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Citation for published version (APA):

Spierings, G. A. C. M., & Stein, H. N. (1976). The influence of Na₂O on the hydration of C3A II. Suspension hydration. *Cement and Concrete Research*, 6(4), 487-496. [https://doi.org/10.1016/0008-8846\(76\)90077-6](https://doi.org/10.1016/0008-8846(76)90077-6)

DOI:

[10.1016/0008-8846\(76\)90077-6](https://doi.org/10.1016/0008-8846(76)90077-6)

Document status and date:

Published: 01/01/1976

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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THE INFLUENCE OF Na_2O ON THE HYDRATION OF C_3A .

II. SUSPENSION HYDRATION.

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(Communicated by H. F. W. Taylor)
(Received March 25, 1976)

ABSTRACT

The influence of Na_2O on the hydration of C_3A was studied in suspensions from the start of the reaction onwards. The heat evolution rate in very early stages of the hydration, measured at varying NaOH concentrations, and SEM, indicate that at NaOH concentrations larger than 0.1 M the reaction mechanism differs from that in water. In these solutions the hydration is thought to be controlled at first by a more or less amorphous $\text{Ca}(\text{OH})_2$ layer.

Der Einfluss von Na_2O auf die Hydratation des C_3A wurde untersucht vom Anfang der Reaktion an. Die Wärmeentwicklungsgeschwindigkeit in den ersten Hydratationsstadien, gemessen bei verschiedenen NaOH-Konzentrationen, und SEM-Aufnahmen deuten auf einen anderen Reaktionsmechanismus bei NaOH-Konzentrationen grösser als 0.1 M. In diesen Lösungen ist die Hydratation im Anfang beherrscht durch eine mehr oder weniger amorphe $\text{Ca}(\text{OH})_2$ -Schicht.

Introduction

In a previous paper (1) the influence of Na_2O on the hydration of C_3A in pastes was reported. To elucidate some of the aspects of the hydration mechanism, especially during the first minutes of hydration, C_3A hydration in suspension ($w/s = 100$) was studied from the start of the hydration onwards using isoperibolic calorimetry.

Experimental

Methods for SEM, X-ray analyses and the arresting of hydration were as described previously (1). Conductivity measurements were performed as described by de Jong, Stein and Stevels (2).

The heat evolution rates in the suspensions were measured using a precision calorimeter LKB 8700-1. The principles of these measurements have been described by Wadsö (3). An isoperibolic calorimeter consists in principle of a nearly adiabatic reaction vessel in an environment of constant temperature. The total heat $Q(t_1)$ developed after a certain hydration time t_1 can be calculated from the following equation (4):

$$Q(t_1) = \alpha \Delta T(t_1) + \beta \int_0^{t_1} \Delta T(t) dt, \text{ where}$$

α = heat capacity of reaction vessel + contents,
 $\Delta T(t)$ = temperature difference between environment and reaction vessel after time t (presumably),
 $\beta \int_0^{t_1} \Delta T(t) dt$ = total heat leak during t_1 seconds.

$\Delta T(t)$ was calculated by measuring the change in resistance of a thermistor ΔR with a Wheatstone bridge. The heat leak from the reaction vessel to the environment was found to be proportional to $\Delta T(t)$.

The experiments were conducted with an environment temperature of $25^\circ \pm 0.01^\circ\text{C}$ and the maximum temperature rise in any experiment was 0.7°C .

The materials used and methods for determining sodium and calcium were those described previously (1). Aluminium was determined as described by Pribil and Vesely (5).

Hydration of C_3A in NaOH Solutions in Suspensions

Results

Fig. 1 shows the cumulative heat evolution for C_3A hydrated in suspension in water and NaOH solutions ($w/s = 100$). Fig. 2 shows the heat evolution rate obtained by differentiating the curves in Fig. 1. In all cases the heat evolution rate is high during the first seconds and decreases rapidly as hydration proceeds. At higher pH ($>0.1\text{M}$ NaOH) a second peak in the heat evolution rate appears which is accelerated by increasing NaOH concentrations.

In Fig. 3 the initial heat evolution rate is plotted against

FIG. 1

Cumulative heat evolution from C_3A hydrated in water and NaOH solutions

FIG. 2

Heat evolution rates of C_3A hydrated in water and NaOH solutions

FIG. 3

Initial heat evolution rate
versus the NaOH concentration

perpendicularly to the surface of a particle instead of the predominantly parallel orientation in paste hydration (1).

the NaOH concentration. This "initial" heat evolution rate is the maximum rate of increase of the thermistor temperature, which is reached a few seconds after the first contact between the reactants. A time lag arises because of the delay in the response of the thermistor.

At low NaOH concentration ($<0.1M$) the initial heat evolution rate decreases rapidly with increasing NaOH concentration while higher NaOH concentrations effect only a minor additional decrease. X-ray analyses of the hydration products are shown in Table I.

