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INFLUENCE OF QUARTZ SURFACES ON THE
REACTION $C_3A + CaSO_4 \cdot 2H_2O + WATER$.

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ABSTRACT

Quartz surfaces counteract the retarding action of SO_4^{2-} on the hydration of C_3A , by presenting additional sites for ettringite crystallization. Strong retardation requires the presence of ettringite near the C_3A , influencing the local concentrations there.

Quarzoberflächen wirken der Verzögerung der Hydratation des C_3A durch Sulfationen entgegen, indem sie Extraplätze für die Kristallisation des Ettringits bieten. Eine starke Verzögerung erfordert die Anwesenheit des Ettringits dicht neben dem C_3A , wodurch die lokalen Konzentrationen dort beeinflusst werden.

Introduction

In studies of the reaction $C_3A + CaSO_4 \cdot 2H_2O + H_2O$ in pastes, quartz is frequently added as an "inert" filler in order to prevent demixing and sedimentation (1, 2). The inert character of the quartz may, however, be doubted, if only because the presence of a foreign surface might influence nucleation of hydrates. Indications of this have been reported for cement pastes (3). It was thought desirable to perform similar experiments with pure C_3A since they may give a clue on the mechanism responsible for the retardation of its hydration by SO_4^{2-} .

Experimental

The $CaSO_4 \cdot 2H_2O$ was *ex Merck pro analysi*.

C_3A , sample a, had 0.1% free CaO and Blaine surface area $0.075 \text{ m}^2\text{g}^{-1}$; sample b had 0.3% free CaO and N_2 adsorption surface area $0.321 \text{ m}^2\text{g}^{-1}$. The samples were either kept in a sealed glass ampoule, or heated to 1000°C for 2 h shortly before use. The quartz was *ex Riedel de Haën*; Blaine surface area $0.60 \text{ m}^2\text{g}^{-1}$. On treating with $HF + H_2SO_4$, 0.6% of residue remained. It was heated to 1000°C for 2 h shortly before use. The water was twice distilled, and then again distilled under reduced pressure shortly before use.

The conduction calorimeter, mixing and X-ray diffraction procedures were the same as described previously (4). The SEM was a Cambridge MK-2A instrument. The hydration reaction was stopped by washing with absolute ethanol and drying in a stream of nitrogen freed from CO_2 . In some cases the drying was effected by sucking air through the precipitate in a glove-box in an atmosphere free of CO_2 .

Results

In Fig.1 heat evolution rate is plotted against time for pastes with C_3A sample b, weight ratios $C_3A:CaSO_4 \cdot 2H_2O:H_2O:SiO_2 = 1.5:1.43:5.0:z$ (z in caption). Groups of three graphs in the same horizontal position refer to one experiment; the breaks correspond to scale adjustments. The main features of Fig.1 were also shown by pastes with $C_3A:CaSO_4 \cdot 2H_2O:H_2O:SiO_2$ weight ratios $1.5:0.77:5.0:z$ ($0 < z < 5.0$), for both C_3A samples. For $z \neq 0$, the effects of increasing quartz content can be summarized as follows:

- 1) The first heat evolution rate peak (A) is intensified and shifted slightly forward.
- 2) After some time the heat evolution rate decreases further (shortly after stage B). For $0.82 < z < 1.65$, a peak is found at stage B. At large z values the transition to the low heat evolution stage C is smooth.
- 3) The transition to stage C starts earlier, and once started is faster with increasing z .
- 4) The final heat evolution peak D occurs earlier.

Experiments with pastes mixed in a glove-box in an atmosphere free of CO_2 did not show significant differences from

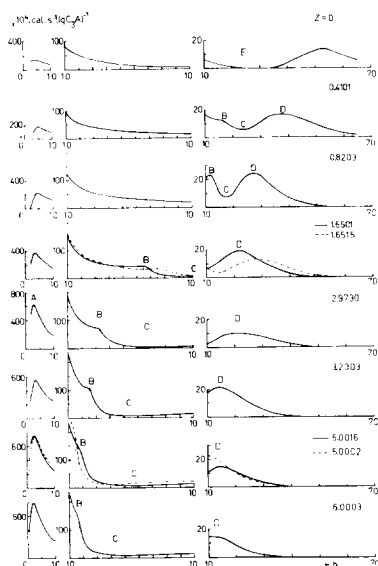


FIG 1

Heat evolution rate vs. time for pastes C₃A + CaSO₄.2H₂O + H₂O + SiO₂, weight ratios 1.50:1.43:5.00:z; C₃A sample b. The vertical bars indicate the reaction stages up to which integration of the curves was carried out (see text).

observed by electron microscopy in other cases (9, 10, 11). After stage D, ettringite was still present, in addition to monosulphate and the 8.2 Å hemicarbonate, which is considered to be formed from C₄AH₁₉ during the preparation of the sample for X-ray analysis.

