

INTERACTION OF ALKALIES WITH HYDRATING AND
HYDRATED CALCIUM SILICATES

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Abstract

Calcium silicate hydrates ranging in C/S mole ratios of 0.88 to 1.45, and C_3S and C_2S have been reacted with different alkali solutions such as LiOH, NaOH, and KOH, of different concentrations for various times to determine the amount of alkali retained by the hydrating and hydrated calcium silicates. It has been found that low C/S ratio hydrates retain more alkali than the high lime to silica ratio hydrates. The amount of alkali retained does not always increase with increasing hydration time since a competition between the alkali and the lime sets in resulting in the recirculation of alkali. The amount of alkali retained also varies with the concentration of alkali in the contact solution. The effect of mixed alkalies has also been studied.

Introduction

Although considerable work has been done since 1940 when T. E. Stanton⁽¹⁾ first discovered that alkali-aggregate reactions were responsible for the deterioration of pavements in California, we have not yet been able to deal with the situation with confidence. In addition, due to new technological developments, strict environmental regulations and kiln dust recycling, the amount of alkalis in cement in future will probably increase. The existing and forecast circumstances point out that it will neither be feasible nor practicable to suggest the use of a low-alkali cement or a non-reactive aggregate to eliminate the problem of expansion caused by the alkali-aggregate reactions. The ultimate objective of this work is to gain an understanding of the basic chemistry of the alkali-aggregate reactions such that the allowable limits of alkalis in cements can be increased without deleterious effects. This paper presents some data from the studies of the reactions between alkalis and pure calcium silicate hydrates, C_3S , and C_2S which helps us understand the more complicated alkali-cement system.

Previous work indicates that cements containing a certain amount of alkali, about 0.6%, usually do not produce deleterious

expansion effects. If the cement contains 0.6% alkali as equivalent Na_2O and 20% SiO_2 , then the $\text{Na}_2\text{O}/\text{SiO}_2$ (N/S) mole ratio is less than 0.03 for a cement that usually does not produce deleterious effects. This is because calcium silicate hydrate (CSH), as we will show, retains much of the cement alkali at these lower (<.60) alkali levels so that little alkali is available to react with the aggregate. The amount of alkali retained varies with the extent of hydration and also the concentration of alkali in the solution.

Experimental

The studies reported in this paper have been performed in two stages over several years. Therefore, the methods of preparation of mixtures differ slightly. In more recent studies, 5 grams of each of the calcium silicate hydrates, C_3S and C_2S , were reacted with 25 grams of different concentrations of different alkali hydroxides. In the earlier studies, the reactants were mixed in slightly different proportions; such differences will be noted in this report when appropriate. All the mixtures were reacted in polyethylene bottles with continuous agitation. After various time periods, the mixtures were filtered and the filtrates were analyzed for alkali and in some cases for silica. The difference in the original concentration of alkali and the concentration of alkali in the filtrate gave the amount of alkali retained by the solid. Once the alkali retained in the solid was obtained, the soda to silica mole ratio (N/S) of the solid was calculated.

The early studies were started by preparing mixtures of potassium silicate, high surface area $\text{Ca}(\text{OH})_2$, and potassium hydroxide to obtain three different calcium oxide to silica mole ratio (C/S) hydrates. The mixtures were reacted for 60 days. Fig. 1 shows the plot between potassium oxide mole ratio (K/S) and contact solution for various C/S ratio hydrates calculated from the analytical data. For different C/S ratio hydrates, the K/S ratio is not a straight line function of the amount of K_2O in the contact solution except for the 0.92 C/S ratio hydrate.

The x-ray diffraction patterns of the solids (filter cakes) obtained after filtration and dried over $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ showed from traces to some amounts of $\text{Ca}(\text{OH})_2$ in all the patterns except the three low C/S ratio mixtures. Another interesting feature was that the filter cakes obtained from less than 2% K_2O solution were physically different from all the other cakes. The cakes were bulky and easily broke up whereas the high K_2O (6-7%) cakes shrank to one tenth of their original volume on drying and were very hard to grind.

In Figure 2, the data from Figure 1 shown as Curves 1, 2, and 3 in Figure 2, have been plotted in combination with data from Kalousek. Several interesting features are apparent from this data. At C/S ratio less than one, the Kalousek data shows that the sodium oxide to silica ratio in the solids ranges from 0.16 to 0.22 over a wide range (5 to 50 grams) of Na_2O per liter as shown by the boxed area. When C/S ratio exceeds one as shown by the dashed line, the N/S ratio in the solids

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Because the reactions in the higher limed samples had not reached what was thought to be equilibrium (there was still Ca(OH)_2 present), further experiments were carried out by first preparing the calcium silicate hydrates and then reacting them with alkalis.

Reaction of Calcium Silicate Hydrates with Various Alkalies of Different Concentrations

The reaction of calcium silicate hydrates with various alkalis has been studied in two series of experiments. These are described separately. Calcium silicate hydrates were prepared using calculated amounts of SiO_2 gel and Ca(OH)_2 in excess water at 73°F . The mixtures were continuously agitated for 3 to 6 months and filtered. At one month the slurries were ground in a mortar and pestle (CO_2 free atmosphere) to pulverize the harder particles which had formed. The x-ray diffraction patterns of solids showed no Ca(OH)_2 . The solids were dried at 70-85% relative humidity.

In the first series of experiments, 5 grams of each of the three calcium silicate hydrates having C/S ratios of 0.88, 0.97, and 1.45 were reacted for 90 days with 20 grams of alkali hydroxide solutions containing 0.125, 0.25, 0.50, 0.75, 1.0, 1.25, 1.5, and 2.0 molar of either LiOH , NaOH , and KOH . Figure 3 shows plots of alkali oxide/ SiO_2 mole ratios as a function of moles of alkali oxides in contact solution for each calcium silicate hydrate. The graph has been purposely drawn

by a set of broken lines rather than as smooth curves because it is thought that the jogs in the curves show that the equilibrium has not been attained. The Li_2O curves are less erratic compared to Na_2O and K_2O curves for the hydrates. The most noticeable variations in the alkali/ SiO_2 ratios mostly occur between 0.25 and 0.5 molar concentrations of Na_2O and K_2O for 0.88 and 0.97 C/S ratio hydrates while for 1.45 C/S ratio hydrate between 0.50 to 0.75 molar concentration. The x-ray diffraction patterns show the presence of $\text{Ca}(\text{OH})_2$ in 1.45 C/S ratio hydrate only above 0.5 molar alkali oxide.

