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MECHANISM OF THE HYDRATION OF TRICALCIUM ALUMINATE AND GYPSUM OF 1:3 MOLE RATIO AT LOW WATER/SOLID RATIO AND IN SUSPENSION

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ABSTRACT

The hydration kinetics of tricalcium aluminate, C_3A, with gypsum or anhydrite at 1:3 mole ratio were studied using hydration periods of 5 min up to 7 days. These studies were assessed with the aid of differential thermal analysis, thermogravimetric analysis and X-ray diffractometry as well as chemical analysis.

The results revealed that hydration periods of up to 7 days of tricalcium aluminate with gypsum in paste form and in suspension, forms ettringite with unhydrated components of C_3A and gypsum. On the other hand, the only hydration product of the slurry of C_3A with anhydrite is ettringite after 7 days of hydration. The kinetics of hydration were studied by the quantitative determination of ettringite from the TG analysis. The results also illustrate that the rate of ettringite formation is slower in the presence of gypsum than in the presence of anhydrite and also that hydration of the slurry gives more ettringite than the hydration of the paste.

INTRODUCTION

Gypsum has been used as a retarder in Portland cement. The retarding action is mainly based on the reaction of gypsum with the tricalcium aluminate, C_3A, phase to form calcium sulphoaluminate hydrates. Jones [1], D'Ans and Eicke [2], and Shwiete, Ludwig and Jäger [3], in their studies on the equilibria in the quaternary system $CaO–Al_2O_3–CaSO_4–H_2O$, obtained a stable compound $C_3A \cdot 3\ CaSO_4 \cdot 32\ H_2O$ (ettringite) and evidence of a metastable compound of composition $C_3A \cdot CaSO_4 \cdot 12\ H_2O$ (monosulphate hydrate).

A study of the two forms of calcium aluminate hydrates is of interest in cement chemistry as these are detected in hydrated Portland cement. It was shown in an earlier work [4] that the hydration of tricalcium aluminate and

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gypsum with a 1 : 1 mole ratio gave monosulphate and trisulphate hydrates. It can also be concluded that the monosulphate hydrate is a metastable form.

The aim of the present investigation is to study the hydration characteristics of tricalcium aluminate and gypsum in a 1 : 3 mole ratio in paste and in suspension as a function of curing time. The effect of using synthetic anhydrite fired at 600°C instead of raw gypsum on the hydration characteristics of tricalcium aluminate was also investigated.

EXPERIMENTAL

The tricalcium aluminate (C_3A) was synthesized as described in a previous work [4]. The dry constituents of C_3A and gypsum as well as anhydrite (1 : 3 mole ratio) were dry-mixed in a ball mill for 1 h. The hydration was effected with 0.50 and 10.0 water/cement ratios for the paste and slurry, respectively. The preparation of the paste and slurry was discussed earlier [4].

The phases of the hydrated samples were identified by the X-ray diffraction technique using Ni-filtered Cu K_α radiation. A Philips Pw 1390 was used at 40 kV and 20 mA. Differential thermal and thermogravimetric analyses were carried out under a nitrogen atmosphere using a thermal analyser DT-30 (Shimadzu, Japan) with a heating rate of 10°C min^{-1}.

The free $CaSO_4$ was also determined as discussed by Forsen [5]. In this method, 1 g of powdered sample and 300 ml of half-saturated lime water were stirred in a beaker placed on a magnetic stirrer for 1 h at room temperature. The mixture was filtered through a sintered glass funnel, G4, and washed with half-saturated lime water and then with distilled water. As unreacted $CaSO_4$ dissolves, it was determined gravimetrically in the filtrate by using barium chloride solution. From the results of TG analysis, the amounts of ettringite and chemically combined water contents, W_n, were calculated. The chemically combined water contents were estimated from the total losses at 600°C minus the water of unhydrated gypsum.

