₂O per liter). By increasing the concentrations of SiO₂ in solution, at fixed Na₂O levels (6, 13, 50, and 96 g per liter), the Na₂O:SiO₂ molar ratio of the gel was shown to increase to a value of about 0.2 and remain approximately constant at this value. The CaO:SiO₂ molar ratio, however, decreased at all Na₂O levels.

The compositions of gels from concrete containing "reactive" aggregates are compared with those of the synthetic gels.

It is shown that the low-lime gels formed in concrete approximate in composition those in the study in contact with solutions the SiO_2 : Na_2O ratio of which approaches a value of 3.

VII. REFERENCES

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