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THE EFFECT OF C_3S ON THE EARLY HYDRATION OF C_3A

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Abstract

The hydration of C_3A, C_3S and C_3A+C_3S mixtures was examined by thermogravimetry, differential thermogravimetry and calorimetry. The results showed the early hydration (15 min) of C_3A+C_3S is of two types: If the content of $C_3S<40\%$, then C_3A hydrates as it does alone, but if the content of $C_3S\geq40\%$, then the hydrate with the lowest temperature and the cubic one do not appear together up to 15 min.

Keywords: hydration of C_3A, C_3S and C_3A+C_3S

Introduction

C_3A and C_3S* are two of the compounds in ordinary Portland cement (OPC). It is accepted that tricalcium aluminate, C_3A, is the major component of clinker, which has a significant effect on the early hydration of cement. C_3S hydrates more slowly, but it is the main factor responsible for the strength of OPC concrete.

The hydration of C_3A and C_3S has been widely examined [1]. The hydration products of C_3A are hexagonal and cubic hydrates. The latter is the more stable. The hydration products of C_3S are a calcium silicate hydrate known as C–S–H, and calcium hydroxide, $Ca(OH)_2$ (portlandite).

Only a few investigations have been carried out on C_3A+C_3S, but merely with limited proportions of C_3A and C_3S. Corstane *et al.* [2] studied only mixtures with $C_3A/C_3S=3$ by weight. By X-ray diffraction, they found, only the cubic hydrate up to 30 h.Ghorab *et al.* [3] investigated mixtures with the following mole ratios of alite (C_3S with traces of Mg and Al) to C_3A: 0.1, 1, 10 and 20. They noted that in <2.3% alite solution, C_3A grains are coated by both hex-

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* Conventional cement nomenclature is as follows: C=CaO, $A=Al_2O_3$, $F=Fe_2O_3$, $S=SiO_2$, $H=H_2O$

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agonal and cubic aluminate hydrates; in >2.3% alites solution, the size of the products is below the detection of the X-ray method. They concluded that the effect of alite on C_3A hydration depends on the water/solid ratio. Plowman and Cabrera [4] observed that for C_3A+C_4AF extracted from clinker, the cubic hydrate appears in less than 15 min. Besides the hexagonal hydrates, Ramachandran and Chun-Mei [5] detected a DSC peak at 100°C, attributed to the desorption of water, but they did not find the cubic hydrate before 1 h. Loprayon and Rossington [6] studied a mixture of C_3A+0.125% calcium lignosulfonate by means of DTA, and demonstrated C_2AH_8 and the cubic hydrate C_3AH_6 even at 5 min. Monosi *et al.* [7] noted a DTG peak at 100°C, which was particularly evident in the presence of hexagonal hydrates. They confirmed the hypothesis of Ramachandran [5] that this peak is related to the thermal desorption of water adsorbed on the hexagonal hydrates. This is not in agreement with the view of researchers who suggest that this peak is present only in the presence of admixtures such as lignosulfonate [8] or gluconate [9].

The aim of the present work was to study the hydration of C_3A without and with the addition of C_3S in different proportions, ranging from 10 to 90%.

Experimental procedure

Materials

C_3A was synthesized from reagent grade $CaCO_3$ and Al_2O_3, by heating the mixture in appropriate molar ratio at 1350°C in several consecutive runs. C_3S was synthesized from reagent grade $CaCO_3$ and SiO_2 by heating the mixture in appropriate molar ratio at 1500°C for 60 h. The samples were ground in a laboratory mill to a Blaine specific surface of about 3000 cm^2/g. Distilled water was added to C_3A, C_3S and C_3A+C_3S. Hydration of pastes with a water/solid ratio of 0.5 was examined at room temperature. After definite times, the hydration was stopped by grinding the pastes with acetone. The pastes were dried at room temperature under vacuum.

Methods

Thermal analysis

TG and DTG curves were obtained with a Thermoanalyseur G70 SETARAM at a heating rate of 6.66 $deg \cdot min^{-1}$. The temperature range was from room temperature to about 1000°C.

Conduction calorimetry

The calorimeter for measuring heat development was a Biocalorimètre BCP ARION. For each experiment, the distilled water was added by syringe at a water/solid ratio of 1.

Results and discussion

X-ray diffraction measurements

Figure 1 shows the X-ray diffraction patterns of synthesized C_3A(1a) and C_3S(1b). They are in excellent agreement with published patterns [10, 11].

