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HYDRATION MECHANISM OF TRICALCIUM ALUMINATE WITH GYPSUM AT 1:1 MOLE RATIO AT LOW WATER/SOLID RATIO AND IN SUSPENSION

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ABSTRACT

The mechanism and kinetics of the hydration of a mixture of tricalcium aluminate and $CaSO_4 \cdot 2\ H_2O$ at 1:1 mole ratio have been studied in paste and in suspension. X-Ray diffraction, DTA and TG analyses were used throughout the investigation.

Ettringite was detected after 5 min of hydration in suspension and after a longer time in paste. As the hydration proceeded, ettringite increased up to deflection point, then transformed to monosulphate hydrate. Deflection points were observed after about 12 h in the case of paste and about 3 h in suspension. The presence of excess water in the case of the suspension accelerates the transformation period. Monosulphate hydrate was found to be a metastable phase.

INTRODUCTION

Tricalcium aluminate (C_3A), and gypsum ($CaSO_4 \cdot 2\ H_2O$) are among the constituents of commercial Portland cement. In hydrating cement paste, they react in a solution saturated towards $Ca(OH)_2$. Earlier investigations [1,2], therefore, concentrated on the reaction of C_3A and $CaSO_4 \cdot 2\ H_2O$ in a saturated calcium hydroxide solution. After the conversion of nearly all the sulphate ions into ettringite, an intensification of the reaction is observed. The mechanism of the latter, however, remained largely obscure.

The early hydration of C_3A has been known to be retarded by the presence of $CaSO_4 \cdot 2\ H_2O$. The kinetics and mechanism of this reaction have been discussed by many authors [1–5]. In general, it has been found that $CaSO_4 \cdot 2\ H_2O$ can retard the hydration of C_3A by the formation of a coating of ettringite on the surface of C_3A grains. This retardation proceeds with the diffusion of sulphate ions through the coating layer in the earlier stage, forming more ettringite in the latter hydration periods [1,2]. In

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addition, other investigators [3] have discussed the formation of monosulphate hydrate on the C_3A grains in the very early hydration period. The retardation by the formation of calcium aluminate hydrate and not of ettringite has been reported.

The aim of this work is to elucidate the hydration mechanism and the kinetics of the complicated behaviour of C_3A in the presence of $CaSO_4 \cdot 2\ H_2O$ (1 : 1 mole ratio) in paste and in suspension.

EXPERIMENTAL

Tricalcium aluminate was synthesized by blending together stoichiometric proportions of analytical reagent-grade calcium carbonate and aluminium oxide in a sintered alumina ball mill using two balls. The intimate mixture was fired in a platinum dish at 1375°C for 2 h in a silicon carbide resistance heating furnace. It was cooled to room temperature, crushed and powdered in an agate mortar to -73 μm. The mixture was fired again in the same manner and checked by X-ray powder technique and chemical analysis. Heating was repeated untill the X-ray powder pattern was in full agreement with the lattice spacing of published data (ASTM card No. 8–5). No free CaO was detected by chemical or X-ray methods in the final product.

The gypsum ($CaSO_4 \cdot 2\ H_2O$) used in this work was provided by B.D.H. Chemical Co., Gt. Britain.

The dry constituents of C_3A and $CaSO_4 \cdot 2\ H_2O$ (1 : 1 mole ratio) were mechanically mixed for 1 h. The hydration was done by two methods; as a paste and in suspension. The suspension was done by mixing the dry constituents with distilled water, using a water/solid ratio of 10.0. Samples were weighed into polyethylene bottles with the appropriate volume of water and sealed during the hydration period. The polyethylene bottle was mechanically stirred on a magnetic stirrer from time to time.

The mixing of the paste was carried out by mixing the dry constituents with distilled water using a water/solid ratio of 0.50. The mixing was made in a porcelain mortar for 2 min, then left in a desiccator saturated with water vapour (100% R.H.) and covered with moistened cotton to minimize the carbonation of the hydrated paste.

After the predetermined curing time, the hydration of the sample was stopped using the technique described previously [6–8]. The phase constitution of each paste and suspension after the prescribed period was followed using DTA and X-ray analysis. Moreover, the mechanism of hydration was also determined using TG analysis.

The crystalline phases present in the unhydrated as well as the hydrated specimens were identified using an X-ray diffraction technique. Ni-filtered CuK_α radiation ($\lambda = 1.5405$ Å) at 40 kV, 20 mA was used throughout in a Philips Pw 1390 diffractometer. Differential thermal and thermogravimetric analyses were carried out using a DT-30 thermal analyzer (Schimadzu Co., Koyoto, Japan). Calcined alumina was used as inert material. A sample of 50 mg (−53 μm) was housed in a small platinum–rhodium crucible using a standard procedure for packing, with a heating rate of 10°C min^{-1}. In the thermogravimetric analysis, a sample of 20 mg (−53 μm) was used. Constant conditions of sensitivity ±5 mg, heating rate 10°C min^{-1}, and an atmosphere of nitrogen (30 ml min^{-1}) were applied in all the experiments.

