

The influence of Na₂O on the hydration of C3A I. Paste hydration

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THE INFLUENCE OF Na_2O ON THE HYDRATION OF C_3A .

I. PASTE HYDRATION

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ABSTRACT

The influence of Na_2O on the hydration of C_3A was studied both by following the hydration of $x\text{Na}_2\text{O} \cdot (3-x)\text{CaO} \cdot \text{Al}_2\text{O}_3$ ($0 < x < 0.25$) in water, and of C_3A in solutions of NaOH . Low NaOH concentrations prevent a very early appearance of the second heat evolution peak, indicating a more controlled formation of C_3AH_6 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 Na_2O auf die Hydratation des C_3A wurde untersucht sowohl mittels der Hydratation von $x\text{Na}_2\text{O} \cdot (3-x)\text{CaO} \cdot \text{Al}_2\text{O}_3$ ($0 < x < 0.25$) in Wasser und von C_3A in NaOH -Lösungen.

Niedrige NaOH -Konzentration verhindern ein sehr frühes Auftreten des zweiten Wärmeentwicklungspeaks; dieses deutet auf eine besser beherrschte Keimbildung des C_3AH_6 hin. Höhere NaOH -Konzentrationen verfrühen den zweiten Peak; dieses wird einer abnehmenden Stabilität der hexagonalen Hydrate mit steigender NaOH -Konzentration zugeschrieben.

Introduction

The alkalis 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 alkalis on the hydration mechanism of portland cement minerals has to be studied.

The alkalis can be incorporated into a number of phases in the clinker. Part of the Na_2O is normally taken up by the C_3A . Recent work (3,4) has shown that there exist several series of solid solutions of general formula $x\text{Na}_2\text{O} \cdot (3-x)\text{CaO} \cdot \text{Al}_2\text{O}_3$, 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_2O on the hydration of C_3A have been investigated (5-9) but no detailed study has been reported. The present investigation deals with the paste hydration of C_3A in solutions of NaOH and of $x\text{Na}_2\text{O} \cdot (3-x)\text{CaO} \cdot \text{Al}_2\text{O}_3$ in water.

Experimental

Methods

Specific surface was determined by N_2 adsorption in an Areometer ("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 ($v\text{vw} < v\text{w} < w < m\text{w} < m < m\text{s} < s < v\text{s}$). The peaks used were the same as those used by Corstanje, Stein and Stevels (11) together with the 10.7 Å peak for C_2AH_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_2O containing C_3A samples were prepared from mixtures of CaCO_3 (p.a. Merck), Al_2O_3 (U.C.B.; loss on ignition 0.57%) and Na_2CO_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_3A 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_3A and $\text{N}_{0.05}\text{C}_{2.95}\text{A}$ are cubic while $\text{N}_{0.25}\text{C}_{2.75}\text{A}$ is monoclinic, and $\text{N}_{0.15}\text{C}_{2.85}\text{A}$ 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

Data on Materials Employed

	Specific surface cm ² g ⁻¹	Free lime %	Ca/Na	
			Theoretical	Analysis
C ₃ A	3210	0.3	--	--
N _{0.05} C _{2.95} A	2890	<0.1	27.5	28.1
N _{0.15} C _{2.85} A	3060	0.3	9.5	10.6
N _{0.25} C _{2.75} A	2670	0.7	5.5	6.0