The basal spacings of the moist solids decreased with an increase in alkali from 14.24 Å to 13.8 Å and 14.12 Å to 12.61 Å in 0.88 and 0.97 C/S ratio hydrates, respectively. The x-ray diffraction peaks became sharper and increased in intensity with increasing Na_2O concentration. For 1.45 C/S ratio hydrate, the basal spacing of 12.27 Å did not change significantly. The mixtures containing Li_2O and K_2O behaved similar to those with Na_2O .

In another series of experiments, the reaction of three calcium silicate hydrates having C/S ratios of 0.97, 1.25, and 1.32 with 1N NaOH solution was studied. The analysis of these calcium silicate hydrates is shown in Table 1. Figure 4 shows the relationship between N/S mole ratio and the reaction time for various calcium silicate hydrates. The figure shows the following main features:

1. It is apparent that the N/S ratio of the alkali retained increases with the increase in reaction time up to 300 days except for 1.32 CSH.

2. Considering the individual calcium silicate hydrates one at a time, it is seen that in the case of CSH having C/S mole ratio of 0.97, the N/S ratio is coming to a plateau. It is possible that the system has already reached an equilibrium state.
3. The x-ray patterns of the alkali reacted hydrates having C/S ratio of 0.97 and 1.25 were similar to the original hydrates in that no calcium hydroxide was found. We interpret this to mean that both the alkali and calcium were retained in the structure of these CS hydrates, producing an NCS hydrate in the latter case with a maximum calcium content for equilibrium with 1N NaOH.
4. The 1.32 C/S ratio hydrate behaved differently as seen in Figure 4. The x-ray patterns of the reacted solid showed the presence of $\text{Ca}(\text{OH})_2$ at all ages. However, there was no indication of $\text{Ca}(\text{OH})_2$ in the 1.32 C/S ratio hydrate starting material. The $\text{Ca}(\text{OH})_2$ obtained after reaction was produced by the replacement of calcium from CSH by sodium. This indicates that in this case, the reaction is a substitution reaction rather than an addition reaction as seen in earlier cases. The extent of substitution is especially apparent in the 90 days reaction time where the N/S ratio shows a large increase, but the ratio decreases sharply after 90 days indicating the complexity of the reaction. This phenomenon of

alkali circulation has been termed as recycling of the alkali.

5. The low C/S ratio hydrate (0.97) retains twice the amount of alkali as the high C/S ratio hydrate (1.25).
6. These experiments also show that calcium silicate hydrate in equilibrium with 1N NaOH solution has a maximum C/S ratio between 1.25 and 1.32. The C/S ratio of calcium silicate hydrate formed as a result of hydration of cement is about 1.5. Therefore, recycling of the alkali can be expected in cement systems. When we add a pozzolan to the cement, the C/S ratio is reduced and it is probable that the reduction in the soluble alkali reduces the rate of the alkali-aggregate reaction.

Hydration of C_3S and C_2S in the Presence of Different Alkalies of Different Concentrations

The hydration of C_3S and C_2S was studied in two series of experiments. In the first series, 6.5 grams of C_3S or 5 grams of C_2S were reacted with 20 grams of alkali hydroxide solutions containing 0.125, 0.25, 0.50, 0.75, 1.0, 1.5, and 2.0 molar NaOH for 90 days. Figure 5 shows a plot of the data between the N/S ratio in the solids and the final concentration of the contact solution. For the purpose of comparison, the retention of Na_2O for calcium silicate hydrate ($C/S = 1.45$) has also been shown in Figure 5. Since the amount of actual combined water used in the hydration of C_3S and C_2S is not known, two curves for each silicate has been drawn to show the

effect of variations in the combined water. The data for the two curves for C_3S have been calculated taking into consideration that either 3 moles of water or 5 moles of water are needed for the hydration of C_3S . It is thought that the water needed for the hydration lies between these limits. For C_2S , the calculations have been made for 4 and 7 moles of water.

The curves for C_3S , C_2S , and CSH ($C/S = 1.45$) show variations in N/S ratios at various concentrations of contact solution but for all the compounds, the N/S ratios have upward trends as the concentration of the contact solution increases to 5 wt % Na_2O . The jogs in these curves probably indicate that equilibrium has not been attained.

The x-ray diffraction patterns show that C_3S and C_2S have completely hydrated. All the patterns showed an increase in the intensity of the diffraction lines due to $Ca(OH)_2$ as the concentration of alkali increased except that a slight correlation appeared between the jogs in the curves and the intensities of the lines for $Ca(OH)_2$. That is, when the N/S ratio decreased, so did the intensity of the $Ca(OH)_2$ lines compared to the $Ca(OH)_2$ intensities on either side of the low points. At NaOH concentrations below 0.75 molar, the basal spacings were either broad and weak or tended toward a peak at 10 Å. At higher NaOH concentrations this 10 Å peak tends to disappear and a new strong peak appears at 12.6 Å. Without alkali present, the basal spacing for wet tobermoroids increases as the C/S ratio of the solid decreased to about 14 Å at $C/S = 0.9$. Therefore, the increase in basal spacings observed during

reaction in NaOH solutions suggests that the C/S ratio of the initially high lime silicate hydrate decreases to about 0.9.

In the second series of experiments, the hydration of C_3S and C_2S was studied in the presence of different concentrations of NaOH solutions (0.25N to 5N) for various time periods. The N/S ratio of the solid is plotted as a function of Na_2O concentration of the mixtures containing C_3S at five ages (7, 14, 28, 90, and 1 year) in Figure 6. The water used in the hydration of C_3S and C_2S has not been taken into account while calculating the N/S ratio of the solids in these results. Therefore, the N/S ratio might be slightly higher than those seen in the first series of experiments of C_3S and C_2S .

The N/S ratio in the solids increases very slowly up to 1N NaOH (or 3% Na_2O) concentrations at all ages. In fact, there is no significant difference with age below 1N NaOH concentration. The N/S ratio is about 0.05 for 1N NaOH concentration. When the concentration of NaOH increases from 1N to 5N, it is seen that the N/S ratios in the solids increase very rapidly. Although in hydrated cements we might not expect to have such high alkali to silica ratios, it is possible that high ratios may exist because of the concentration of alkali solutions produced by the removal of water by cement hydration.

To further understand this part of the system, we need to know the amount of lime in these solids. We tried to calculate the C/S ratio of the CSH from the difference between the total lime and the amount of lime as $Ca(OH)_2$ determined by DTA/TGA. DTA/TGA runs of solids having a very high N/S ratios were not

successful for determining the $\text{Ca}(\text{OH})_2$ generated during the hydration in the presence of high concentrations of alkali in the solids. Several peaks which interfere with the $\text{Ca}(\text{OH})_2$ determination in DTA/TGA plots are thought to be due to various reactions of sodium or calcium silicates during heating. One washing of the solids with ethyl alcohol did not remove all the alkali.