RESULTS AND DISCUSSION

Paste hydration

Figure 1 shows the X-ray diffraction patterns of the mixtures of $C_3A + CaSO_4 \cdot 2\ H_2O$ (1 : 3 mole ratio) hydrated in paste form as a function of curing time from 5 min up to 7 days. Hydration of this mixture for 5 min shows an insignificant change in its phase composition. After 30 min, a minute amount of ettringite was found to co-exist. When hydration was continued for 1 h the peak due to ettringite increases. The only hydration product was ettringite and no monosulphate hydrate was formed. On prolonged hydration up to 7 days, the peak intensities due to ettringite increase. The unhydrated components, C_3A and $CaSO_4 \cdot 2\ H_2O$, are still present at 7 days.

Figure 2 shows the DTA thermograms of C_3A + gypsum paste (1 : 3 mole ratio) as a function of curing time. It shows the appearance of a small broad

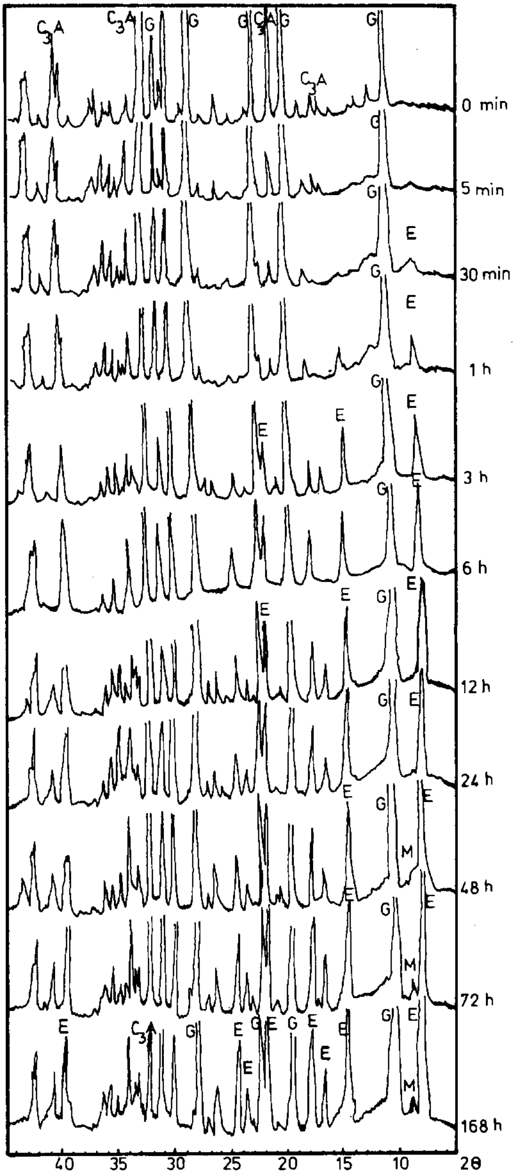

Fig. 1. X-Ray diffraction patterns of $C_3A + CaSO_4 \cdot 2\ H_2O$ (1 : 3 mole ratio) hydrated in paste form at different curing times. G = gypsum; E = ettringite; M = monosulphate.

endothermic peak at 120°C which is related to the dissociation of minute amounts of ettringite. After 30 min, the thermogram shows an increase in this endothermic peak together with two other endothermic effects at about 140 and 180°C and an exothermic peak at 350°C which is related to the dissociation and recrystallisation of gypsum. As the hydration proceeds, the intensity of the ettringite peak increases, whereas the endothermic peaks of the gypsum decrease. After 72 h hydration, the paste shows an endothermic peak at about 270°C. This effect may be attributed to the monosulphate hydrate and/or a solid solution with ettringite [6,7].