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

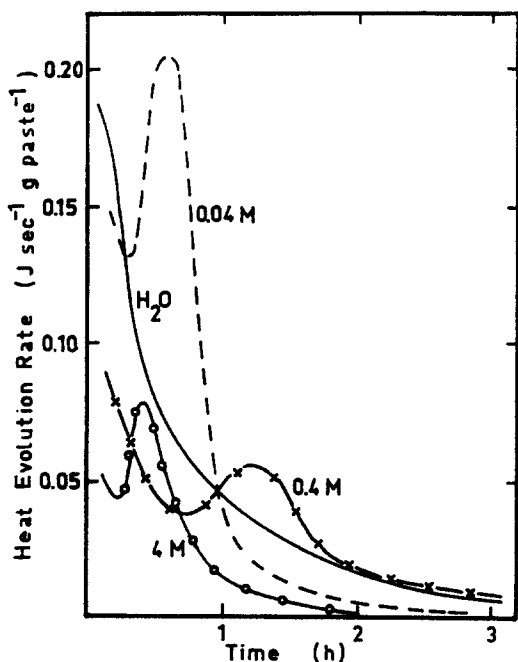


FIG. 1

Heat evolution rates of pastes (w/s = 1) made using water and aqueous NaOH

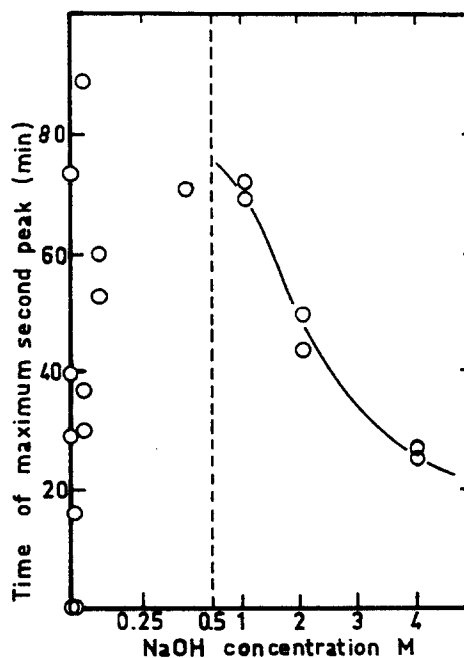


FIG. 2

Time of second heat evolution peak

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 C_3AH_6 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 C_3AH_6 . These had a platy 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 C_3AH_6 to give $Ca(OH)_2$, C_4AH_{13} and aluminate ions in solution, but Jones (17) found in a study of the C-A-N-H system that C_3AH_6 is stable in 1% NaOH, even



FIG. 3

SEM of C_3A hydrated
for 10 minutes in water

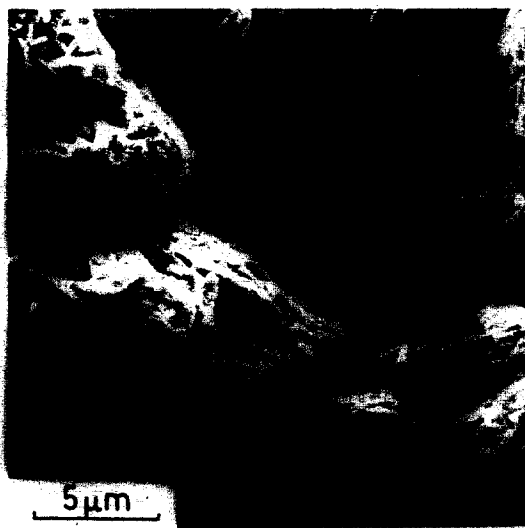


FIG. 4

SEM of C_3A hydrated for
10 minutes in 2M NaOH

C₃A PASTES, ALKALI HYDROXIDE, HYDRATION

Table II

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

NaOH Hydration (M)	time (min)	C ₃ A	C ₂ AH ₈	C ₃ AH ₆
0	10	vs	-	vw
0	30	vs	-	m
0	120	s	-	s
0.04	10	vs	-	vw
0.2	10	vs	-	vw
0.2	50	vs	-	mw
0.2	1200	vs	vvw	m

*Neither Ca(OH)₂ nor C₄AH_x was ever detected.

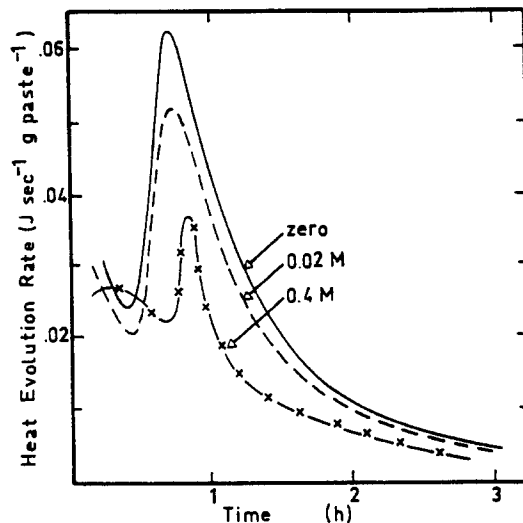


FIG. 5

Heat evolution rates of pastes ($w/s = 1$) containing both NaOH (2M) and NaAl(OH)₄ of concentrations shown

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.

