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CALORIMETRIC STUDY OF REACTIONS IN THE SYSTEM $C_4A_3\bar{S}$ - CH - $C\bar{S}$ - H

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ABSTRACT

The formation of ettringite ($C_6A\bar{S}_3.32H$) in diluted water suspensions was studied. The solid components were taken in mole rations 1:8:6 ($C_4A_3\bar{S}$, $C\bar{S}H_2$ and CS respectively). The reaction rate, in the first period of hydration, depends on the granulometry of $C_4A_3\bar{S}$. It is independent on the granulometries of $C\bar{S}H_2$ and CH.

Results indicates that the ettringite forms topochemically, by heterogenous nucleation, on the active sites of solid surfaces.

INTRODUCTION

One of the phases formed in the above system is ettringite-$C_6A\bar{S}_3.32H$ (C = CaO, A = Al_2O_3, $\bar{S}$ = SO_3, H = H_2O), an important constituent of hydrated rapid hardening cements (ref. 1).

The reactions in the system were reported in several papers (ref. 2, 3, 4). These studies dealt in most cases with pastes, at water content comparable to the amount of solid components.

Up to now, there exists no unified view upon the mechanism of ettringite formation, the possible mechanisms were reviewed in (ref. 5).

In our case the reactions took place in diluted suspensions. The reactants ($C_4A_3\bar{S}$, $C\bar{S}H_2$ and CH) were taken in stoichiometric proportion to form ettringite (in mole ratios 1:8:6 respectively). The main emphasis was given on the influence of the granulometry of phases $C_4A_3\bar{S}$, $C\bar{S}H_2$ in the reactions and on the sequence in which the solid components were introduced into suspensions.

EXPERIMENTAL

The heat evolution connected to the reactions studied was measured by a quasi-adiabatic calorimeter (Directhermom, MOM, Budapest). The weight of solid components that reacted was 6 grams.

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The weight of water was 200 or 300 grams. $C_4A_3\bar{S}$ was synthesised from $CaCO_3$, $Al(OH)_3$ and $CaSO_4.2H_2O$ (all reagents grade) at 1300°C. Its phase purity was checked by X-ray diffraction. The X-ray diffraction was used also to determine the phase composition of hydration products.

Solid components were ball-milled and sieved on the individually specified fractions (in legends to figures).

The degree of saturation of solutions, when tempering suspensions with individual solid reactants, was determined by the continuous measurement of their conductivity.

RESULTS AND DISCUSSION

The results of the measurements are summarised in (Figs. 1-3). According to them the following conclusions can be drawn :

1. The particle size of $C\bar{S}H_2$ does not influence the heat evolution of the reaction in a significant manner (Fig. 1.).
2. The heat evolution is also independent on the quantity the reaction surface of CH in suspension (Fig. 2.).
3. The reaction rates depend on the sequence in which solid components are brought into the liquid phase (Fig. 3.).

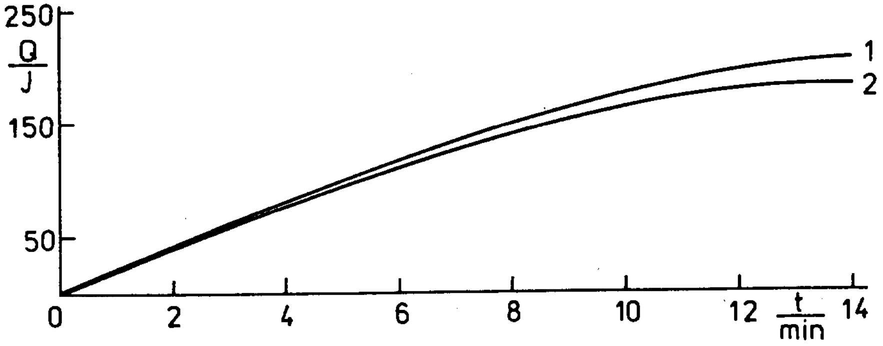

Fig. 1. The heat evolution during the hydration of $C_4A_3\bar{S}$ (particle size < 0,063 mm) in the suspension of $C\bar{S}H_2$ and CH
1 - particle size of $C\bar{S}H_2$ < 0,063 mm
2 - particle size of $C\bar{S}H_2$ > 0,063 mm

The heat evolution rate is nearly the same when either a mixture of $C\bar{S}H_2$ and $C_4A_3\bar{S}$ is brought into saturated tempered solution of CH, or when a mixture of CH and $C_4A_3\bar{S}$ is brought into the suspension of $C\bar{S}H_2$. If $C_4A_3\bar{S}$ is brought into the common suspension of $C\bar{S}H_2$ and CH the rate of the heat evolution is appreciably lower.

