THE INFLUENCE OF Na₂O ON THE HYDRATION OF C₃A.
I. PASTE HYDRATION

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ABSTRACT

The influence of Na₂O on the hydration of C₃A was studied both by following the hydration of xNa₂O.(3-x)CaO.Al₂O₃ (0<x<0.25) in water, and of C₃A in solutions of NaOH. Low NaOH concentrations prevent a very early appearance of the second heat evolution peak, indicating a more controlled formation of C₃AH₆ nuclei. Higher NaOH concentrations advance the second peak; this is ascribed to a decreased stability of the hexagonal hydrates with increasing NaOH concentrations.

Der Einfluss von Na₂O auf die Hydratation des C₃A wurde untersucht sowohl mittels der Hydratation von xNa₂O.(3-x)CaO.Al₂O₃ (0<x<0.25) in Wasser und von C₃A in NaOH-Lösungen. Niedrige NaOH-Konzentration verhindern ein sehr frühes Auftreten des zweiten Wärmeentwicklungspeaks; dieses deutet auf eine besser beherrschte Keimbildung des C₃AH₆ hin. Höhere NaOH-Konzentrationen verfrühen den zweiten Peak; dieses wird einer abnehmenden Stabilität der hexagonalen Hydrate mit steigender NaOH-Konzentration zugeschrieben.
Introduction

The alkalies in a portland cement clinker have a distinct influence on the strength development of a cement paste prepared from it (1,2). As a first step in understanding this effect the influence of alkalies on the hydration mechanism of portland cement minerals has to be studied.

The alkalies can be incorporated into a number of phases in the clinker. Part of the Na\textsubscript{2}O is normally taken up by the C\textsubscript{3}A. Recent work (3,4) has shown that there exist several series of solid solutions of general formula xNa\textsubscript{2}O.(3-x)CaO.Al\textsubscript{2}O\textsubscript{3}, of which a cubic one with 0<x<0.08, an orthorhombic one with 0.16<x<0.20 and a monoclinic one with 0.20<x<0.25 are relevant to the present investigation. When 0.08<x<0.16 a mixture of two phases is found.

Some aspects of the influence of Na\textsubscript{2}O on the hydration of C\textsubscript{3}A have been investigated (5-9) but no detailed study has been reported. The present investigation deals with the paste hydration of C\textsubscript{3}A in solutions of NaOH and of xNa\textsubscript{2}O.(3-x)CaO.Al\textsubscript{2}O\textsubscript{3} in water.

Experimental

Methods

Specific surface was determined by N\textsubscript{2} adsorption in an Areameter ("Ströhlein"). Free lime was determined by the method of Pressler et al. (10). Scanning electron micrographs (SEM) were made using a Cambridge MK-2A instrument.

X-ray analysis was performed using a Philips diffractometer PW1010 with filtered Cu radiation; the quantities of the compounds present were estimated from the intensities of characteristic peaks, which are given in arbitrary units (vw<vw<w<mw<m<s<s). The peaks used were the same as those used by Corstanje, Stein and Stevels (11) together with the 10.7 Å peak for C\textsubscript{2}AH\textsubscript{8}.

Isothermal calorimetry was performed at 25°C as described previously (12). The pastes were prepared and the hydration reactions arrested as described by de Jong, Stein and Stevels (13). Calcium was determined by a spectrophotometric titration method (Slanina et al. (15)). Sodium was determined using a sodium ion electrode (Swasey (16)).

Materials

The Na\textsubscript{2}O containing C\textsubscript{3}A samples were prepared from mixtures of CaCO\textsubscript{3} (p.a. Merck), Al\textsubscript{2}O\textsubscript{3} (U.C.B.; loss on ignition 0.57%) and Na\textsubscript{2}CO\textsubscript{3} (p.a. Merck). The starting materials were mixed in an agate ball mill, heated three times in platinum crucibles for two hours at 1325°C with intermediate grinding, and sieved. The fractions with particles smaller than 36 μm were used. C\textsubscript{3}A was prepared as described by de Jong, Stein and Stevels (13). Table I contains some data for the materials.