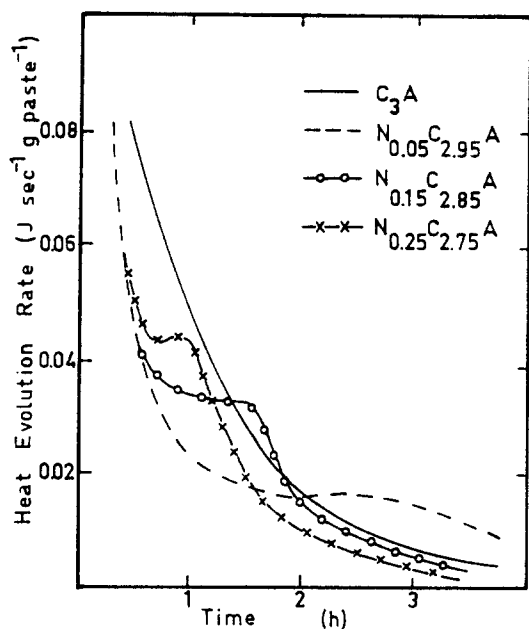


FIG. 6

Heat evolution rates
for pastes of water
and $N_xC_{3-x}A$ preparations

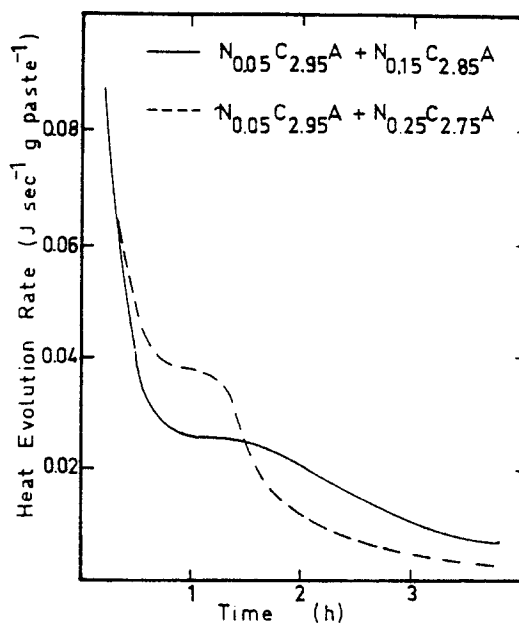


FIG. 7

Heat evolution rates
for pastes of water
and mixtures of $N_xC_{3-x}A$ pastes

Hydration of $xNa_2O \cdot (3-x)CaO \cdot Al_2O_3$ Solid Solutions

Figs. 6 and 7 give heat evolution curves for several preparations and mixtures thereof. As with hydration of C_3A in NaOH solutions, Na_2O causes the first peak to occur later though no increase in the effect with Na_2O 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 Na_2O contents.

X-ray results (Table III) showed that C_2AH_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 Na_2O -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 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 OH^- concentration is about 1M. The alkali will have similar effects to those found on hydration of pure C_3A 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 N_{0.25}C_{2.75}A*

Hydration time (h)	C ₃ A	C ₂ AH ₈	C ₃ AH ₆
0.83	vs	m	m
2.50	s	w	s
48	s	-	vs

*C₄AH_x was not found.

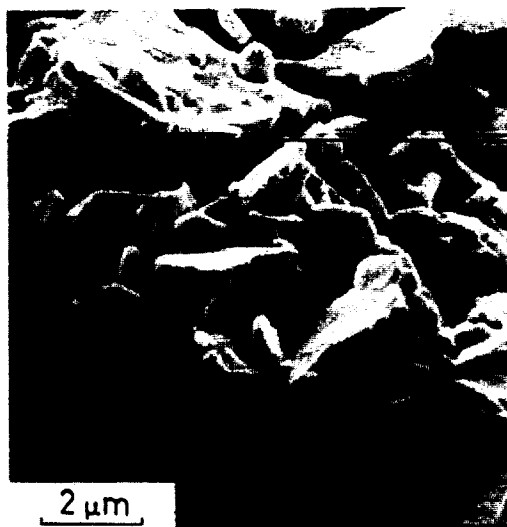


FIG. 8

SEM of N_{0.25}C_{2.75}A hydrated
for 50 min. in water

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.

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