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

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ABSTRACT

The hydration mechanism of tricalcium aluminate C_3A with CaO at 1:1 mole ratio was studied in paste as well as slurry from 5 min up to 7 days of hydration. These studies were made with the aid of X-ray diffractometry, differential thermal analysis and thermogravimetric analysis. The results illustrate that the hydrate phases C_4AH_{13} and C_3AH_6 are still formed in the paste and slurry hydrations from 5 min up to 7 days. It was concluded that the free $Ca(OH)_2$ is also found in the two hydrated systems after 7 days. The amount of C_3AH_6 is maximum at 24 h and then decreases, whereas the amount of C_4AH_{13} increases with curing time.

INTRODUCTION

The quaternary system comprising CaO, Al_2O_3, SiO_2 and Fe_2O_3 as well as H_2O are of importance in studying the chemistry and morphology of hydrous calcium silicates and aluminates in hydrating cement. Portland cement is composed of four major phases: tricalcium silicate C_3S, B-dicalcium silicate B-C_2S, tricalcium aluminate C_3A, and tetracalcium aluminoferrite C_4AF. C_3S and B-C_2S liberate $Ca(OH)_2$ during the hydration of portland cement. It has been pointed out by some workers, such as Forsen [1], Seligman and Creening [2], Mori [3], Stein [4] and Copeland and Kantro [5], that calcium hydroxide liberated from the hydration of calcium silicates controls the formation of ettringite even in the early stage of C_3A hydration. Tricalcium aluminate [6] reacts with excess water to form C_2AH_8 and either or both C_3AH_6 and C_3A. $Ca(OH)_2 \cdot 12\ H_2O \cdot C_2AH_8$ reacts with $Ca(OH)_2$ to form C_4AH_{13} or C_3AH_6, depending on the hydration conditions.

The aim of the present investigation is to elucidate the hydration mechanism of C_3A in the presence of $Ca(OH)_2$ (1:1 mole ratio) in paste and in

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suspension. The hydration is studied from 5 min up to 7 days by differential thermal analysis and X-ray diffraction technique.

EXPERIMENTAL

Tricalcium aluminate C_3A was synthesized as described previously [7]. The dry components of C_3A and $Ca(OH)_2$ (1 : 1 mole ratio) were dry-mixed in a ball mill for 1 h to ensure homogeneity. The hydration was made with 0.50 and 10.0 water/solid ratios by weight for the paste and slurry, respectively. The preparation of the paste as well as slurry was discussed in an earlier work [7]. The hydration kinetics and products were determined by X-ray diffraction technique and differential thermal analysis and thermogravimetry. From the results of TG analysis, the amount of C_4AH_{13},

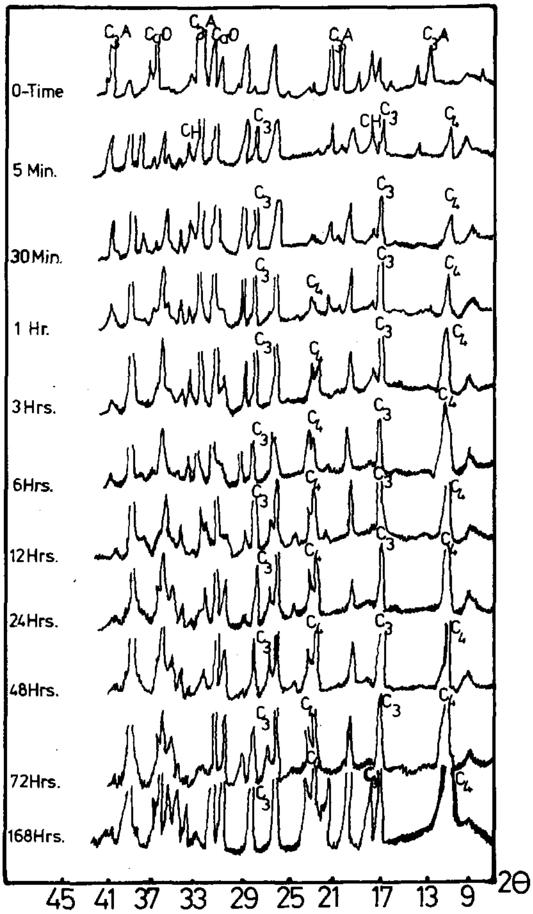

Fig. 1. X-Ray diffraction patterns of C_3A+CaO paste (1 : 1 mole ratio) in relation to curing time. $C_3 = C_3AH_6$, $C_4 = C_4AH_{13}$, and $CH = Ca(OH)_2$.