RESULTS AND DISCUSSION

Paste hydration

Figure 1 illustrates the X-ray diffraction pattern of the hydrated mixtures of $C_3A + CaSO_4 \cdot 2\ H_2O$ in relation to curing time. The curing period begins

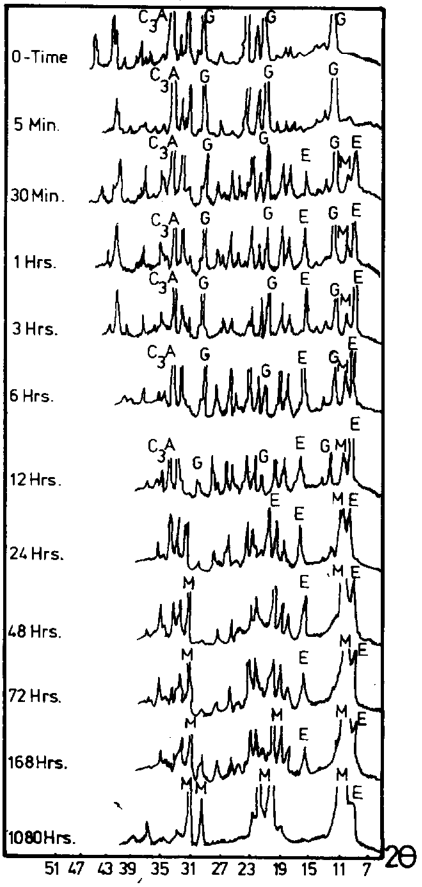

Fig. 1. X-Ray diffraction patterns of the hydrated paste of $C_3A + CaSO_4 \cdot 2\ H_2O$ of (1 : 1 mole ratio) for different curing times. E = Ettringite, M = monosulphate, G = gypsum.

after 5 min up to 45 days. The hydration products change with curing time. It was observed that no hydration products appear after 5 min of hydration, whereas at 30 min the peak of ettringite was higher than monosulphate hydrate. On the other hand, the unhydrated components, i.e. C_3A and $CaSO_4 \cdot 2\ H_2O$, were still present. On prolonged hydration, the extent of ettringite increases up to 12 h. After 24 h, it was observed that the ettringite transforms to monosulphate hydrate, with a noticeable decrease of the unhydrous materials. Gypsum disappeared after 72 h of hydration, whereas tricalcium aluminate was completely hydrated after 45 days. As far as the hydration proceeds from 72 h up to 45 days, the results show that the monosulphate hydrate increases and the ettringite diminishes.

DTA thermograms of the above paste as a function of curing time are shown in Fig. 2, which shows the appearance of one endothermic peak at ~ 140°C related to the formation of ettringite after 30 min of hydration. As the hydration proceeds, after 3 h, the intensity of ettringite increases, with the appearance of monosulphate hydrate with an endothermic peak at ~ 240°C. The endothermic peak of gypsum is present after 6 h, whereas it is overlapped by the ettringite after 12 h. After 24 h, the two endothermic peaks of monosulphate hydrate at 210 and 290°C increase as the degree of hydration increases, whereas the peak of ettringite decreases. It is also clear from the DTA thermograms that 12 h hydration can be considered as a

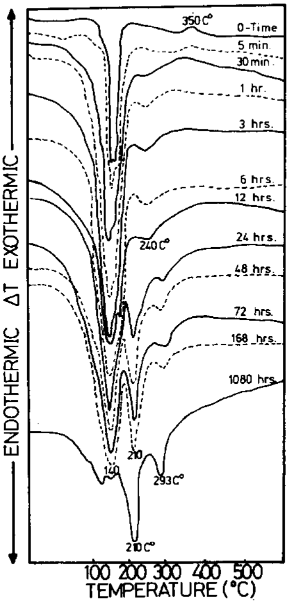

Fig. 2. Differential thermograms of paste hydrated $C_3A + CaSO_4 \cdot 2\ H_2O$ as a function of curing time.

deflection point of ettringite–monosulphate transformation. At this time, the ettringite decreases whereas the monosulphate hydrate increases.