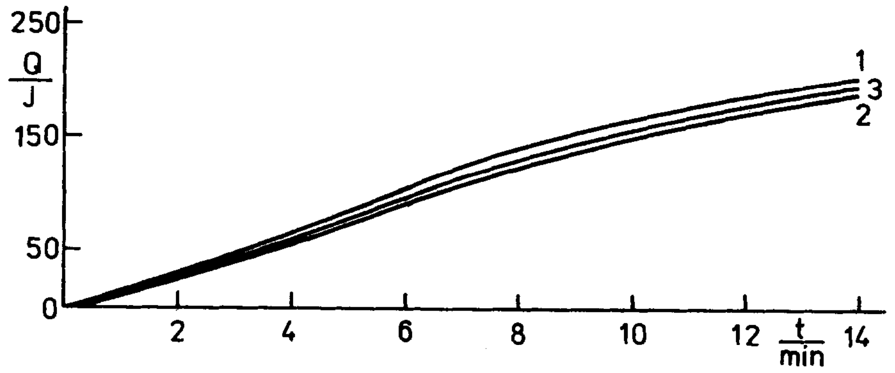

Fig. 2. The heat evolution during the hydration of $C_4A_3\bar{S}$ (particle size < 0,063 mm) as dependent on the quantity of CH (the suspension of $C\bar{S}H_2$ and CH)
1 - stoichiometric ratio
2 - 50% of the stoichiometric quantity
3 - 200% of the stoichiometric quantity

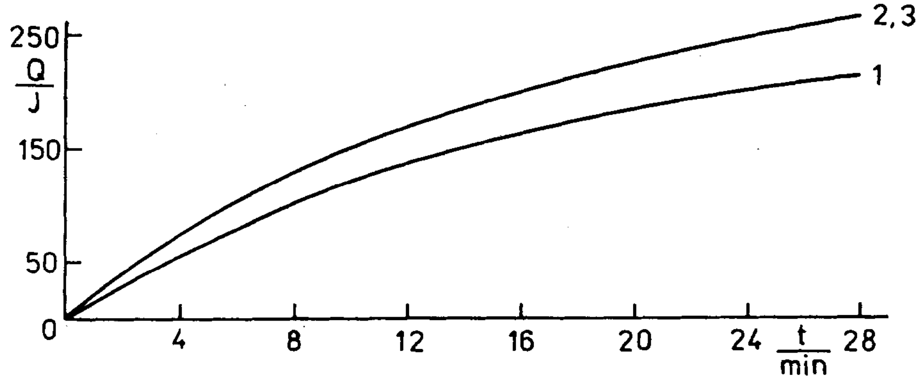

Fig. 3. The heat evolution during the hydration of $C_4A_3\bar{S}$ (particle size < 0,063 mm) as dependent of the sequence in which the solid components are brought into suspension
1 - $C_4A_3\bar{S}$ into tempered suspension of CH and $C\bar{S}H_2$
2 - $C_4A_3\bar{S}$ and $C\bar{S}H_2$ into tempered suspension of CH
3 - $C_4A_3\bar{S}$ and CH into tempered suspension of $C\bar{S}H_2$

To explain the behaviour of the system studied the following tentative inferences are drawn, concerning the possible mechanism of ettringite formation.

The dissolution rates of $C\bar{S}H_2$ and CH during the reaction are not rate limiting factors (Fig. 1 and 2.).

In two cases according to (Fig. 3. /2,3/), in which one of the solids ($C\bar{S}H_2$, CH) is brought into suspension, partial precipitation of the second phase (CH, $C\bar{S}H_2$) takes place.

We hypothesize therefore that the formed nuclei, at their properly grown up size, serve as the nucleating centres for ettringite nucleation. Their smaller size (in orders) in comparison to the rest of particles of solid phases ensures their high concentration in solution.

When the number of nucleating sites is not the rate limiting factor, the rate of reaction is controled by the rate of $C_4A_3\bar{S}$.

These results, pertinent to diluted mixed suspensions, indicate that the ettringite forms topochemicaly, by heterogeneous nucleation on the active sites of solid phases. The conclusion is conform to the ideas on the mechanism of ettringite formation in cement pastes proposed by Budnikov (ref. 6.). The hypothesis declared is prone, however, to firther testing.

CONCLUSION

The results, which were obtained studying the heat evolution rate in reactions to form ettringite in diluted water suspensions, indicate that the rate limiting factor is the availability of active sites on the surfaces of solid particles. These serve as sites at which the nucleation of ettringite take plase.

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