The results of the hydration of C_2S in the presence of various concentrations of alkali are shown in Figure 7. The N/S ratios show a continuous increase for all ages with increasing concentration and increasing time from 7 days to 1 year. For 1N NaOH, the average N/S ratio is less than 0.05. A similar average ratio was obtained with C_3S at 1N NaOH concentration.

Figure 8 shows the hydration of C_3S in the presence of different alkalies such as 1N LiOH, NaOH, and KOH at different times. The mixtures were prepared using 5 grams of C_3S and 15 grams of alkali solution.

In this hydrating system, it is readily apparent that the alkali/silica ratio increases to a maximum around 28 days and then shows a decrease.

The continuously hydrating system of C_3S will be continuously producing both CSH and $\text{Ca}(\text{OH})_2$ which are also the two major phases produced by cement hydration. CSH reacts with alkali to produce alkali CSH. The increasing amount of CSH will keep on reacting with alkali to produce increasing amount of alkali CSH. In this way, the increasing alkali retention of the system is understandable.

After 28 days or so, it is seen that the alkalies are being released, and lime is probably being substituted for the alkali.

Another interesting feature of Figure 8 is that at later ages lithium has the highest retention compared to the sodium and potassium.

C_2S has also been hydrated in the presence of 1N LiOH, NaOH, and KOH for different times and the results are plotted in Figure 9.

The alkali to silica ratios increase with increasing hydration time for all the alkalies studied up to 90 days, but after 90 days up to 1 year, the alkali to silica ratios show a decrease for LiOH and a very slight increase in the alkali to silica ratio for NaOH and KOH.

The continuous increase in the alkali retention up to 90 days is understandable as it is due to the formation of increasing amount of CSH as a result of continuous hydration of C_2S . This trend is very similar to that which has been observed for C_3S . However, it should be kept in mind that the hydration rates of C_3S and C_2S are different: it takes about 90 days for C_3S and 1 year for C_2S for nearly complete hydration.

Again, the amount of lithium retained at later ages is more than sodium and potassium. This is similar to what is observed in C_3S -alkali system.

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Retention of Alkalies in Calcium Silicate Hydrates in the Presence of Chloride

Calcium silicate hydrates having C/S ratios of 0.88, 0.97, and 1.45 were reacted with mixed solutions of LiCl and NaOH, NaOH and NaCl, and LiOH and NaOH. The reaction times were 20 and 98 days. Table 2 summarizes the data. The interesting features are as follows:

1. In a medium containing sodium hydroxide and sodium chloride, the solids appear to absorb sodium ion and then to lose it again especially at high C/S ratio. (Sample Nos. 2, 5 & 8)
2. No such alkali loss occurs in the presence of sufficient lithium ion during the 98-day period of observation. (Nos. 1, 3, 4, 6, 7 & 9.) In fact, there is a gain in the total alkali in the solids in the presence of lithium within this time frame. This may explain why lithium salts help to ameliorate alkali-aggregate expansion.
3. In the mixed alkali media, the alkalies appear to act relatively independently of each other. If one estimates the alkalinity of the solution by subtracting the chloride ion from the total number of moles of alkali, one finds that the alkali oxide to silicate ratio for the low-limed silicate is higher than that for either alkali separately because of this additive effect of the separate ions.

4. The adsorption of the alkalis does not appear to change the moisture contents of the solid phases. This conclusion is drawn from measurements of the chloride ion which was introduced into the original solutions for this purpose. A significant loss or gain of water by a solid phase would have resulted in a corresponding change in the chloride ion concentration, since chloride ion is not adsorbed by these silicates. The changes in the chloride ion shown in the last column of the table indicate, within the analytical accuracy, no change in the hydration water.

Summary

The results presented provide a basis for better understanding of the behavior of alkalis in the cement system. The main products of hydration of portland cement are calcium silicate hydrate and Ca(OH)_2 . The average lime to silica ratio of the hydrates of the major calcium silicates is about 1.5. The present results show that such high lime to silica ratio hydrates do not have as high a capacity for alkali retention as hydrates of lower lime to silica ratio.

It is also seen that when high lime to silica ratio hydrates react with alkali, some lime is released by the alkali from the hydrate and more alkali is retained. However, some alkali may then be released resulting in the recycling of alkali which may then be available for deleterious reactions.

The results also show that Li_2O is retained more than Na_2O and K_2O in the hydrating C_3S and C_2S .