C_3AH_6, $Ca(OH)_2$, as well as the chemically-combined water content, W_n, were calculated. The chemically-combined water content was estimated from the total loss at 600°C minus the water of calcium hydroxide.

RESULTS AND DISCUSSION

Paste hydration

Figure 1 illustrates the X-ray diffraction patterns of $C_3A + CaO$ (1 : 1 mole ratio) hydrated in paste form in relation to curing time from 5 min up to 7 days. The patterns show the formation of C_4AH_{13} and C_3AH_6 after 5 min of hydration. After 30 min, the amount of calcium aluminate hydrate increases and C_3A decreases. The pattern of C_3A as well as $Ca(OH)_2$ is still present up to 7 days. At 7 days of hydration, the hydrated phases are

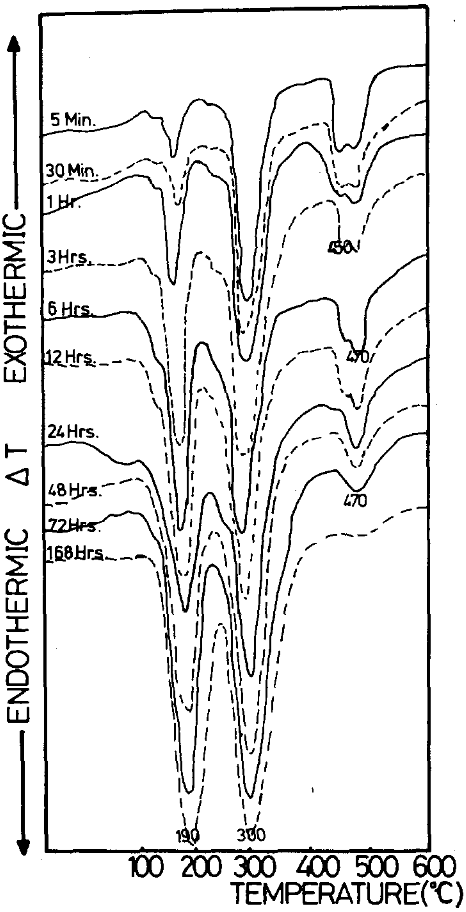

Fig. 2. DTA thermograms of $C_3A + CaO$ paste (1 : 1 mole ratio) as a function of curing time.

C_3AH_6 and C_4AH_{13}; unhydrated C_3A and $Ca(OH)_2$ are also present.

The DTA thermograms of $C_3A + Ca(OH)_2$ paste (1 : 1 mole ratio) as a function of curing age are shown in Fig. 2. After 5 min, four endothermic peaks at 170, 290, 460 and 480°C are shown. The first effect is attributed to the dissociation of C_4AH_{13}, the second and third peaks are due to C_3AH_6, and the last endothermic peak at 480°C is attributed to the decomposition of $Ca(OH)_2$ [2–8]. On prolonged hydration, the amount of C_4AH_{13} and C_3AH_6 increases. The free $Ca(OH)_2$ content decreases with increasing hydration time. It is seen that C_3AH_6 and C_4AH_{13} as well as a small amount of $Ca(OH)_2$ are found in the hydrated system after 7 days of hydration.

Suspension hydration

Figure 3 shows the X-ray diffraction patterns of $C_3A + CaO$ in suspension (1 : 1 mole ratio) as a function of curing time. After 5 min, the patterns

