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DISSOLUTION AND HYDRATION OF C_3A-Na_2O SOLID SOLUTIONS

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ABSTRACT

This presentation highlights the dissolution and hydration data obtained on several C_3A preparations in solid solution with varying amounts of Na_2O . Almost all Na_2O present in the solid solution was released into the liquid phase of the hydrating system within a few hours, indicating nearly complete dissociation and hydration of the solid solution. With increasing Na_2O content in the solid solutions, the concentration of CaO decreased and that of Al_2O_3 increased in the liquid phase. The effect was apparently independent of the source of Na_2O . The Na_2O concentrations in the liquid phase were unaffected when the solid solutions were hydrated in the presence of C_3S . The data show that the hydration of solid solutions is not significantly affected by the incorporation of different amounts of Na_2O .

Keywords: cement, alkali, liquid phase, C_3A

INTRODUCTION

Alkalies in portland cement clinker have become increasingly important for two principal reasons: firstly, they can become incorporated in the structure of clinker minerals resulting in several polymorphs or solid solutions of different hydration reactivities with subsequent effect on the mechanical properties of cement and concrete; secondly, their presence in the concrete pore fluid may lead to the well-known alkali-silica reaction. Until recently, the subject of hydration reactivity of clinker minerals as a result of alkali incorporation has received relatively little attention [1-5]. Also, only limited and indirect evidence is available concerning, if and to what extent, the distribution of alkalies among cement phases affects the alkali-silica reaction. Although correlations between alkali content of cement and alkali-silica expansion have been reported [6-9], there appears to be no published data relating the alkali content of individual clinker minerals and the alkali-silica expansion.

Since hydration of portland cement is essentially a dissolution-precipitation process, the rate of hydration and dissolution of various alkali-containing cement clinker minerals is of great importance for both reasons mentioned above. The nucleation and precipitation of hydration products is affected by the composition of the liquid phase of the hydrating system. It is, therefore, of special interest to determine how the alkali content of clinker minerals would affect the concentration of alkalies and other species in the liquid phase of the hydrating system. Of all cement clinker minerals, tricalcium aluminate (C_3A) is the most reactive with water and can also incorporate substantial amounts of alkalies in its structure. This note describes some initial studies on the hydration and dissolution of C_3A phases containing various amounts of Na_2O in solid solution.

EXPERIMENTAL

The various Na₂O-C₃A solid solutions were prepared by sintering mixtures of reagent grade CaCO₃, Al₂O₃ and Na₂CO₃ in the same proportions as used by Boikova et al. [2]. Each mixture was first calcined at 1000°C and then burned and cooled three times as follows: heated at 1400°C for 2 hours in a platinum crucible, cooled to 1200°C in the furnace and then air-quenched. After each burn, the samples were ground in a vibratory mill. By using the same thermal treatment for all mixtures, we hoped to avoid any reactivity differences that could be caused by different thermal histories.

Table 1 gives chemical and X-ray diffraction (XRD) analyses of our preparations. As shown there, all samples are either cubic or mixtures of cubic and orthorhombic C₃A. No other sodium-containing compounds were detected, but all samples contained trace amounts of C₁₂A₇.

Table 1
Chemical Analyses of Na₂O-C₃A Preparations

Sample Number	%CaO	%Al ₂ O ₃	%Na ₂ O	Polymorph*
1	63.48	36.46	0.34	Cu
2	61.68	36.84	1.70	Cu
3	61.25	36.41	2.65	Cu + Or
4	59.26	36.79	3.85	Or + Cu
5	58.84	36.46	4.90	Or + Cu

* Cubic (Cu) or orthorhombic (Or) with the polymorph listed in order of decreasing amount.