Fig. 4 shows SEM's of the hydration products on the surfaces of particles after 10 seconds and 10 minutes hydration. In water without NaOH addition the plate-like hydrates are, in many cases, orientated more or less

TABLE I

X-ray Data for hydration of C_3A in NaOH solutions

NaOH (M)	Hydration time (min)	C_2AH_8	C_4AH_{13}	C_3AH_6	C_3A
0	10	w	-	w	vs
0.04	10	-	vw	vw	vs
2	10	-	w	vvw	vs
2	1200	-	-	s	s

Fig. 5 shows the change in conductivity of C_3A suspensions during the hydration in H_2O and dilute NaOH solutions

Discussion

The decrease in conductivity (Fig. 5) after a certain hydration time (5.7 h for a suspension of C_3A in water) indicates the point during the hydration at which the conversion of hexagonal hydrates into C_3AH_6 becomes important enough to cause the solution to leave the metastable point of coexistence of C_2AH_8 , C_4AH_{13} and aqueous solution (9). Both the conductivity experiments and the behaviour of the second heat evolution peak shows that this conversion is accelerated when the NaOH

FIG. 4

SEM's of C_3A hydrated in suspension (w/s = 100) for

a 10 sec in H_2O
 b 10 sec in 0.1M NaOH
 c 10 sec in 2M NaOH

d 10 min in H_2O
 e 10 min in 0.1M NaOH
 f 10 min in 2M NaOH

FIG. 5

Increase in specific conductivity with regard to initial conductivity of suspensions of C_3A in water and aqueous NaOH

concentration increases. In 0.1M NaOH, the conductivity increases at the time of the second heat evolution peak (compare Figs. 2 and 5). For suspensions without NaOH, a very early appearance of the second peak and the accompanying conductivity decrease that were observed in pastes (1) were not found, presumably because of difficulty in nucleation of C_3AH_6 . Thus, the influence of NaOH on the second peak in suspensions is always an accelerating one.

In the early hydration stages, the heat evolution rate in pastes is about equal to that in suspensions after the same time. This is remarkable in view of the different orientation of the platey crystals in the hydrate layer in the two cases, and rules out a direct screening action of the hydrates.

The SEM results show that a hydrate layer exists on the C_3A surface. Because of misfit between the latter and the hydrates, some space will exist between them. Three possible explanations of retardation of C_3A hydration will be considered.

1) This space is filled by an aqueous solution saturated towards the anhydrous C_3A , the hydration rate of the C_3A then being determined either by the diffusion of ions out of the space concerned and of water into it, or by the growth of the hexagonal hydrates in the layer.

2) Feldman and Ramachandran (10) proposed that the hydration of C_3A is impeded, not by hydrates, but by the blocking of movements of surface dislocations by adsorption of ions, such as OH^- . In this case, the second peak would be caused by the

C_3A , HYDRATION, NaOH SOLUTION

recrystallization of hexagonal hydrates because the latter is accompanied by some changes in the concentrations of these ions.

3) An aqueous solution occurs in the space between the C_3A and the hexagonal hydrates, in which conditions differ from those in the outside solution; this leads to the formation in this space of an amorphous solid that can match the C_3A surface on an atomic scale more closely than can a hexagonal hydrate (11). The role of the hexagonal hydrates is then an isolating one, and the rate determining step is the transport between the crystals of the hexagonal hydrates of ions, which tend to attack the retarding agent.

Regarding these three reaction mechanisms the following remarks can be made:

According to the "saturated solution" mechanism the heat evolution rate at $t \rightarrow 0$ corresponds to a situation in which the dissolution of C_3A is not hindered by hydrates, and follows the equation

However, the dependence of the heat evolution rate at $t \rightarrow 0$ on the NaOH concentration is too weak, especially at higher concentrations, to be compatible with the mechanism, at least if equal volumes of liquid are assumed to be saturated per unit of time in all cases. This mechanism could account for the facts only if with increasing NaOH concentration either a larger volume would be accessible to saturation by C_3A , or increasing contributions of hydrate precipitation to the heat evolved at $t \rightarrow 0$ are assumed. Both alternatives are improbable; the former because large NaOH concentrations promote precipitation of $Ca(OH)_2$, the latter because this precipitation is an endothermic process.

According to the mechanism postulated by Feldman and Ramachandran (10), the influence of increasing NaOH concentrations at $t \rightarrow 0$ is caused by increasing difficulty in movement of dislocations; the levelling off with higher NaOH concentrations is due to all surface sites being occupied by OH^- ions, the decrease of the heat evolution rate is due to gradual exhaustion of surface dislocations, and the second peak can be ascribed to a decrease in OH^- concentration, as has indeed been observed in suspensions at that particular stage of reaction by de Jong, Stein and Stevels (9). However, this effect is small (the pH changes from 12.2 to 12.1), especially when compared with the OH^- concentrations present, for instance, in 4M NaOH where the second peak remains quite remarkable (Fig. 2). Thus, the data do not support a surface dislocation movement inhibition by absorbed OH^- ions.