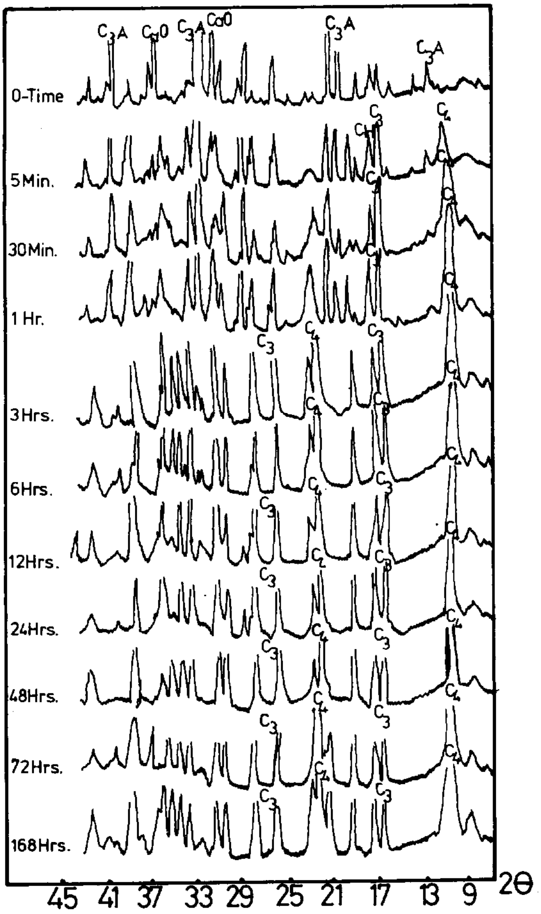

Fig. 3. X-Ray diffraction patterns of $C_3A + CaO$ suspension (1 : 1 mole ratio) in relation to curing time. $C_3 = C_3AH_6$, $C_4 = C_4AH_{13}$, and $CH = Ca(OH)_2$.

show the lines of C_4AH_{13}, C_3AH_6 with the lines of unhydrated C_3A and $Ca(OH)_2$. As the hydration progresses, the amount of hydrated calcium aluminate increases, whereas the C_3A disappears after 24 h of hydration. As in the case of the paste hydration, the hydrated phases in the suspension are C_4AH_{13} and C_3AH_6, with some unhydrated $Ca(OH)_2$.

The DTA derivatograms of the hydrated mixture of $C_3A + CaO$ in suspension (1 : 1 mole ratio) as a function of curing time are shown in Fig. 4. After 5 min of hydration, the thermogram illustrates three endothermic effects at about 190, 300 and 480°C. The low endothermic peak at 190°C is attributed to the decomposition of C_4AH_{13}, whereas the endothermic effect at 300°C is due to the dissociation of C_3AH_6, and the third endothermic peak at 480°C is due to $Ca(OH)_2$. As the hydration proceeds, the extent of two endothermic peaks at 190 and 300°C increases and the third peak of $Ca(OH)_2$ at 480°C decreases. It can be seen that after 7 days of hydration

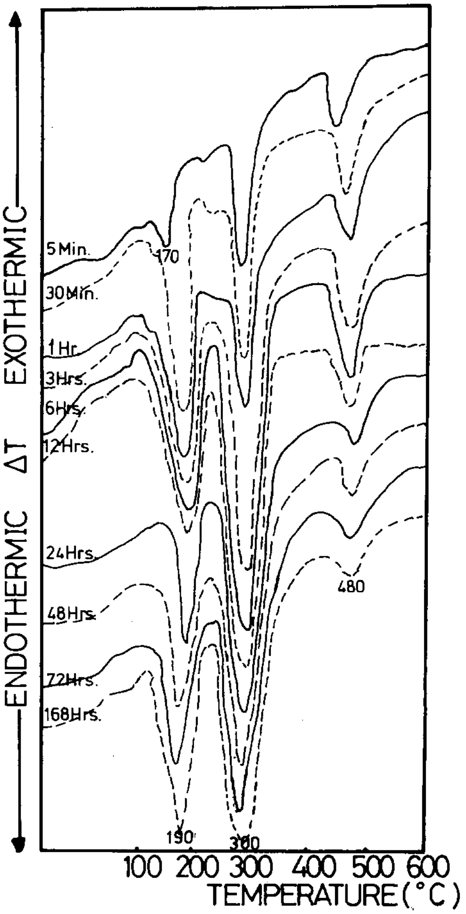

Fig. 4. DTA thermograms of $C_3A + CaO$ suspension (1 : 1 mole ratio) as a function of curing time.

the hydrated phases are C_3AH_6 and C_4AH_{13}, with some unhydrated $Ca(OH)_2$.