Hydration experiments were carried out on fractions of each sample between 325 mesh and 400 mesh (after grinding in a vibratory mill). Suspensions of 2 g sample and 150 ml distilled water or NaCl solution (w/s = 75) were continuously stirred at room temperature. At the selected times (between 5 minutes and 24 hours) approximately 5 ml of each suspension were withdrawn using a syringe and filtered through a 0.45 micron millipore filter. The clear filtrate was acidified and analyzed for Na, Ca, and Al by atomic absorption spectrophotometry. The solid residue was washed with acetone, vacuum dried at room temperature and examined by XRD, differential thermal analysis (DTA) and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Results of the analyses of the liquid phase during the hydration of various solid solutions are shown in Figures 1-3. For clarity, the figures include only C₃A samples 1 and 5, the highest and lowest in Na₂O content. Liquid phase

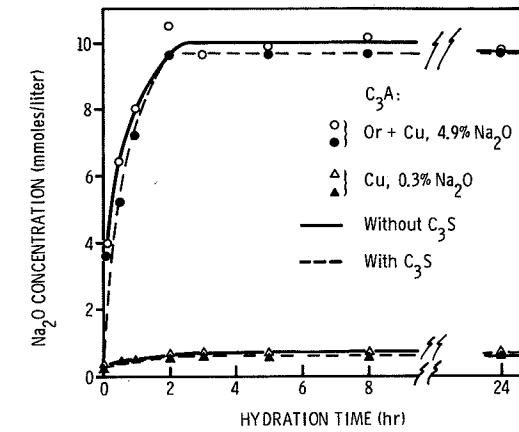


Fig. 1. Na₂O concentration in the liquid phase of the C₃A-Na₂O solid solutions (w/s = 75).

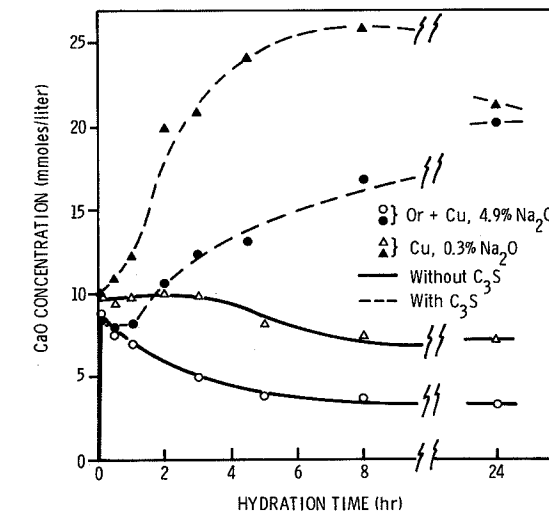


Fig. 2. CaO concentration in the liquid phase of the C₃A-Na₂O solid solutions (w/s = 75).

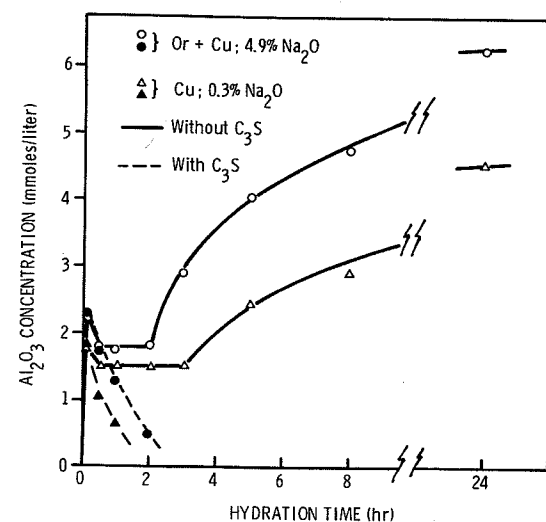


Fig. 3. Al_2O_3 concentration in the liquid phase of the $\text{C}_3\text{A-Na}_2\text{O}$ solid solutions ($w/s = 75$).