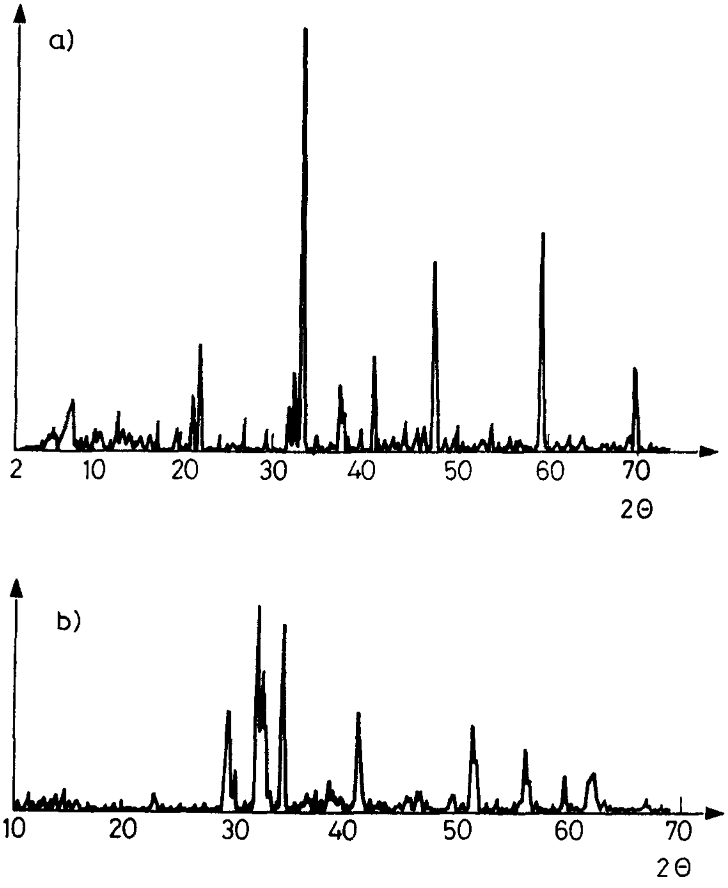

Fig. 1 (a) X-ray pattern of C_3A, (b) X-ray pattern of C_3S

TG and DTG measurements

Figure 2 depicts the TG and DTG curves of C_3A hydrated for 15 min without C_3S. Four peaks are observed, at about 100, 180, 320 and 500°C. A shoulder can also be observed at about 470°C. The peak at 180°C is attributed to dehydration of the hexagonal hydrate C_2AH_8. The peak at 100°C is stronger and sharper than the others. The peaks at 320 and 500°C correspond to the cubic