According to Regourd and Guinier(3), C\textsubscript{3}A and N\textsubscript{0.05}C\textsubscript{0.95}A are cubic while N\textsubscript{0.25}C\textsubscript{0.75}A is monoclinic, and N\textsubscript{0.45}C\textsubscript{0.55}A a mixture of the cubic and orthorhombic phases. The samples were characterized by their X-ray diffractograms which agreed completely with the data given by Regourd and Guinier.

The water used was distilled twice and boiled and cooled to room
temperature shortly before use. The alkali hydroxide solutions were prepared from LiOH·H₂O (Koch light >99%), NaOH and KOH (Titrisol Merck) and RbOH (Koch light >99.8%). The NaAl(OH)₄ solutions were prepared by dissolving Al ribbon (p.a. Merck) in aqueous NaOH solution. All preparations were carried out using a glove box with a N₂-atmosphere free from CO₂.

TABLE I

<table>
<thead>
<tr>
<th>Specific surface</th>
<th>Free Ca/Na</th>
<th>Theoretical</th>
<th>Analysis</th>
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<tbody>
<tr>
<td>cm²/g</td>
<td>%</td>
<td>C₃A</td>
<td>Na₂O</td>
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<td>C₃A</td>
<td>3210</td>
<td>0.3</td>
<td>2890</td>
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<td>N₀.₀₅C₂.₉₅A</td>
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<td>0.15</td>
<td>2.75</td>
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<tr>
<td>N₀.₁₅C₂.₈₅A</td>
<td>3060</td>
<td>0.3</td>
<td>2.75</td>
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<tr>
<td>N₀.₂₅C₂.₇₅A</td>
<td>2670</td>
<td>0.7</td>
<td>2.75</td>
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</table>

Hydration of C₃A in Solutions of Alkali Hydroxide or Hydroxoaluminate

Results

Fig. 1 gives typical heat evolution curves for pastes (w/s = 1) made with C₃A and water or aqueous NaOH. In Fig. 2, the time...
of the second heat evolution peak is plotted against NaOH concentration. Heat evolution in the first 15 minutes decreases with increasing NaOH concentration. With water or NaOH less concentrated than about 0.5M, the time of the second peak is not very reproducible. With more concentrated NaOH, the reproducibility is much better, and the occurrence of this peak at very short times is prevented. The time of the second peak falls with concentration above 1M. Mori et al. (6) also found this.

X-ray results (Table II) show that C₃AH₆ is formed within 10 minutes and that its amount increases with time thereafter. At short times the amount is virtually independent of NaOH concentration. Hexagonal hydrates were only once found (after 20h in 2N NaOH) with X-rays, but the SEM (Figs. 3 and 4) showed the presence after 10 minutes of hydrates other than C₃AH₆. These had a platey habit reminiscent of that of hexagonal hydrates. The absence of the characteristic X-ray peaks indicates that hexagonal hydrates, if formed, are much disordered.

The effect of varying the alkali cation was studied using 2M solutions. The only observed effect was a small decrease in heat evolution rate over the whole period of hydration when the cation radius was increased.

Fig. 5 shows the effect of adding NaAl(OH)₄ as well as NaOH. The second heat evolution peak is depressed and slightly retarded.

Discussion

Addition of NaOH lowers the solubility of Ca(OH)₂ and increases that of Al(OH)₃. Berger, Kotsupalo and Pushnyakova (16) found that aqueous alkali partly decomposes C₃AH₆ to give Ca(OH)₂, C₄AH₁₃ and aluminate ions in solution, but Jones (17) found in a study of the C-A-N-H system that C₃AH₆ is stable in 1% NaOH, even

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FIG. 3
SEM of C₃A hydrated for 10 minutes in water

FIG. 4
SEM of C₃A hydrated for 10 minutes in 2M NaOH
Table II

X-ray Data on Paste
Hydration of C₃A in
water and NaOH solutions*

<table>
<thead>
<tr>
<th>NaOH Hydration (M)</th>
<th>C₃A</th>
<th>C₂AH₈</th>
<th>C₃AH₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0.2</td>
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<td></td>
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<tr>
<td>0.2</td>
<td></td>
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<tr>
<td>0.2</td>
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</tbody>
</table>

Neither Ca(OH)₂ nor
C₄AHₓ was ever detected.

at low aluminate ion concentrations. The result of Berger,
Kotsupalo and Pushnyakova can be ascribed to the initial absence
in the solution of Al(OH)₄⁻. It nevertheless seems strange that no
solid Ca(OH)₂ could be detected in the present work.