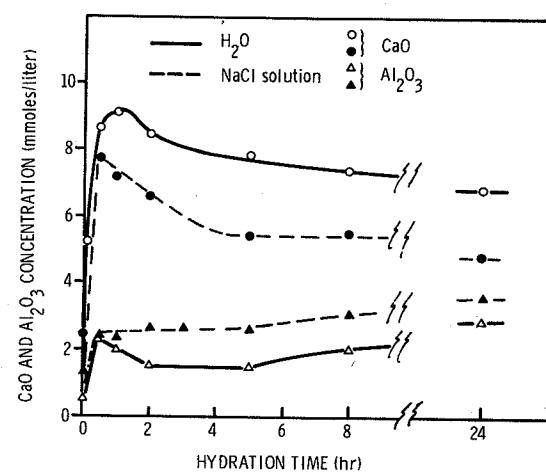


Fig. 4. Effect of NaCl on CaO and Al_2O_3 concentrations of $\text{C}_3\text{A-Na}_2\text{O}$ solid solutions ($w/s = 75$).

analyses were also carried out on the other three samples that are intermediate in Na_2O contents. These samples were in every case likewise intermediate in the liquid phase composition. The Na_2O concentration in the liquid phase increased rapidly (Figure 1) and by 5 hours nearly all the Na_2O present in the solid solution passed into the liquid phase indicating complete dissolution of the material. The XRD patterns of the solid residues collected on the filters also did not show any unhydrated C_3A after 5 hours. The data do not indicate any significant differences in the dissolution rate of various solid solutions. The CaO concentrations (Figure 2), after an initial increase in the very early stages, gradually decreased up to about 2-5 hours, after which there was very little change up to 24 hours. The CaO concentration is seen to depend on the Na_2O content of the solid solution and decreases with increase in its Na_2O content (even when the decreased CaO content with increased Na_2O content in the starting material is considered). Our data on Na_2O and CaO concentrations show good qualitative agreement with those of Shin and Glasser [5]. Also, in agreement with their observations, we noticed a maximum in the CaO curve for the low- Na_2O solid solution which was suppressed at high Na_2O content. The Al_2O_3 concentration (Figure 3), after an initial drop at about 1-2 hours, continued to increase up to 24 hours. Like CaO, it also showed a dependence on the Na_2O content of the solid solution, being higher for the high- Na_2O solid solution.

The hydrating C_3A system is a very complex system involving numerous species. The dissolution of C_3A results in soluble species such as Ca^{+2} , CaOH^+ , OH^- , $\text{Al}(\text{OH})_4^-$ and some polynuclear complexes as a result of hydrolysis of aluminum ions. The hydrating system also involves presence of several solid species such as C_2AH_8 , C_4AH_{13} (or C_4AH_{19}), and C_3AH_6 , in addition to unhydrated C_3A . The various reactions during hydration can also produce $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$. For these reasons, it is very difficult to single out one factor accounting for the observed changes in the liquid phase composition. Presence of NaOH in the liquid phase increases the solubility of $\text{Al}(\text{OH})_3$ [10], and decreases that of $\text{Ca}(\text{OH})_2$ [11]. Conversion of hexagonal C_2AH_8 to cubic C_3AH_6 can produce Al-containing species in the liquid phase. According to Spierings and Stein [1], the Al-O network of C_3A can be destroyed by high OH^- concentrations such as would be present in NaOH solution. The liquid phase data for Na_2O and the XRD results show that almost all C_3A has hydrated within the first few hours and, therefore, at later periods, the dissolution and electrokinetic properties of the various hydrates become increasingly important.

Alkalies from soluble alkali sulfates in portland cement pass readily into the liquid phase of the hydrating system, whereas those present in solid solution with clinker minerals may take much longer to dissolve. It is, therefore, of interest to see if any difference exists between the effect of alkalies already present in the liquid phase of the hydrating system and those present in solid solutions on the dissolution and hydration of clinker minerals. Suspension hydration of pure C_3A was performed in the same manner as described above in distilled water and NaCl solution (600 ppm with respect to Na_2O to approximate the Na_2O content of the liquid phase of high- Na_2O solid solution). NaCl, rather than NaOH, was used to avoid any effect that any change in pH of the liquid phase may have on the dissolution behavior of C_3A . The data on the liquid phase analysis, shown in Figure 4, are qualitatively the same as for the Na_2O -containing solid solutions. These results indicate that the effect of Na_2O on the dissolution behavior of hydrating C_3A is independent of its source. This is in contrast to the observation of Shin and Glasser [5] who reported a decrease in both the calcium and aluminum concentrations after 30 hours of hydration of C_3A when sodium was added as NaOH. They tentatively ascribed this observation to the formation on the C_3A surface of $\text{Ca}(\text{OH})_2$ which subsequently reacted with Al in the liquid phase to form C_3AH_6 and depleted the