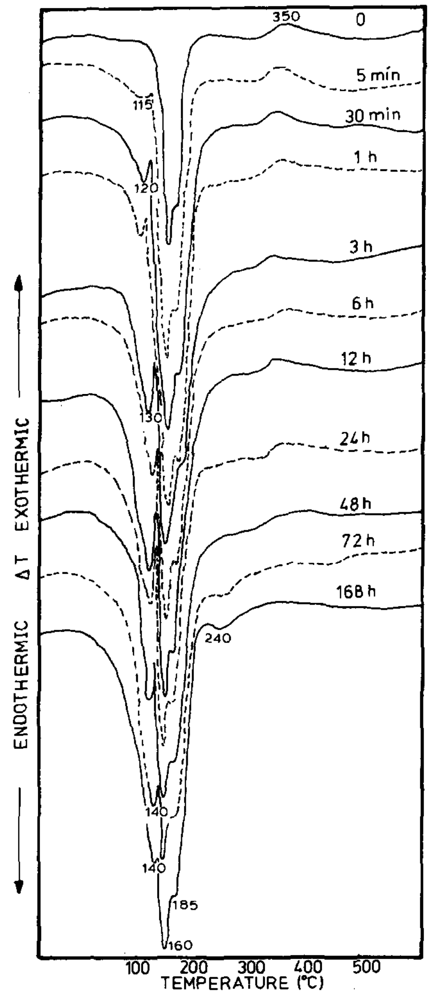

Fig. 2. Differential thermograms of $C_3A + CaSO_4 \cdot 2\ H_2O$ (1 : 3 mole ratio) hydrated in paste form as a function of curing time.

Suspension hydration

The X-ray diffraction patterns of hydrated mixtures of $C_3A + CaSO_4 \cdot 2\,H_2O$ in suspension (1 : 3 mole ratio) as a function of curing time are shown in Fig. 3. The sample hydrated for 5 min shows the lines due to ettringite with greater intensity than that found for hydration of the paste. After 30

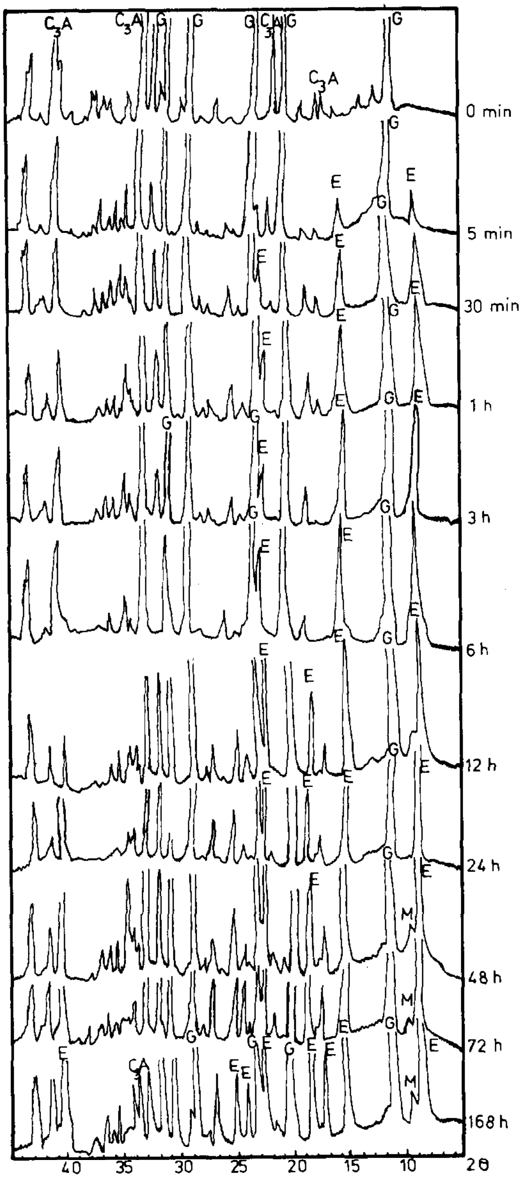

Fig. 3. X-Ray diffraction patterns of $C_3A + CaSO_4 \cdot 2\ H_2O$ (1:3 mole ratio) hydrated in suspension at different curing times. G = gypsum; E = ettringite; M = monosulphate.

min, the amount of ettringite increases. Longer curing times exhibit the presence of ettringite as the main hydration product together with the unhydrated C_3A + gypsum.