0.30
0.28
* Ca(OH)_2 Found in Solid by X-Ray

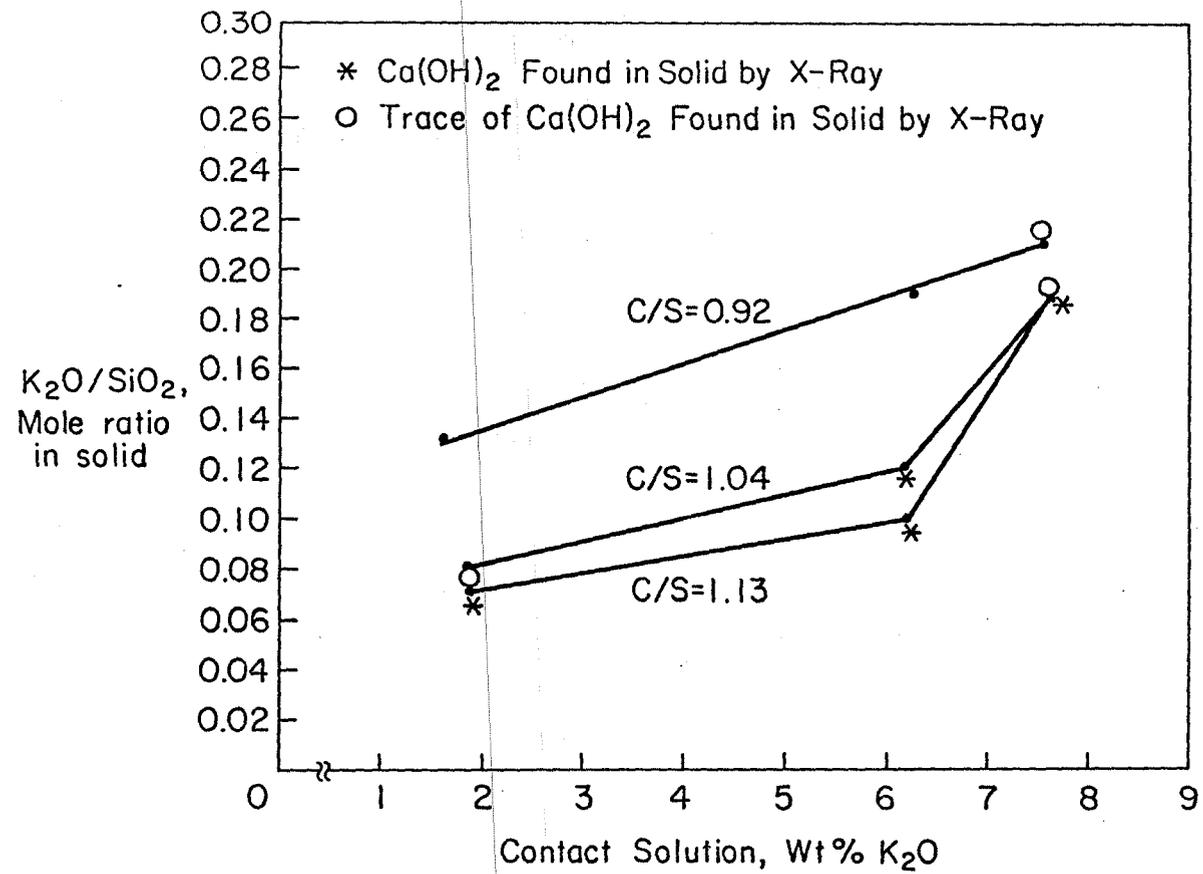


FIGURE 1: RETENTION OF POTASSIUM OXIDE BY VARIOUS CALCIUM SILICATE HYDRATES

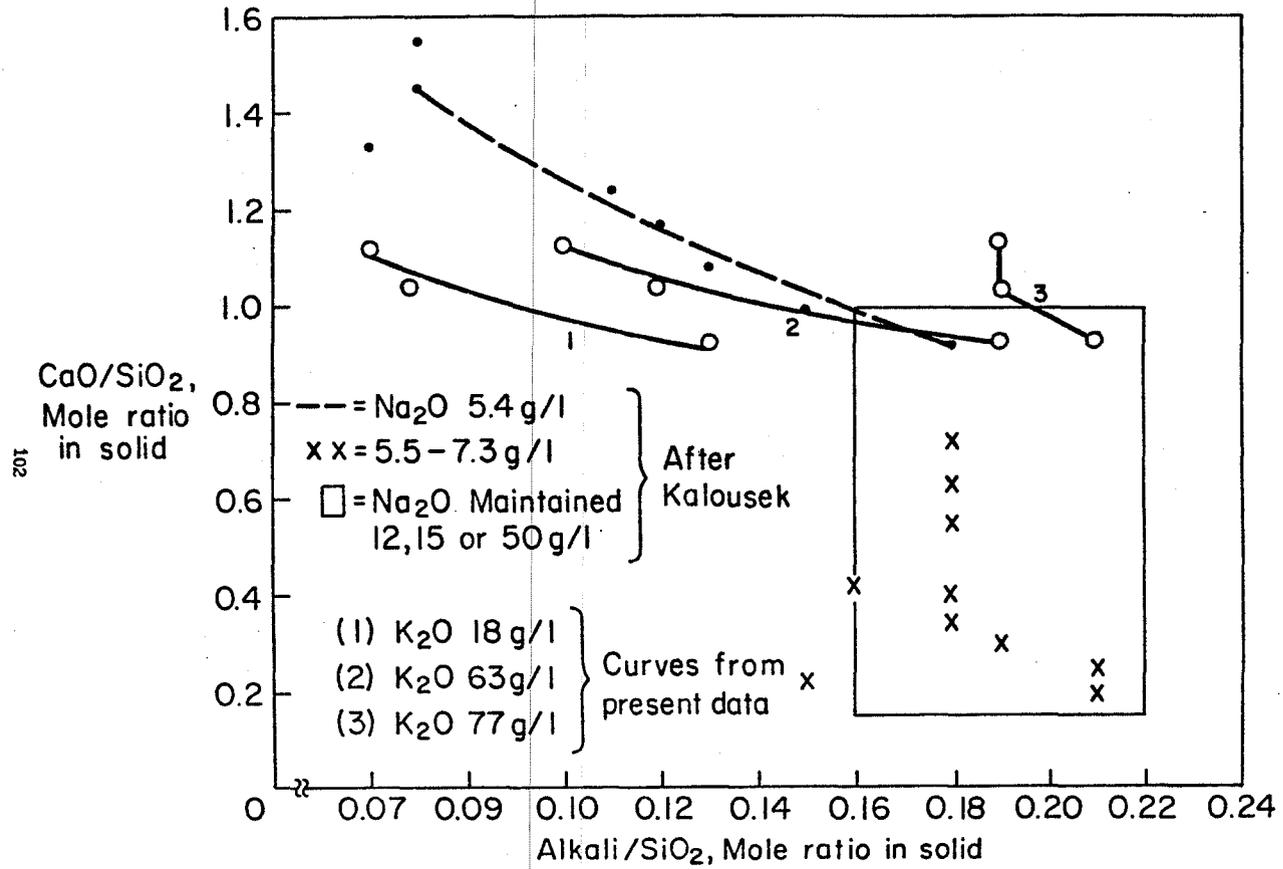


FIGURE 2: ALKALI RETENTION OF VARIOUS CALCIUM SILICATE HYDRATES
(DATA FROM KALOUSEK AND FIGURE 1)