If $z = 0$, the enthalpy change up to stage E (Fig. 1) was $-0.14 \text{ kcal (g C}_3\text{A)}^{-1}$. This indicates inhomogeneity of this paste, because of the high water/solids ratio: the C₃A settles more rapidly than the CaSO₄.2H₂O and a SO₄²⁻ shortage arises near the C₃A grains before exhaustion of the CaSO₄.2H₂O. With large z , however, no demixing occurred; this was checked in a separate experiment with C₃A (sample b; weight ratios 1.5:1.43:5.0:2.97), carried out in a glass vessel of dimensions similar to those of the calorimeter vessels. Shortly after being mixed, the paste had a reflecting top surface, but after 8 minutes the top surface had become non-reflecting. Apparently, coagulation caused the sediment volume to coincide practically with the total paste volume. Separate X-ray analyses of top and bottom material, in a reaction stage where only small amounts of CaSO₄.2H₂O remained, showed good mutual agreement.

Discussion

An increasing quartz content of the paste has a distinct influence which, at least for $z > 2.97$, cannot be ascribed to counteraction of demixing. An ever increasing counteraction of demixing with increasing z might be held responsible for the

those shown in Fig. 1. Neither had previous saturation of the water with CaSO₄.2H₂O any influence.

Stage B corresponds to nearly complete exhaustion of the CaSO₄.2H₂O. This was found by X-ray diffraction, agreeing with previous data (2), and by the total enthalpy change exhibited by the reaction to stage B as found by graphical integration of the heat evolution rate curves. In the latter case, values were found in slight excess (0.20-0.24 kcal (g C₃A)⁻¹) of the theoretical value for total conversion of CaSO₄.2H₂O into ettringite (0.2065 kcal (g C₃A)⁻¹, calculated from the enthalpies of formation of C₃A (5), H₂O (6), CaSO₄.2H₂O (7) and ettringite (8). This indicates the formation of some other product besides ettringite. No product except ettringite was found up to stage C by X-ray diffraction, but hydration products resembling AFm phases, not showing the corresponding X-ray diffraction lines, have been

intensification of the first peak and the shifting forwards of stage B, but not for the fact that the transition to stage C, once started, is quicker (i.e., the hydration of C_3A is slowed down faster) in the presence of more quartz. The experimental evidence against demixing at $z = 2.97$ has also been mentioned.

Three possible mechanisms for the retardation of hydration in the presence of SO_4^{2-} will be considered:

I. The solution between the C_3A grains is saturated towards the anhydrous C_3A , and C_3A reacts only to the extent that reaction replaces ions withdrawn from the solution by precipitation of hydrates. SO_4^{2-} lowers the solubility of C_3A , causing a slower precipitation of ettringite as compared with the precipitation of AFm phases from a medium less rich in SO_4^{2-} . Hydrate precipitation is the rate-determining step (12, 13).

II. C_3A reacts only where its surface is met by dislocations; the hydration is accompanied by movement of the dislocations, and ions adsorbed onto the surface impede this movement (14).

III. A hydration product, e.g. ettringite (15), forms a protective layer.

Mechanism II is contradicted by the fact that quartz has any influence at all. C_3A and $CaSO_4 \cdot 2H_2O$ dissolve quickly in water, as shown by electrical conductivity data in systems $C_3A + H_2O$ (16) and $C_3A + CaSO_4 \cdot 2H_2O + H_2O$ (17), and by the fact that no difference is seen between pastes prepared with pure water and with water previously saturated towards $CaSO_4 \cdot 2H_2O$. The reaction of quartz with the ions concerned is much slower (quartz has no influence on the concentrations in C_3A suspensions during the initial stages (16)). Thus, the presence of quartz cannot reasonably be supposed to influence either the concentrations of ions in the solution, or their adsorption onto the C_3A .

Mechanism I might account for the intensification of the first peak, and the shifting forwards of stage B with increasing z . Although quartz cannot change the concentrations in a solution saturated towards C_3A and $CaSO_4 \cdot 2H_2O$, the quartz surfaces could facilitate nucleation of hydrates, thus accelerating what is, according to this mechanism, the rate-determining step. However, the following arguments are adduced against mechanism I:

1) The concentrations in a solution saturated towards C_3A , as calculated from thermodynamic data (18), are at least 100 times larger than those found experimentally in $C_3A + CaSO_4 + H_2O$ systems (2).