The following mechanism appears to be compatible with the results: In NaOH solutions of high concentration the amount of Ca^{2+} going into solution as a result of hydration of the C_3A must be small. Aluminate ions may go into solution but Ca^{2+} ions stay behind, their charge being compensated by OH^- ions. Rearrangement into crystalline $Ca(OH)_2$ is prevented by the adjacent C_3A . The resulting primary layer thus formed prevents contact between C_3A and the solution, and can follow the C_3A

surface closely because of its in situ formation. Figs. 4a-c show that after 10 seconds hydration in water a structure consisting of plates reminiscent of the hexagonal hydrates is formed, while in 2M NaOH a dense layer is formed which might be capable of preventing contact between the C_3A and the solution. Some H_2O and OH^- will penetrate through this layer and react with aluminate ions from the C_3A to form $Al(OH)_4^-$. These aluminate ions replace part of the OH^- ions in the layer, and at some distance from the C_3A rearrangement into hexagonal hydrates may occur, as is shown by X-ray analyses (Table I) and SEM (Fig. 4d-f).

The decrease in the heat evolution rate with time (Fig. 2) is ascribed to the layer becoming thicker, and the second peak to recrystallization of the hydrates into C_3AH_6 , which affects the concentration gradients in the vicinity of the C_3A sufficiently to destabilize the primary layer. This hypothesis would explain the absence of X-ray reflections due to crystalline $Ca(OH)_2$ and the presence of only weak lines due to the hexagonal hydrates (Table I).

It appears from the conductivity curve that, after the formation of the layer seen in Fig. 4b, some hydrate nucleates in the surrounding liquid. This is shown by the conductivity maximum found after about 1 minute (Fig. 5; the SEM shown in Fig. 4b was taken after 10 sec., which is before the conductivity maximum). This supports the existence of two hydrates: one at the C_3A surface, a second one somewhat further away from it. The second one is the one seen in Figs. 4e-f, and is thought to be a disordered form of one of the hexagonal hydrates playing an isolating rather than a retarding role.

The mechanism described is not necessarily the mechanism operative in H_2O or in $Ca(OH)_2$ solutions. On the contrary, the shape of the heat evolution rate at $t \rightarrow 0$ versus the NaOH concentration graph (Fig. 3) suggests that a different mechanism becomes operative when the NaOH concentration exceeds 0.1M.

Hydration of $0.25Na_2O \cdot 0.2.75CaO \cdot Al_2O_3$ in Suspensions

Results

The total heat developed up to a certain hydration time and the heat evolution rate at the time concerned are both shown in Fig. 6. The total heat liberated after a certain hydration time and the heat liberation rate during the $N_{0.25}C_{2.75}A$ hydration are somewhat lower than for C_3A (Figs. 1 and 2).

In Fig. 7 the conductivity of a suspension of $N_{0.25}C_{2.75}A$ is plotted against time. At certain times designated by A, B, C and D the hydration was arrested and X-ray analyses of the solid phases and chemical analyses of the liquid phase were performed. Table II shows the results of these analyses.

Discussion

When $N_{0.25}C_{2.75}A$ is hydrated in suspensions with w/s = 100 no second peak in the heat evolution rate curve appears (Fig. 7). The total heat developed up to a certain hydration time is only slightly less than the total heat developed during the hydration

FIG. 6
Cumulative heat evolution and heat evolution rate during the hydration in suspension (w/s = 100) of N_{0.25}C_{2.75}A in H₂O

FIG. 7
Specific conductivity of a suspension (w/s = 100) of N_{0.25}C_{2.75}A in H₂O

TABLE II

X-ray and chemical analyses data
for hydration of N_{0.25}C_{2.75}A in H₂O

Time		concentration in mmol/l					
(min)	C ₂ AH ₈	C ₄ AH ₁₉	C ₃ AH ₆	N _{0.25} C _{2.75} A	Ca ²⁺	Al(OH) ₄ ⁻	Na ⁺
A 3	vw	-	-	vs	1.54	1.47	0.58
B 32	w	-	vw	s	0.62	0.75	1.22
C 200	s	m	m	w	0.06	0.91	1.86
D 410	s	-	vs	vw	0.42	1.96	2.40

of C₃A. Thus the hydration characteristics of N_{0.25}C_{2.75}A in suspensions are almost similar to those of C₃A, while in pastes there exists a significant difference (1). The similarity between the hydration in suspension of C₃A and N_{0.25}C_{2.75}A is to

be expected in view of the small NaOH concentrations effected by the former (Fig. 2). Again it appears (see ref. 1) that the NaOH concentration in the solution is more important than changes in solid state properties.

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