OLiOH

103

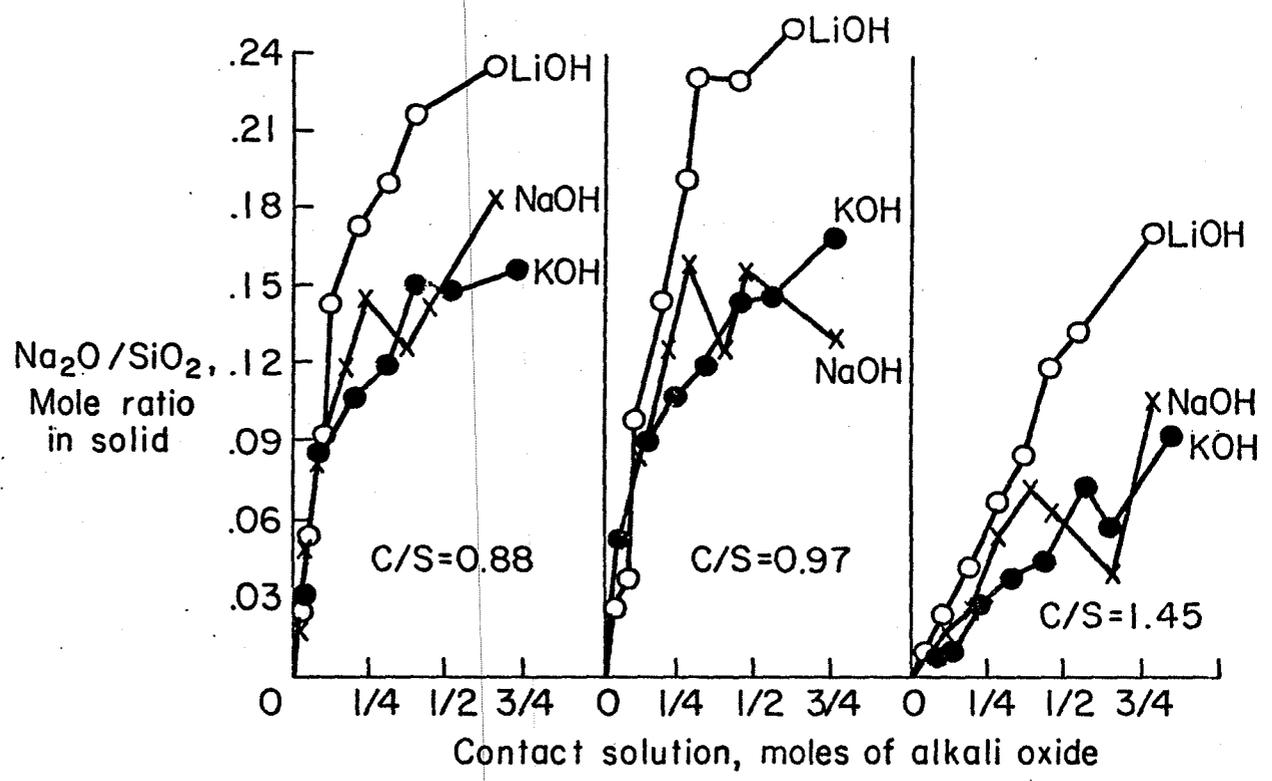


FIGURE 3: REACTION OF VARIOUS CALCIUM SILICATE HYDRATES WITH DIFFERENT CONCENTRATIONS OF DIFFERENT ALKALIES

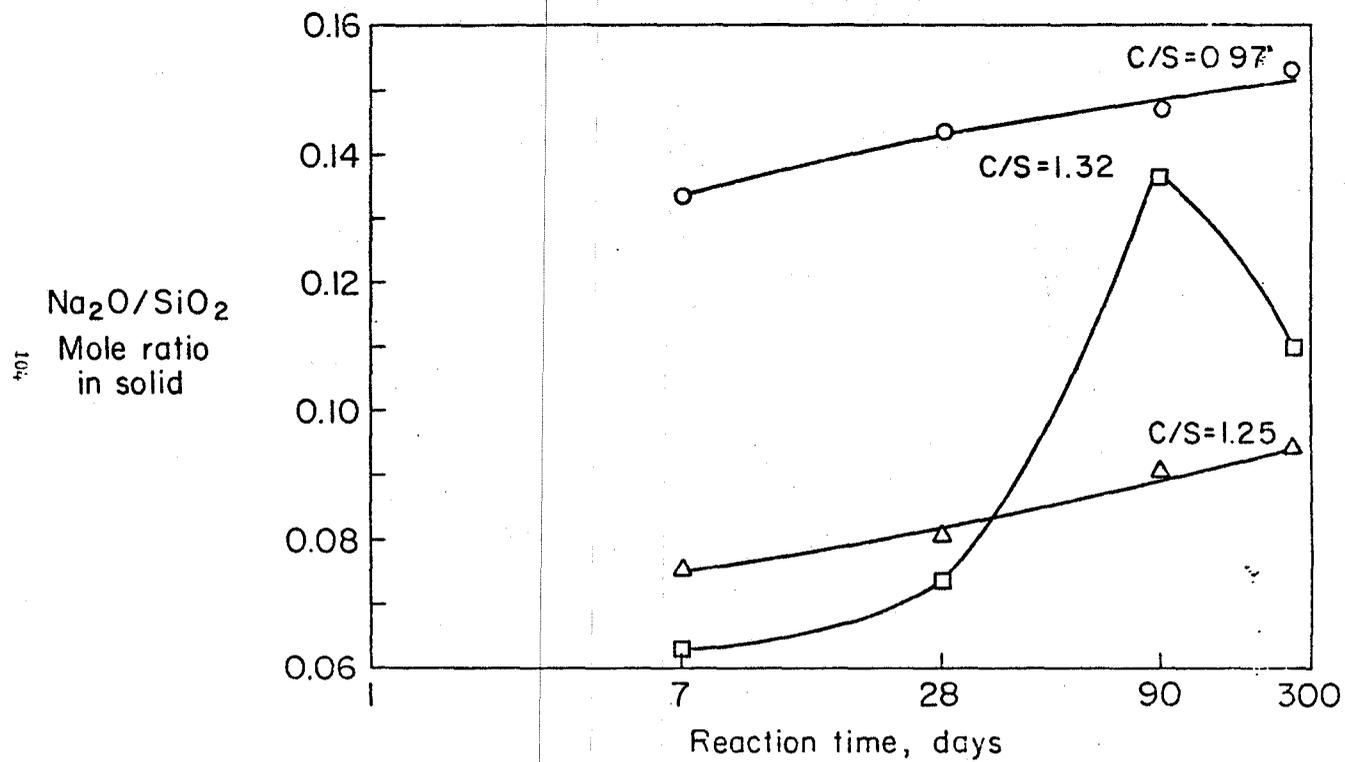


FIGURE 4: REACTION OF CALCIUM SILICATE HYDRATES WITH ONE NORMAL NaOH