Kinetics of hydration

The hydration mechanism of $C_3A + CaO$ (1 : 1 mole ratio) can be studied by the quantitative determination of C_4AH_{13}, C_3AH_6 as well as $Ca(OH)_2$ from the results of TG. The kinetics of hydration can also be studied from the determination of chemically-combined water content, W_n, in relation to curing time for the hydration in paste as well as in suspension.

Figure 5 shows the mechanism of formation of C_4AH_{13} and C_3AH_6 and also the consumption of $Ca(OH)_2$ with curing time. It is clear that C_4AH_{13} and C_3AH_6 are formed after 5 min in the paste and in suspension. The amount of C_3AH_6 is greater than C_4AH_{13}. The paste hydration also shows lower values than the suspension. Values of 14.08 and 12.7% are obtained for C_3AH_6 for suspension and paste hydration, respectively, compared with values of 5.9 and 4.2% for C_4AH_{13}. As the hydration continues, the amount of hydrated calcium aluminate increases and $Ca(OH)_2$ decreases. After 3 h the amount of C_3AH_6 of paste hydration is higher than the value obtained in slurry hydration and then increases up to 24 h. Between 24 and 168 h, the amount of C_3AH_6 decreases. On the other hand, the amount of C_4AH_{13} increases gradually with curing time. After 6 h, the degree of paste hydration is higher than the corresponding slurry hydration. On the contrary, the amount of $Ca(OH)_2$ decreases linearly with increasing curing time.

There is no great difference between the amount of $Ca(OH)_2$ in the case of paste and slurry.

Figure 6 shows the kinetics of hydration as measured from the

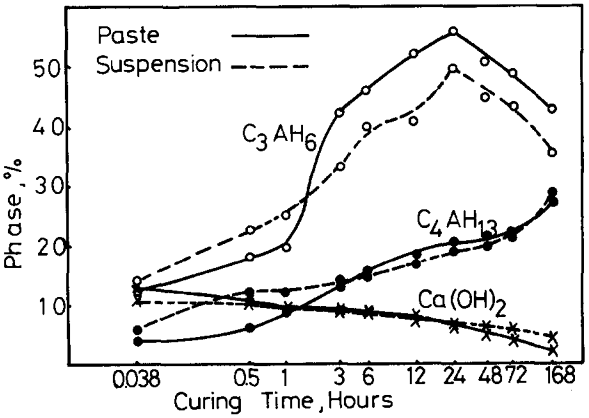

Fig. 5. C_4AH_{13}, C_3AH_6 and $Ca(OH)_2$ in 1 : 1 mole ratio $C_3A + CaO$ in suspension and paste as a function of curing time.

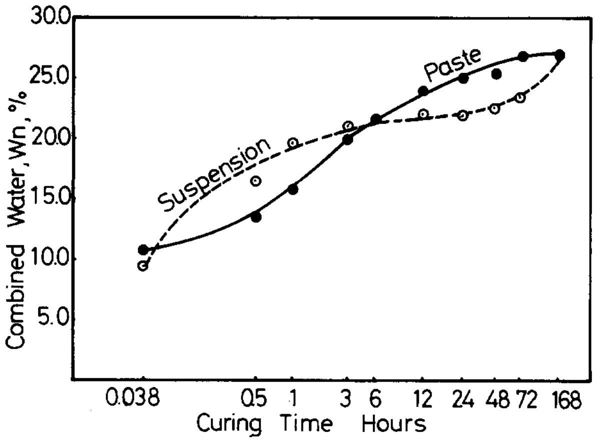

Fig. 6. Kinetics of hydration of suspension and paste of 1:1 mole ratio $C_3A + CaO$ as a function of curing time.

chemically-combined water content, W_n. The combined water is determined from the TG losses minus the amount of water of $Ca(OH)_2$. It is clear from Fig. 6 that hydration of the suspended mixture is faster than the paste hydration at very early stages of hydration then decreases between 4 and 5 h. After 6 h, the paste hydration shows higher values of combined water than the slurry hydration. The behaviour of the chemically-combined water content, W_n, is nearly parallel with the amount of C_4AH_{13} in the paste and slurry hydrations.

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