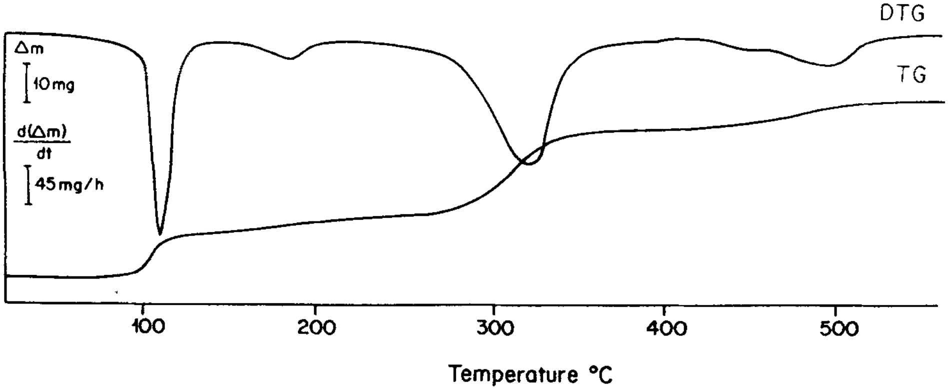

Fig. 2 TG and DTG curves of C_3A hydrated for 15 min

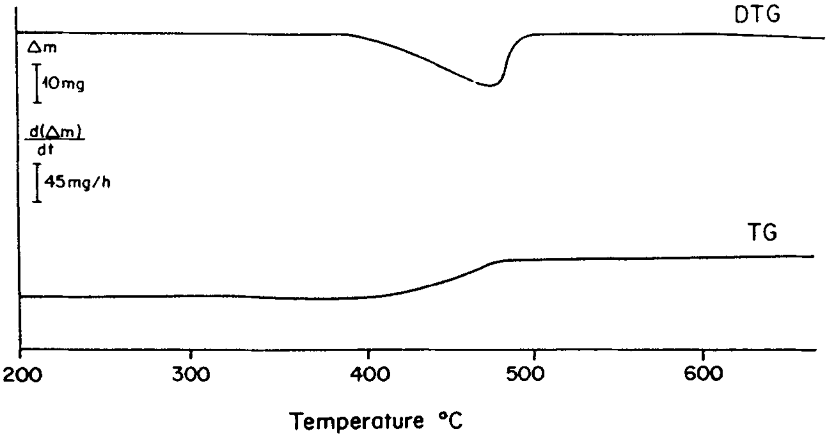

Fig. 3 TG and DTG curves of $Ca(OH)_2$

hydrate C_3AH_6, and the shoulder to $Ca(OH)_2$. The dehydration of pure $Ca(OH)_2$ is seen in Fig. 3, with a DTG peak at about 480°C. Figure 4 depicts the DTG curves of C_3A hydrated for different times, from 5 min up to 3 days. The peak at 100°C increases up to 16 h, after which it decreases, while that at 180°C increases up to 3 days. It is important to note that the peak at 100°C is sharper than that at 180°C. It seems that the loss in mass at 100°C is easier and quicker than at 180°C. The hydrate which transforms at 100°C seems to be less stable than the other one. This observation supports the hypothesis that the peak at 100°C corresponds to the desorption of water [4]. After 24 h, this peak decreases. It is probable that some of the water is not only adsorbed, but strongly bonded as in a hydrate. C_3AH_6 appears simultaneously with the hexagonal hydrate. Figure 5 shows the DTG curves of C_3S hydrated for different times. When C_3S reacts with water, C–S–H and CH are formed. The corresponding DTG peaks occur at about 120–130°C and 500°C, respectively. A peak is also ob-