The DTA derivatograms of the hydrated mixture of $C_3A + CaSO_4 \cdot 2\ H_2O$ in suspension as a function of curing age are shown in Fig. 4. After 5 min hydration, the thermogram shows an endothermic effect at about 110°C which is related to the dissociation of ettringite. It also shows two other endothermic peaks at 140 and 180°C as well as an exothermic peak at 350°C; these are due to the dehydration of gypsum. On prolonged hydration, the extent of ettringite formation increases, whereas the amount of gypsum decreases. After 24 h of hydration, the derivatogram exhibits another endothermic peak at about 100°C; this may be attributed to the dissociation

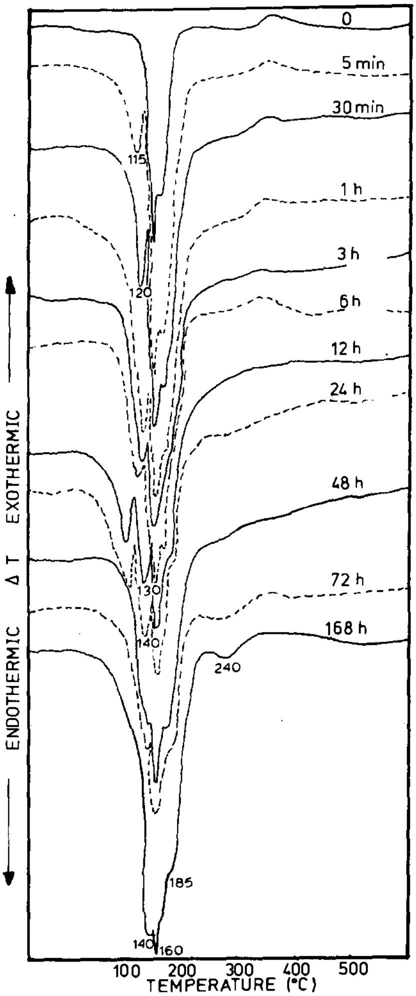

Fig. 4. Differential thermograms of $C_3A+CaSO_4 \cdot 2\ H_2O$ (1:3 mole ratio) hydrated in suspension as a function of curing time.

of another form of ettringite with low water content [8]. The amount of ettringite increases with curing time. Samples hydrated for 72 and 168 h exhibit an endothermic peak at about 250°C. This may be due to the formation of monosulphate hydrate and/or a solid solution with ettringite.

To show the effect of anhydrite on the hydration characteristics of C_3A, gypsum was fired at 600°C for 2 h, mixed with C_3A and hydrated in suspension from 5 min to 7 days. Figure 5 illustrates the X-ray diffraction

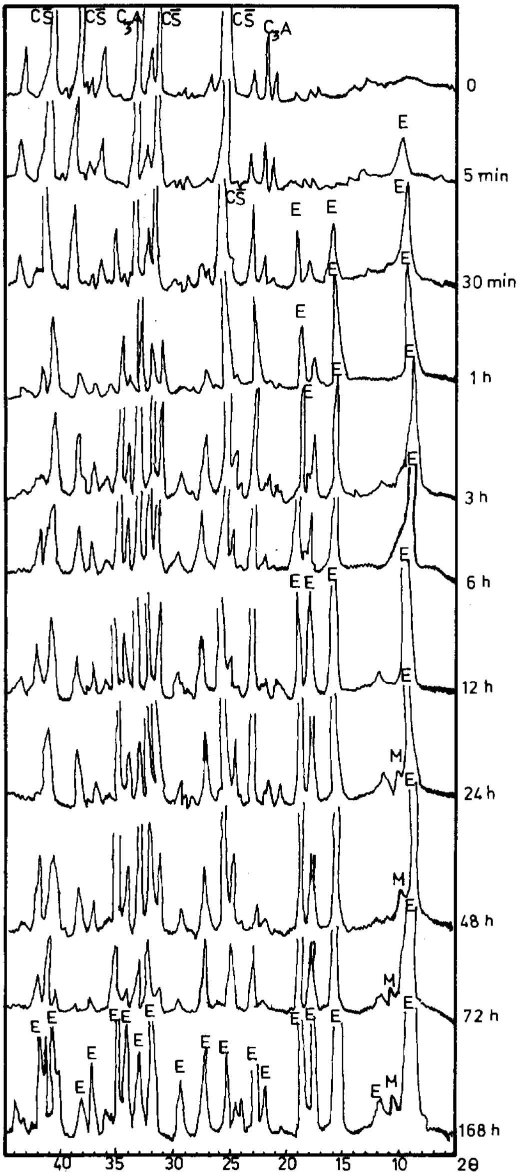

Fig. 5. X-Ray diffraction patterns of $C_3A + CaSO_4$ (1 : 3 mole ratio) hydrated in suspension at different curing times. Cs = $CaSO_4$; E = ettringite; M = monosulphate.