2) The concentrations found experimentally correspond to the solubilities of the hydrates. The large difference between the enthalpies of dissolution of the hydrates on the one hand, and of C_3A on the other, lead to the expectation that the solubility of C_3A should be much larger than those of the hydrates.

3) If such SO_4^{2-} concentrations as are present in a solution saturated towards $CaSO_4 \cdot 2H_2O$ would reduce the solubility of C_3A to the extent required by the mechanism, then SO_4^{2-} must strongly increase the activity coefficients of the other ions present. This is not known in the thermodynamics of electrolyte solutions (cf. data on activity coefficients of 1:1 electrolytes in the

C₃A + GYPSUM HYDRATION, QUARTZ EFFECT

presence of SO₄²⁻ (19)).

According to mechanism III, the quartz presents additional sites for ettringite crystallization and prevents formation of ettringite on the C₃A surface. This is compatible with the heat evolution rate data; however, ettringite layers as formed in hydrating pastes are too incoherent for complete screening of the C₃A (13).

However, there is no need to assume such a complete screening. If ettringite is the sole hydrate formed, and counteracts the transport of ions from the bulk solution towards the vicinity of the C₃A sufficiently for a concentration gradient to exist between those regions, there will arise a local SO₄²⁻ shortage near the C₃A. If initially the solution is saturated towards CaSO₄·2H₂O, H₂O and CaSO₄ reach the C₃A in a weight to weight ratio of 400:1; if ettringite precipitates as the sole hydrate, H₂O and CaSO₄ are withdrawn from the solution in a weight to weight ratio of 14:1. Thus, predominant ettringite formation leads to a local SO₄²⁻ shortage near the C₃A. Nevertheless, the reactivity of C₃A is lower than in SO₄²⁻-free pastes. It has been suggested (2) that amorphous Al(OH)₃ is formed because the ettringite crystals tend to grow further when there is no SO₄²⁻ at hand, with 2OH⁻ replacing SO₄²⁻, causing a locally low pH and Ca²⁺ concentration near the C₃A. Although mixed crystals Ca₆Al₂(OH)₁₂(SO₄²⁻)_{3-x}(OH⁻)_{2x}·25H₂O are not known, the effect suggested here may be a surface effect rather than a bulk effect.

Earlier (2) it was supposed that the amorphous Al(OH)₃ precipitates from solution. However, recent data on the hydration of C₃A in NaOH solutions (10, 20) suggest the formation of a disturbed surface layer on the C₃A, approaching Ca(OH)₂ in composition, by preferential extraction of aluminate ions from the C₃A and their replacement by OH⁻. It would be more in line with these data to think in the present case of a disturbed surface layer on the C₃A approaching Al(OH)₃ in composition, formed by preferential extraction of Ca²⁺ and its replacement by H⁺.

The occurrence at stage B of a peak at small values of z, and a quicker and smoother transition to stage C at larger values, can be explained thus. As long as SO₄²⁻ diffuses between the ettringite crystals towards the C₃A, the ettringite remains stable. The SO₄²⁻ replaces OH⁻ in or on ettringite, and the hydration of C₃A continues slowly. If, however, no SO₄²⁻ reaches the C₃A, the ettringite is converted into monosulphate and C₄AH₁₉, but not C₂AH₈ (2, 17). If C₄AH₁₉ precipitation dominates, the pH and Ca²⁺ concentration near the C₃A decrease again (Ca²⁺ and aluminate ions enter the solution in 3:2 molar ratio, but are withdrawn from it in 2:1 ratio), leading to a rapid new retardation. This will occur when, on ettringite conversion, little SO₄²⁻ is freed for monosulphate formation; i.e. when a large fraction of the ettringite is not formed near the C₃A, but on the SiO₂ surfaces; i.c. at large z.

SEM evidence supported ettringite formation on quartz surfaces and the incoherent character of the ettringite layers near the C₃A, although it was difficult to be sure that no artefacts were introduced during sample preparation.

The final peak (stage D) at z≠0 can be understood by assuming that in the long run the ettringite far from the C₃A is

converted too, converting C_4AH_{19} initially formed into monosulphate and increasing local pH near the C_3A .

The proposed mechanism is regrettably complicated, but the complicated heat evolution rate curves cannot be explained by a simple mechanism.

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