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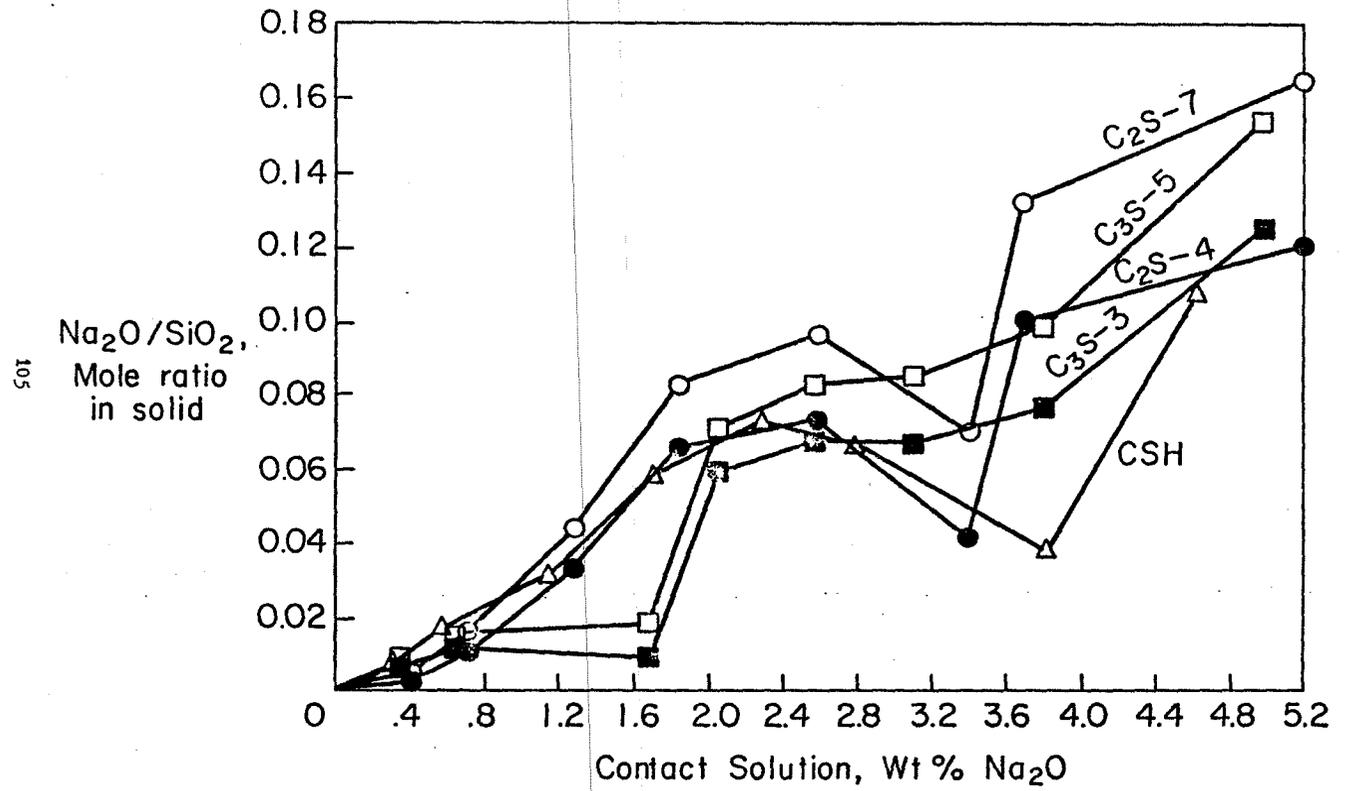


FIGURE 5: HYDRATION OF C_2S AND C_3S IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF NaOH FOR 90 DAYS, DATA FOR CSH TAKEN FROM FIGURE 3.