patterns of $C_3A + CaSO_4$ hydrated in suspension (1 : 3 mole ratio) as a function of curing age. The sample hydrated for 5 min exhibits the lines of ettringite with those of $CaSO_4$ and C_3A. After 30 min, the intensities of the lines due to ettringite increase. As hydration progresses, the quantity of ettringite increases and the unhydrated components, C_3A and $CaSO_4$, decrease in quantity. The sample hydrated for 3 days shows ettringite as the main hydration product with small amounts of C_3A and $CaSO_4$. After 7 days of hydration, the pattern shows only the lines of ettringite. It is postulated that hydration of C_3A with anhydrite is faster than hydration with gypsum.

Figure 6 demonstrates the DTA thermograms of $C_3A + CaSO_4$ hydrated in suspension as a function of curing time up to 7 days of hydration. The

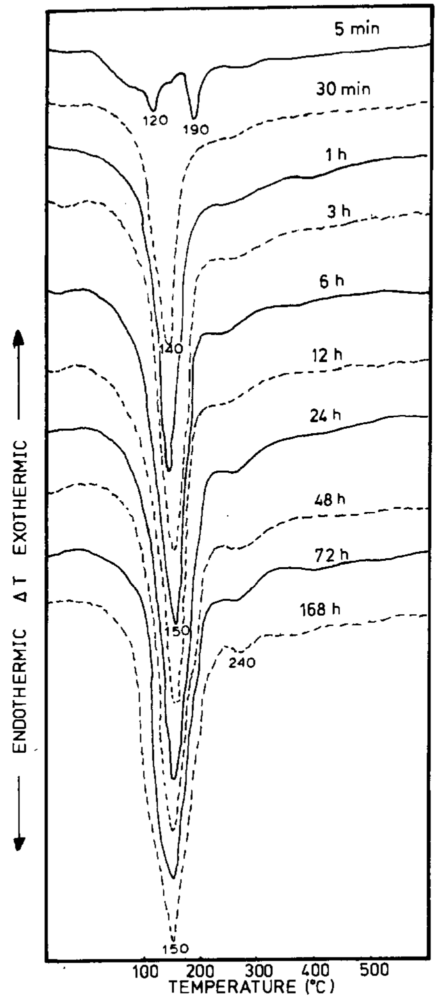

Fig. 6. Differential thermograms of $C_3A + CaSO_4$ (1 : 3 mole ratio) hydrated in suspension as a function of curing time.

sample hydrated for 5 min shows an endothermic peak at 140°C which is due to the dissociation of ettringite. As hydration proceeds, the amounts of ettringite increase sharply. After one day the thermogram shows another weak endothermic peak at about 250°C. This may be attributed to the formation of monosulphate hydrate and/or a solid solution with ettringite. The sample hydrated for 7 days shows ettringite as the only hydration product without any gypsum or unhydrated components.

The kinetics of hydration can be studied by the quantitative determination of ettringite and free $CaSO_4$ in the paste as well as samples hydrated in suspension. It is clear that ettringite is formed after 5 min of hydration in the paste and in the suspended mixture of C_3A with gypsum or anhydrite (Fig. 7). The rate of ettringite formation using gypsum is slower than that of anhydrite. The amount of ettringite is calculated from the results of TG analysis. By using gypsum, it was found that hydration in a slurry yields more ettringite than hydration in a paste. The amounts of ettringite formed after 7 days of hydration are 32 and 37% for C_3A + gypsum as a paste and as a slurry, respectively. On the other hand, the amount of ettringite formed is about 94% for C_3A + anhydrite hydrated in suspension. The kinetics of hydration can also be studied by the quantitative determination of free (unreacted) $CaSO_4$. After 5 min of hydration, the sample hydrated in suspension using $CaSO_4$ gives about 22% free $CaSO_4$. On prolonged hydration, some free $CaSO_4$ is consumed and it is reduced to about 6.50% after 7 days of hydration. On the other hand, the amount of free $CaSO_4$ by using gypsum in the paste and in suspension is 66 and 62%, respectively. On prolonged curing of these samples, the unreacted $CaSO_4$ contents are 53 and 46% for the paste and slurry, respectively. It is also clear that the kinetics of the reaction of anhydrite is faster than the reaction of raw gypsum with C_3A.