solution in Al. Our studies show an increase in Al_2O_3 concentration with increase in Na_2O content. At this stage, however, we are unable to account for this observation. Addition of NaCl will apparently change the ionic strength of the liquid phase, which may affect the electrokinetic behavior and, consequently, the dissolution of C_3A . This phenomenon clearly needs more study.

Figures 1, 2, and 3 also show the liquid phase analysis data for the suspension hydration of solid solutions in the presence of C_3S . The Na_2O concentrations for both low- and high- Na_2O solid solutions follow almost the same curves as those in the absence of C_3S . The low- Na_2O solid solution showed higher CaO concentration than the high- Na_2O material at least up to 8 hours and almost the same at 24 hours. A decrease in CaO concentration from 8 to 24 hours was noted for high- Na_2O solid solution. The Al_2O_3 concentrations for both solid solutions showed a drastic drop and, after about 2 hours, were almost undetectable. These results show that practically all the Na_2O from the solid solutions is released into the liquid phase, indicating absence of any effect by C_3S on the rate of dissolution of C_3A . However, the DTA results indicate that the rate at which hexagonal and cubic hydrates form and at which hexagonal hydrates transform into the cubic hydrates appears to be affected by the presence of C_3S . The results also imply that no Na_2O is incorporated in the calcium silicate hydrates up to 24 hours, at least at the w/s ratios used in the present study. The disappearance of Al_2O_3 from the liquid phase could be due to two reasons: its incorporation in the calcium silicate hydrates and its consumption in the formation of calcium aluminate hydrates.

To complement liquid phase data, the solid residues remaining on the millipore filters were examined using the techniques of XRD, DTA and SEM. Both low and high- Na_2O solid solutions essentially gave the same hydration products and only some minor differences as to their amounts were noticed. Cubic hydrates (C_3AH_6), in addition to hexagonal hydrates such as C_2AH_8 , were observed as early as 5 minutes of hydration in both cases. Similar results have also been reported by Spierings and Stein in their studies of effect of Na_2O on the hydration and hydration products of C_3A [1]. The high- Na_2O solid solution showed somewhat more cubic hydrates in the early stages, but at later stages, the trend reversed. XRD did not show any $Al(OH)_3$ as reported by Shin and Glasser [5]. The DTA showed presence of $Ca(OH)_2$ in the hydration products in both cases at all times after 5 hours. Presence of NaOH in the liquid phase can contribute to the precipitation of $Ca(OH)_2$. Decomposition of cubic C_3AH_6 in alkaline solutions has also been reported to give $Ca(OH)_2$ [12]. In general, the examination of the solid phases of the hydrating systems by XRD, DTA and SEM did not give any conclusive evidence of distinct retardation of C_3A as a result of incorporation of Na_2O as reported by several workers [1-4].

CONCLUSIONS

Present work on the suspension hydration of Na_2O - C_3A solid solutions leads to the following conclusions:

1. Na_2O from the solid solution appears to enter the liquid phase at the same rate as the solid solution dissolves and nearly all Na_2O is in the liquid phase within a few hours.

2. Little difference is apparent in the rate of hydration at different levels of Na_2O in the solid solution.

3. With increasing Na_2O content in the solid solutions, there is a decrease in CaO concentration and increase in the Al_2O_3 concentration of the liquid phase. This trend was found to be independent of the source of sodium in the liquid phase.

4. In the presence of C_3S , the concentration of Na_2O in the liquid phase does not seem to be affected, but the concentration of Al_2O_3 is drastically decreased.

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