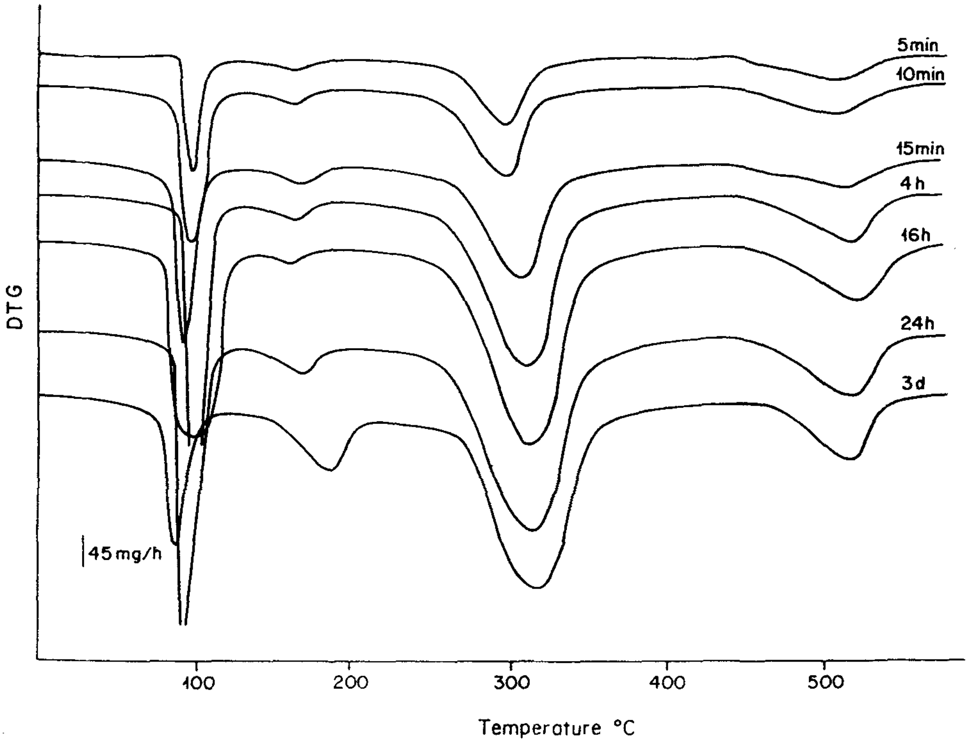

Fig. 4 DTG curves of C_3A hydrated for different times

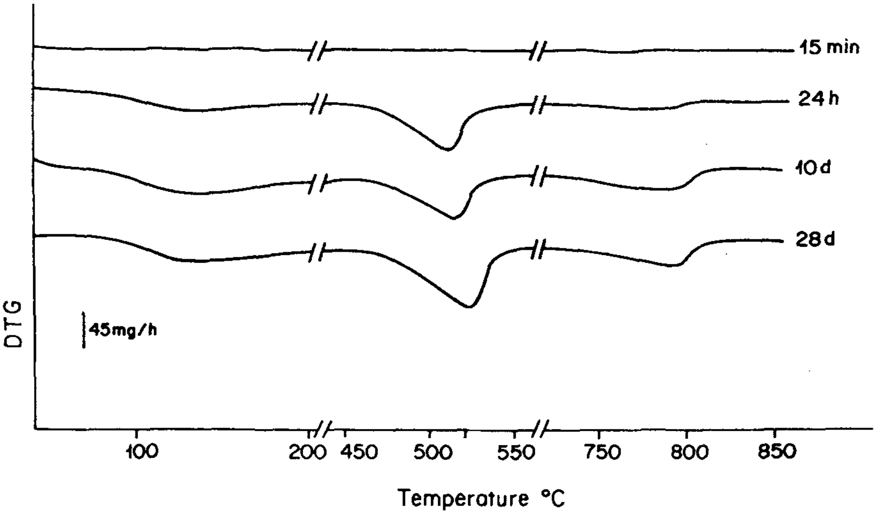

Fig. 5 DTG curves of C_3S hydrated for different times

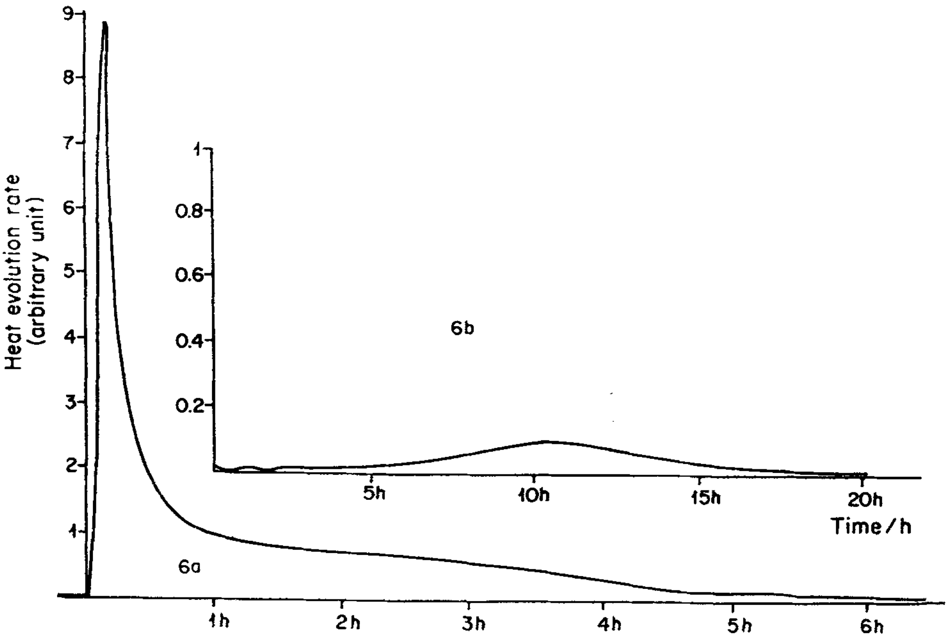

Fig. 6 Rate of heat evolution for C_3A (a), rate of heat evolution for C_3S (b)