Retardation of the hydration reaction after the first peak is
generally attributed to formation of a layer of hydrates, which
impedes the passage of Ca²⁺ and aluminate ions into solution. The
SEM results (Figs. 3 and 4) confirm that such a layer is formed.
However, misfit between C₃A and hexagonal hydrates as regards
interatomic distances and habits will make it difficult to obtain
a fit on an atomic scale, and some space will exist between the
C₃A and the hydrate crystals. Some retardation mechanisms
compatible with the existence of such a space will be discussed
in a later paper (18).

The existence of the second heat evolution peak is generally
attributed to recrystallization of this layer. The effect of
alkali in preventing the very early occurrence of this peak can be
attributed to retardation of the hydration of the C₃A which could
be expected to cause a more controlled growth of C₃AH₆ nuclei.

The fact that the amount of C₃AH₆ formed in the first 10
minutes does not depend on NaOH concentration indicates that the
nucleation of C₃AH₆ is not markedly affected by the type of
aluminate ion present in the solution. The earlier appearance of
the second peak at high alkali concentration might be caused by
changes in the nucleus growth rate of C₃A due to higher aluminate
concentrations. However, the second peak does not occur sooner
when NaAl(OH)₄ is added initially (Fig. 5); therefore the earlier
occurrence of the second peak is attributed to changes in the rate
at which Al(OH)₄ passes into solution from the hexagonal hydrates.
Hydration of $x\text{Na}_2\text{O}.(3-x)\text{CaO}.\text{Al}_2\text{O}_3$ Solid Solutions

Figs. 6 and 7 give heat evolution curves for several preparations and mixtures thereof. As with hydration of $\text{C}_3\text{A}$ in NaOH solutions, $\text{Na}_2\text{O}$ causes the first peak to occur later though no increase in the effect with $\text{Na}_2\text{O}$ content was observed beyond $x = 0.05$ despite the variations in crystal structure. Mori et al. (6) found a similar effect. The second peak occurred sooner at high $\text{Na}_2\text{O}$ contents.

X-ray results (Table III) showed that $\text{C}_2\text{AH}_8$ was formed initially. The amount decreased after the second peak and none was found after 48 h. A SEM (Fig. 8) of a preparation with $x = 0.25$ hydrated for 50 minutes showed particles coated with typical hexagonal plates.

When these $\text{Na}_2\text{O}$-containing phases hydrate alkali hydroxide accumulates in the solution. The concentration depends on $x$, the time or degree of hydration, and the amount of water left. At $w/s = 1$ the $\text{OH}^-$ concentration could easily reach 0.5-1 M, for example, if in a paste of $N_{0.25}C_{2.75}$A that is 33% hydrated, and assuming no change in volume of the liquid phase, the $\text{OH}^-$ concentration is about 1M. The alkali will have similar effects to those found on hydration of pure $\text{C}_3\text{A}$ in NaOH solutions but the situation is more complex because the alkali hydroxide concentration in solution varies with time.

The fact that the mixture of preparations with $x = 0.05$ and $x = 0.25$ behaves in much the same way as the preparation with $x =$
TABLE III

X-ray Data on Paste Hydration of N0.25C2.75A

<table>
<thead>
<tr>
<th>Hydration time (h)</th>
<th>C₃A</th>
<th>C₂AH₈</th>
<th>C₃AH₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>vs</td>
<td>m</td>
<td>m</td>
</tr>
<tr>
<td>2.50</td>
<td>s</td>
<td>w</td>
<td>s</td>
</tr>
<tr>
<td>48</td>
<td>s</td>
<td>-</td>
<td>vs</td>
</tr>
</tbody>
</table>

*C₄AHₓ was not found.

0.15 indicates that the effects are determined by the alkali hydroxide concentration in solution and not by any particular property of the solid phase; this is consistent with the earlier statements about the second peak.

Acknowledgement

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References


18. G.A.C.M. Spierings and H.N. Stein, to be published.