Carlson and Berman [9], prepared trisulphate hydrate (ettringite) by reacting together gypsum-rich mixture of lime, gypsum and calcium aluminate solution. They carried out the thermal dehydration studies on the trisulphate form and registered losses corresponding to about 11–12, 23–24, 25–26, and 32 molecules of water at 60, 110, 145 and 200°C, respectively. Therefore, from DTA thermograms it was revealed that the ettringite formed in this system exists in low water contents, ranging from 23–26 molecules of water.

Suspension hydration

The X-ray diffraction pattern of the hydrated suspended mixture of $C_3A + CaSO_4 \cdot 2\ H_2O$ as a function of curing time is shown in Fig. 3. The

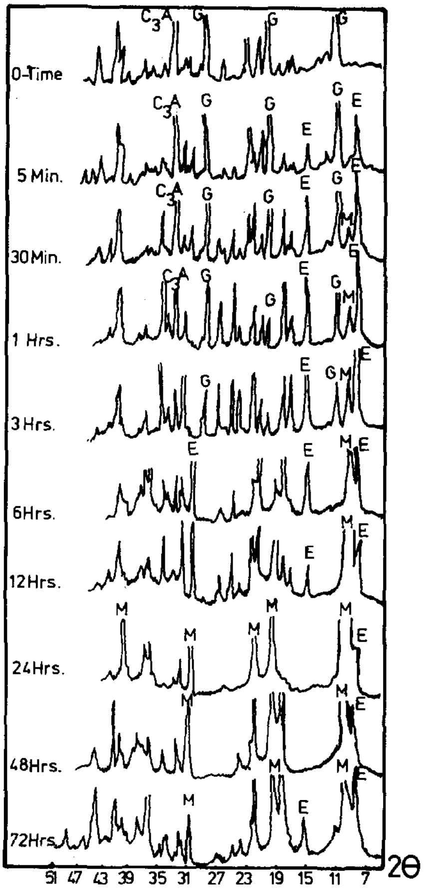

Fig. 3. X-Ray diffraction patterns of the hydrated suspension of $C_3A + CaSO_4 \cdot 2\ H_2O$ (1:1 mole ratio) for different curing times. E = Ettringite, M = monosulphate, G = gypsum.

hydration period extends from 5 min of hydration. After 30 min of hydration, the extent of ettringite increases and the monosulphate hydrate appears. As the hydration progresses, the monosulphate increases and the ettringite decreases with the disappearance of the unhydrated constituents, i.e. C_3A and $CaSO_4 \cdot 2\ H_2O$. Gypsum disappears after 6 h of hydration, whereas C_3A is not detected after 48 h. After 6 h, it was observed that monosulphate hydrate increases and ettringite diminishes. After 24 h, it was seen that the main hydration product is monosulphate hydrate with a very small amount of ettringite. As the hydration proceeds, the ettringite phase increases again and the monosulphate diminishes up to 72 h.

Figure 4 illustrates the DTA thermograms of the suspended hydrated system from 5 min up to 72 h. After 5 min of hydration, the peak of ettringite appears at about 120°C. At 30 min, the amount of ettringite increases and the monosulphate hydrate appears. The endothermic peaks of ettringite and monosulphate hydrate increase with increase in hydrating period up to 3 h. As the hydration proceeds, 6 h, the endothermic peaks of monosulphate hydrate at ~ 210 and 290°C increase with a decrease in the endothermic peak of ettringite. The low endothermic peak at 110°C may be attributed to the dissociation of ettringite with low water of crystallization [9]. The endothermic peak of monosulphate hydrate increases as the hydration proceeds, whereas at 24 h of hydration the amount of dissociated ettringite is a minimum. After 48 as well as 72 h the low water ettringite

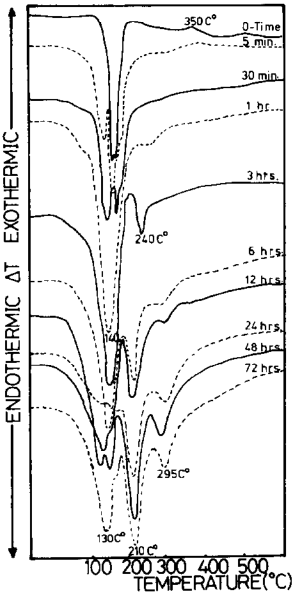

Fig. 4. Differential thermograms of suspension hydrated $C_3A + CaSO_4 \cdot 2\ H_2O$ as a function of curing time.