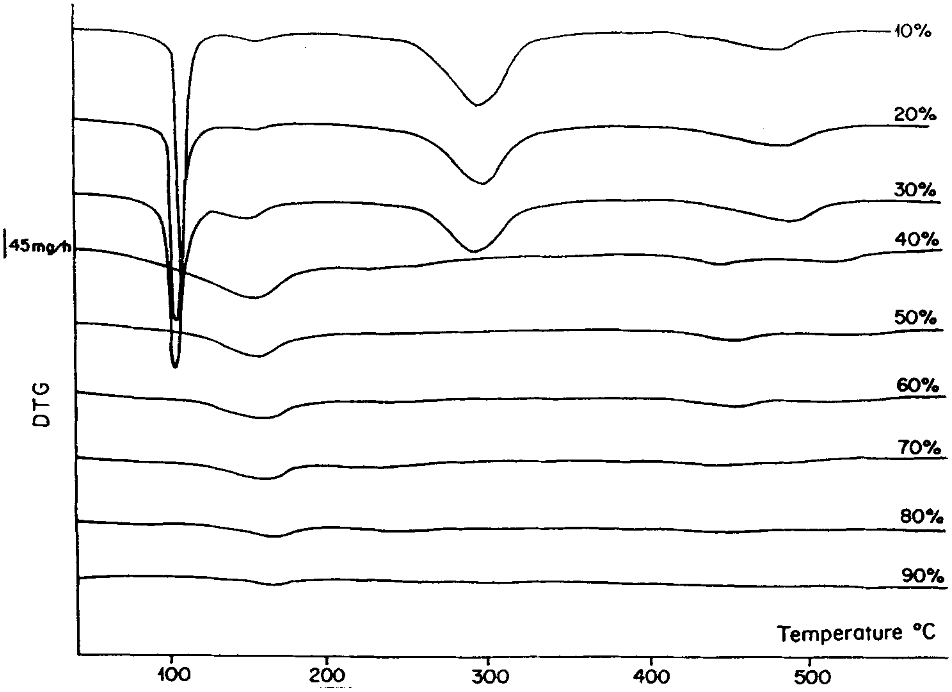

Fig. 7 DTG curves of $C_3A + C_3S$ mixtures containing different proportions of C_3S, hydrated for 15 min