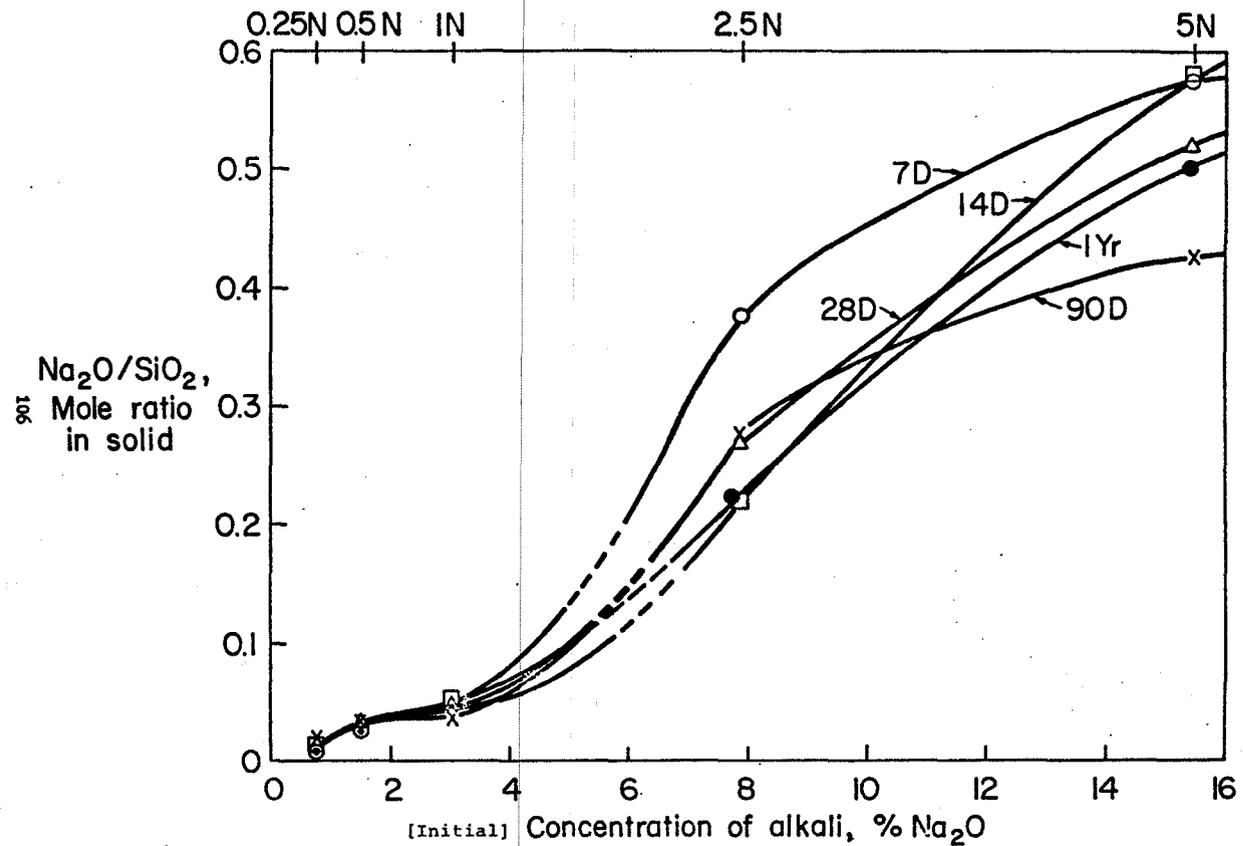


FIGURE 6: HYDRATION OF C₃S IN THE PRESENCE
OF DIFFERENT CONCENTRATIONS OF NaOH

0.5N

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2.5N

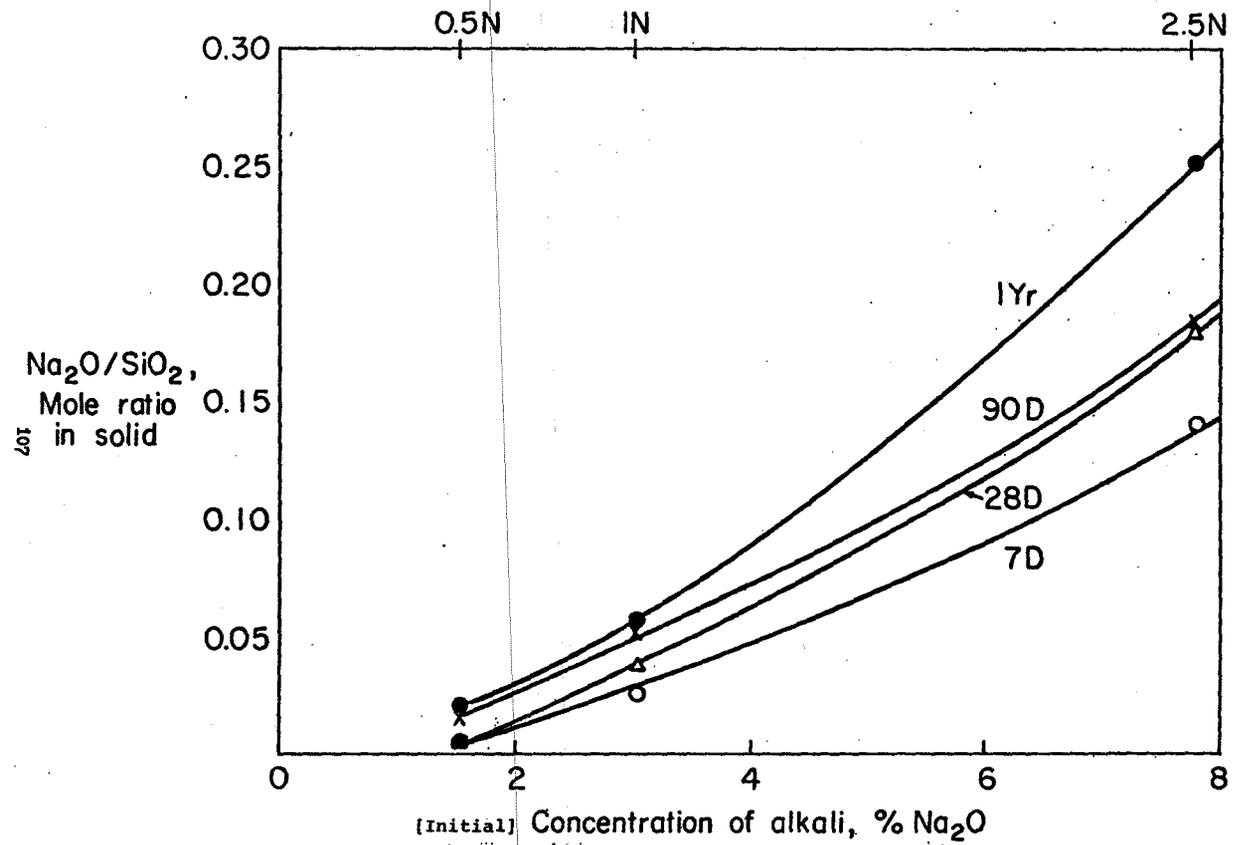


FIGURE 7: HYDRATION OF C₂S IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF NaOH