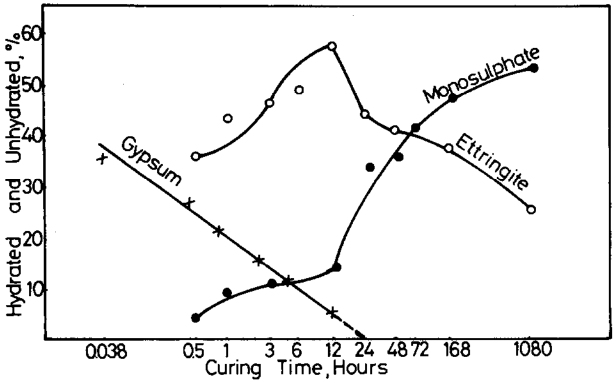

Fig. 5. Ettringite, monosulphate and gypsum in the hydrated paste of $C_3A + CaSO_4 \cdot 2\ H_2O$ (1 : 1 mole ratio) as a function of curing time.

increases and the monosulphate hydrate also increases. Generally, the DTA results are in full agreement with the X-ray analysis.

Kinetics of hydration

The kinetics of hydration can be studied by the quantitative determination of ettringite, monosulphate and gypsum. These amounts can be calculated from the results of TG analysis. The DTA results indicate that the formed ettringite is mainly a phase containing about 24–26 molecules of water [9].

Figures 5 and 6 illustrate the relation between the hydrated constituents (ettringite and monosulphate) as well as unhydrated compound (gypsum) with curing time for paste and suspension, respectively. In paste hydration, it is clear that ettringite and monosulphate hydrate are formed after 30 min. In the suspension hydrated system (Fig. 6) ettringite was formed after 5 min of hydration, whereas the monosulphate hydrate was clearly detected after 30

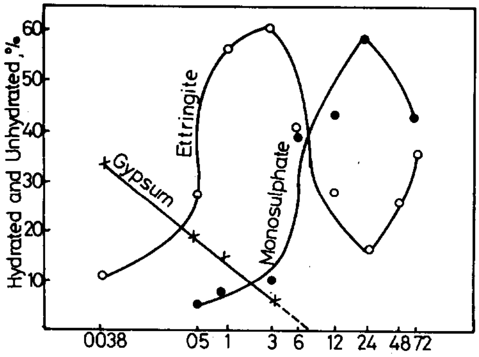

Fig. 6. Ettringite monosulphate and gypsum in the suspension of $C_3A + CaSO_4 \cdot 2\ H_2O$ (1 : 1 mole ratio) as a function of curing time.

min. As the hydration proceeds, the gypsum content decreases and disappears after 12 h in paste hydration and after 3 h in the case of suspension. On prolonged hydration, up to 12 h, the amounts of ettringite and monosulphate hydrate increase slowly. After 12 h up to 45 days in paste hydration, the monosulphate hydrate increases sharply and ettringite decreases. After 45 days, monosulphate hydrate was found to be the predominant phase—55% compared with 25% ettringite.

On the contrary, in the suspension hydration the amount of ettringite increases sharply up to 3 h, whereas the monosulphate hydrate increases slowly. As the hydration proceeds from 3–24 h, the amount of ettringite decreases sharply, whereas the monosulphate increases very quickly. Between 24–72 h, there is further transformation from monosulphate to ettringite, i.e. the ettringite increased and monosulphate hydrate decreased.

From the above results, it is clear that the presence of adequate water, as in suspension hydration, accelerates the hydration mechanism as well as the transformation of ettringite into monosulphate. As can be seen from Fig. 6, there are two transformation steps, whereas in the paste hydration (Fig. 5) one transformation period is observed.

Figure 7 illustrates the kinetics of hydration, as measured by the determination of chemically-combined water contents, W_n, which was determined from the total losses from the TG analysis minus the water content of the unhydrated gypsum. The results indicate that the kinetics of the suspension hydration are faster than the paste hydration. The paste hydration shows a maximum content after 7 days and then decreases up to 45 days. On the contrary, the suspension hydration shows a maximum content after 12 h and minimum after 24 h. This is in agreement with the results shown in Figs. 5 and 6.

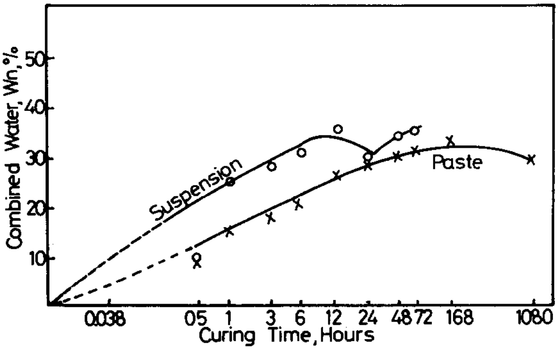

Fig. 7. Kinetics of hydration of suspension as well as paste hydrated $C_3A + CaSO \cdot 2\ H_2O$ (1 : 1 mole ratio) in relation to curing time.

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