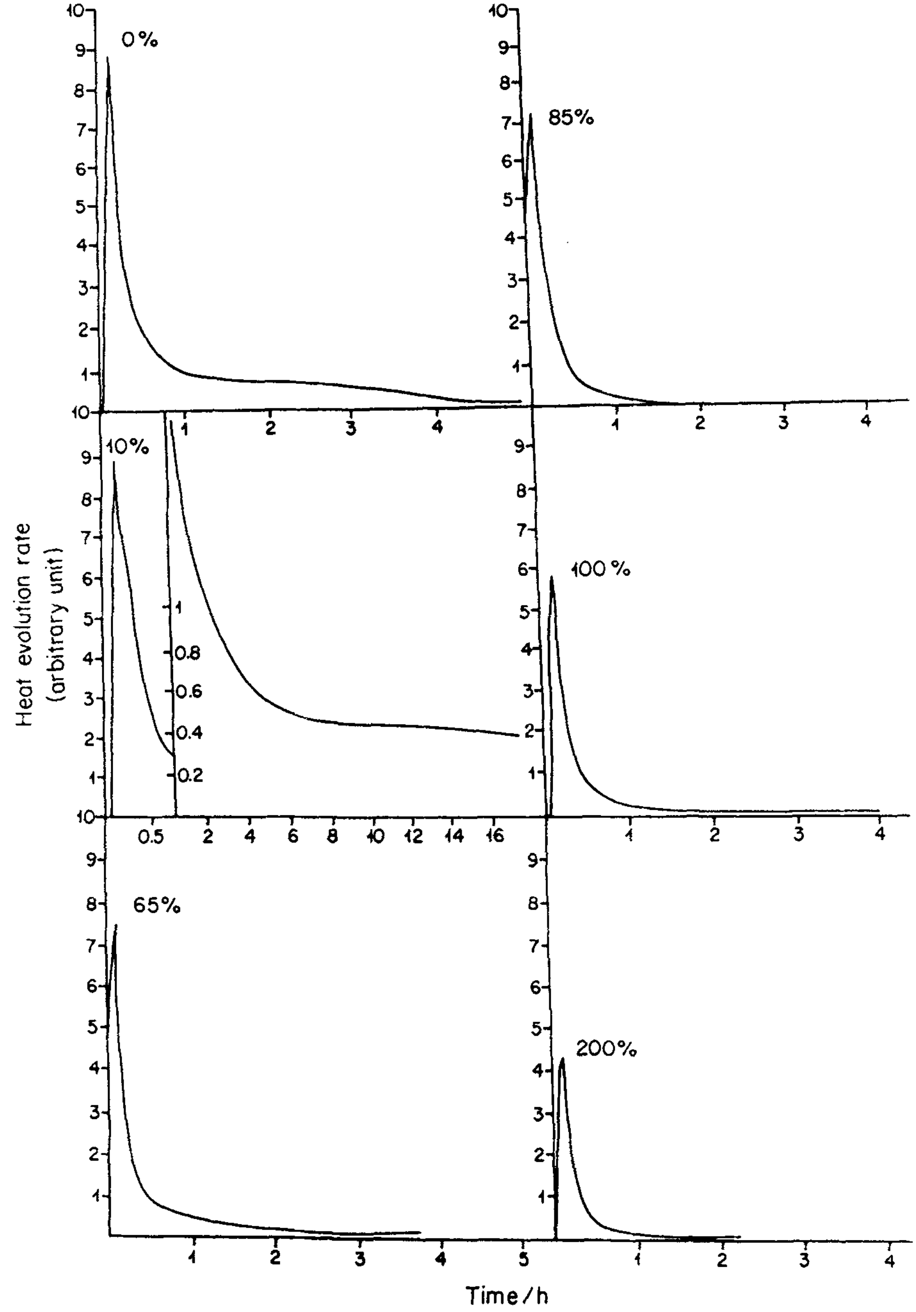

Fig. 8 Rate of heat evolution from C_3A+C_3S mixtures containing different proportions of C_3S

served at about 800°C, due to $CaCO_3$. Figure 7 presents DTG curves of C_3A hydrated with C_3S in different proportions for 15 min. The hydration products are the same as those obtained without C_3S, but only if the content of $C_3S<40$ %. C_3S does not hydrate in this time (Figs 5 and 6b). If the content of $C_3S \geq 40\%$, the peaks at 100, 320 and 520°C are practically not observed. From a comparison of the DTG curves of C_3A hydrated alone with those of C_3A+C_3S at 15 min at a C_3S content $\geq 40\%$, it can readily be concluded that, at this concentration, the formation of cubic aluminate hydrate is blocked. The peak at 100°C is not observed either. On the other hand, the amount of the hexagonal hydrate with DTG peak at 180°C increases. The peaks at 100°C and at 320 and 520°C appear and disappear simultaneously. Since the peak at 100°C certainly corresponds to the desorption of water, it can be concluded that the adsorption of water occurs on both hexagonal and cubic hydrates. After hydration of C_3A+C_3S with a C_3S content $\geq 40\%$ for 15 min, the main hydrate formed is that with DTG peak is at 180°C.

Calorimetric measurements

In Fig. 6, the rate of heat evolution as a function of time is shown C_3A(6a) hydrates more quickly than C_3S. For C_3A, a large heat evolution peak is recorded during the first 30 min. A second, smaller peak can also be observed. C_3A reacts immediately with water and the hydration rate reaches a maximum after about 8 min. Subsequently, the hydration rate decreases. The hydrates form a barrier layer which inhibits the transport of water to the C_3A grain and slows the hydration. On the other hand, the heat evolution peak of C_3A together with C_3S seems to decrease when the proportion of C_3S increases (Fig. 8).

The C_3A grains are surrounded by the formed hydrates and particles of C_3S. The number of these particles coating the C_3A grain increases with the proportion of C_3S and the amount of water in contact with the C_3A then decreases. The sequence of C_3A hydration is modified. However, it is necessary to study this phenomenon at higher times of hydration, especially when the hydration of C_3S begins. This will be the topic of future papers.

Conclusion

The above results and discussion have led to the following conclusions:

C_3A hydration

– The DTG peak at 100°C appears without an admixture and certainly corresponds to the desorption of water.

– The aluminate cubic and hexagonal hydrates appear almost simultaneously, immediately when C_3A comes into contact with water, although ESCA studies reveal only the hexagonal hydrate in a few milliseconds.

C_3A+C_3S hydration

The addition of C_3S modifies the hydration behaviour of C_3A.

– If the content of $C_3S<40\%$, the hydration products of C_3A are the same as for C_3A alone.

– If the content of $C_3S\geq 40\%$, the hydrate with the lowest temperature and the cubic one do not appear together up to 15 min. Further, it seems that water adsorption occurs on both hexagonal and cubic hydrates.

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Zusammenfassung — Mittels Thermogravimetrie, Differentialthermogravimetrie und Kalorimetrie wurde die Hydration von C_3A, C_3S und C_3A+C_3S-Gemischen untersucht. Die Resultate ergeben zwei Arten einer frühzeitigen Hydration (15 min) von C_3A+C_3S: liegt der C_3S-Gehalt unter 40%, hydratiert C_3A allein, beträgt der C_3S-Gehalt jedoch mindestens 40%, dann treten das Hydrat mit der niedrigsten Temperatur und das kubische vor Ablauf von 15 min nicht gemeinsam auf.