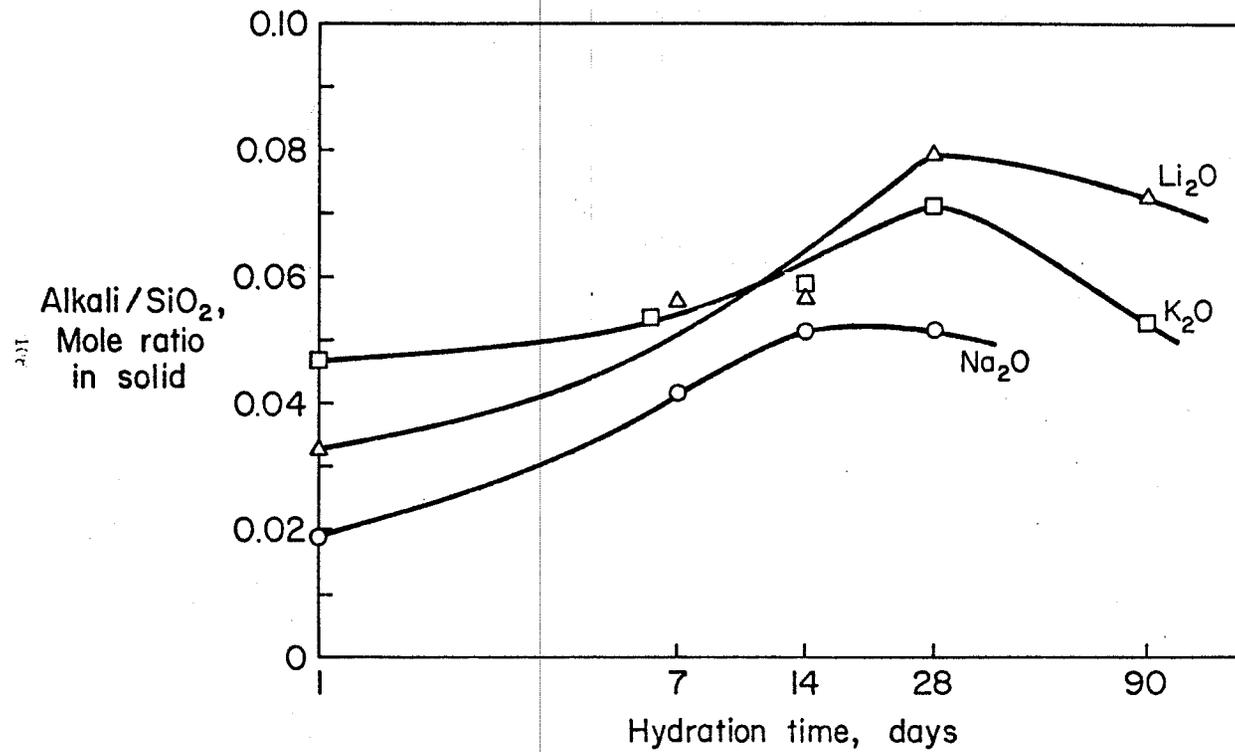


FIGURE 8: HYDRATION OF C₃S IN THE PRESENCE OF DIFFERENT ALKALIES
OF ONE NORMAL CONCENTRATION

0.10

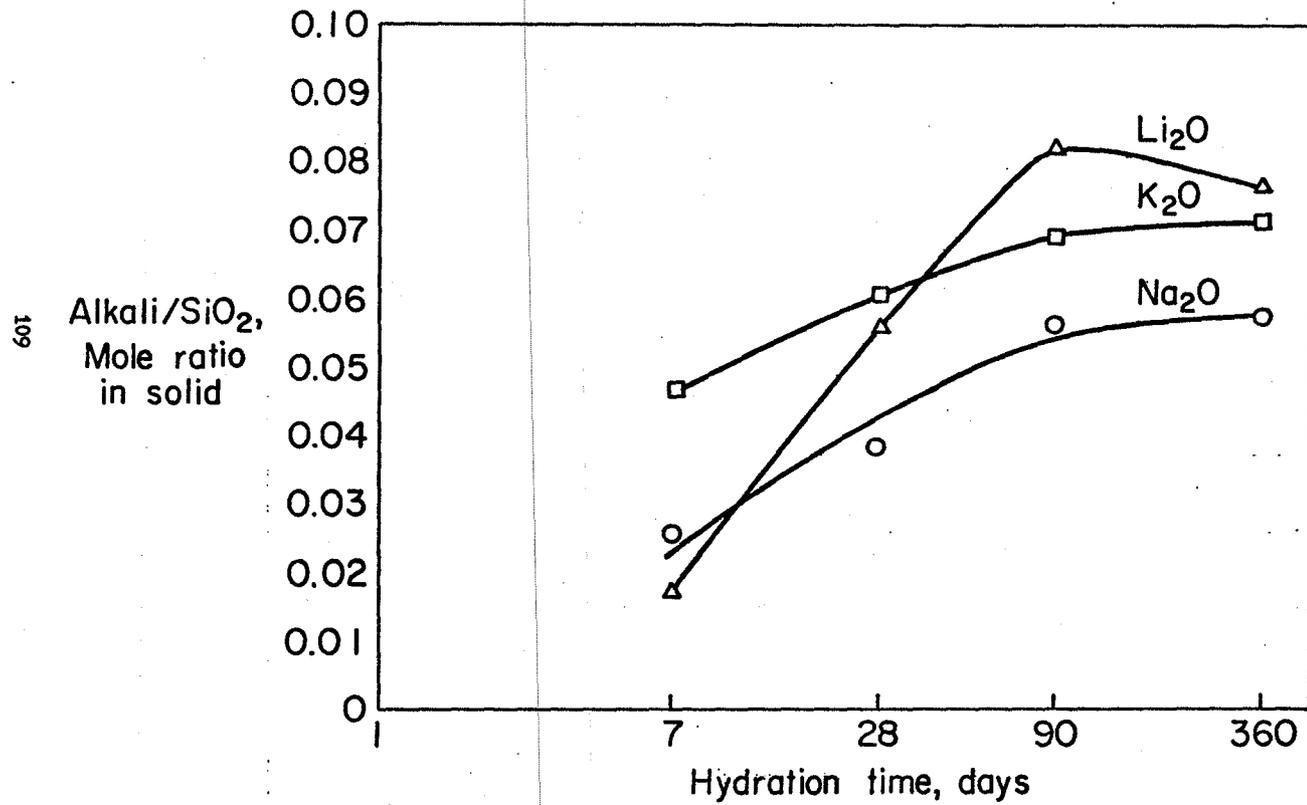


FIGURE 9: HYDRATION OF C₂S IN THE PRESENCE OF DIFFERENT ALKALIES OF ONE NORMAL CONCENTRATION

	SiO ₂	CaO	L.O.I. *	CO ₂	$\frac{\text{CaO}}{\text{SiO}_2}$ mole ratio
(1)	36.93%	33.56%	29.60%	0.84%	0.97
(2)	35.68%	41.72%	22.28%	1.97%	1.25
(3)	34.34%	42.35%	22.95%	1.89%	1.32
* L.O.I. includes CO ₂					

TABLE 1: CHEMICAL COMPOSITION OF CALCIUM SILICATE HYDRATES

TABLE 2: COMPOSITION OF MIXED ALKALI OXIDES BY CALCIUM SILICATE HYDRATES

TABLE 2: SORPTION OF MIXED ALKALI OXIDES BY CALCIUM SILICATE HYDRATES

Sample No.	Mole Ratios of Original Synthetic Ca Silicate Hydrates		Original Solution Concentration, Moles Nominal				Reaction Time, Days	Calculated Final Mole Ratios of Solids			Final Solution		Change in Cl ⁻ %
	CaO / SiO ₂	H ₂ O / SiO ₂	LiOH	LiCl	NaOH	NaCl		M ₂ O / SiO ₂	Na ₂ O / SiO ₂	Li ₂ O / SiO ₂	*OH ⁻ as % Li ₂ O	**M ⁺ as % Li ₂ O	
1a	0.88	2.66	--	0.6894	0.7162	--	20	0.165	0.086	0.079	0.41	1.32	+0.2
1b	0.88	2.66	--	0.6894	0.7162	--	98	0.183	0.089	0.094	0.32	1.25	-0.1
2a	0.88	2.66	--	--	0.6880	0.6712	20	0.15	0.15	--	0.31	1.36	+0.07
2b	0.88	2.66	--	--	0.6880	0.6712	98	0.13	0.13	--	0.42	1.45	+0.05
3a	0.88	2.66	0.4174	--	0.3516	--	20	0.135	0.066	0.069	0.52	0.52	--
3b	0.88	2.66	0.4174	--	0.3516	--	98	0.16	0.075	0.085	0.41	0.41	--
4a	0.97	4.07	--	0.6894	0.7162	--	20	0.17	0.083	0.088	0.51	1.46	+0.03
4b	0.97	4.07	--	0.6894	0.7162	--	98	0.198	0.093	0.106	0.42	1.35	-0.01
5a	0.97	4.07	--	--	0.6880	0.6712	20	0.158	0.158	--	0.43	1.44	+0.01
5b	0.97	4.07	--	--	0.6880	0.6712	98	0.137	0.137	--	0.53	1.52	-0.04
6a	0.97	4.07	0.4174	--	0.3516	--	20	0.142	0.064	0.078	0.60	0.60	--
6b	0.97	4.07	0.4174	--	0.3516	--	98	0.143	0.066	0.077	0.59	0.59	--
7a	1.45	2.41	--	0.6894	0.7162	--	20	0.077	0.033	0.044	0.85	1.80	+0.04
7b	1.45	2.41	--	0.6894	0.7162	--	98	0.103	0.045	0.058	0.73	1.71	--
8a	1.45	2.41	--	--	0.6880	0.6712	20	0.072	0.072	--	0.73	1.76	+0.04
8b	1.45	2.41	--	--	0.6880	0.6712	98	0.009	0.009	--	0.98	2.00	--
9a	1.45	2.41	0.4174	--	0.3516	--	20	0.049	0.016	0.033	0.95	0.95	--
9b	1.45	2.41	0.4174	--	0.3516	--	98	0.065	0.021	0.044	0.86	0.86	--

*Total moles of alkali oxides minus 1/2 number of moles of chloride X 29.88 gives solution % wt. as Li₂O.

**Total alkalies calculated as % by wt. of solution as Li₂O.