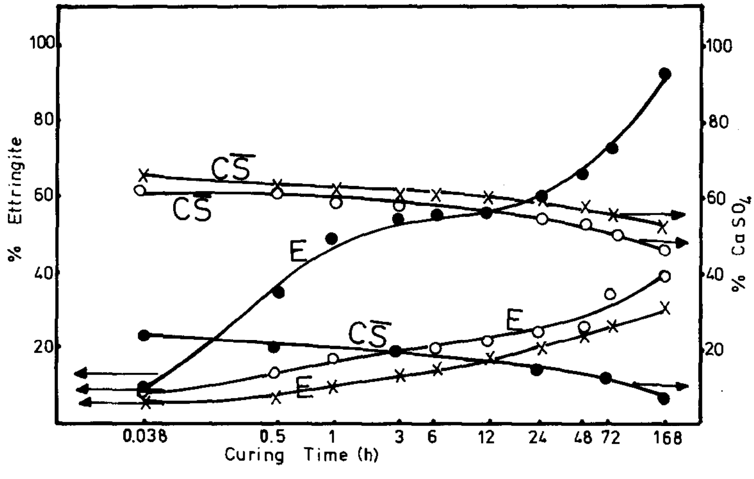

Fig. 7. Ettringite and $CaSO_4$ content in 1 : 3 mole ratio $C_3A + CaSO_4 \cdot 2\ H_2O$ suspensions (○) and pastes (×) and a 1 : 3 mole ratio $C_3A + CaSO_4$ suspension (●) as a function of curing time.

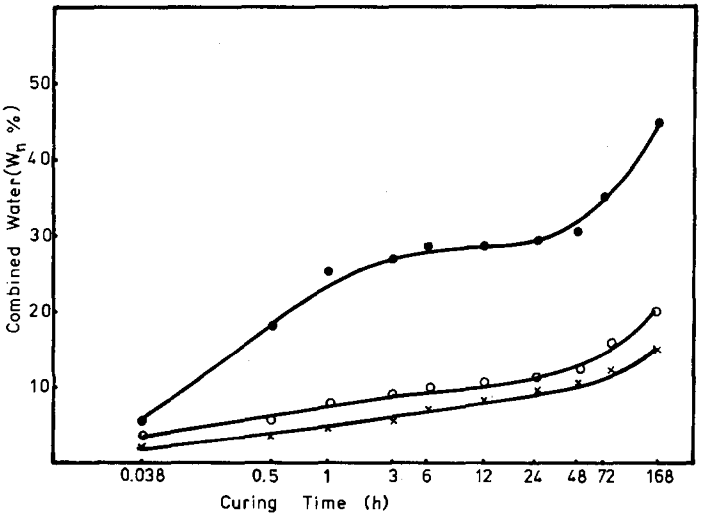

Fig. 8. Kinetics of hydration of a suspension (O) and paste (×) of 1:3 mole ratio $C_3A+CaSO_4 \cdot 2\ H_2O$ and a suspension of 1:3 mole ratio $C_3A+CaSO_4$ (●) as a function of curing time.

Figure 8 illustrates the kinetics of hydration as measured by determination of the chemically-combined water contents, W_n. It is also found that hydration of the suspended mixture is faster than hydration of the paste. It gives about 2.5 and 6.20% of chemically-combined water for the paste and suspended mixture of C_3A + gypsum, respectively, after 5 min of hydration. As hydration proceeds, the amount of chemically combined water increases linearly up to 7 days. The trends of the two curves are parallel to each other, giving 15 and 20% of chemically combined water for the paste and the suspended mixture, respectively, after 7 days of hydration. On the other hand, the hydration of C_3A with $CaSO_4$ gives 7.5% of chemically combined water after 5 min of hydration of the slurry. The amount increases sharply with curing time up to 3 h and then slowly to 48 h and, finally, increases sharply between 48 and 168 h of hydration. It gives about 45% of chemically combined water after 7 days. It is also found that hydration of C_3A with anhydrite is faster than the reaction with raw gypsum.

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