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HYDRATION OF C_3A IN THE PRESENCE OF $CaCO_3$

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Abstract

The hydration of C_3A with and without $CaCO_3$ was studied. The techniques used were X-ray diffraction, thermogravimetry, differential thermogravimetry and calorimetry.

In the presence of $CaCO_3$, the hydration of C_3A is accelerated. The hexagonal hydrates are formed first. They react with $CaCO_3$ to form calcium carboaluminate hydrate. This reaction blocks formation of the cubic hydrate. The latter appears when $CaCO_3$ is completely consumed.

Keywords: C_3A, $C_3A+CaCO_3$, hydration

Introduction

C_3A* is a component of ordinary Portland cement (OPC) which reacts very quickly with water. It is generally accepted that during this hydration the metastable hexagonal hydrates C_2AH_8 and C_4AH_{13} are formed first, before conversion to the stable cubic hydrate C_3AH_6:

$$2C_3A + 21H \rightarrow C_2AH_8 + C_4AH_{13}$$

$$C_2AH_8 + C_4AH_{13} \rightarrow 2C_3AH_6 + 9H$$

It has been shown by different techniques (calorimetry, water desorption, XRD, conductometry, etc.) that the addition of $CaCO_3$ to a Moroccan OPC accelerates its hydration, although its compressive strength decreases by about 18% when 20% of $CaCO_3$ is added [1]. In a recent study. Montanaro *et al.* [2] showed that, in the hydration of C_3S, it seems possible to remove 50% of the gypsum by adding 50% $CaCO_3$. In fact, gypsum is used in cement chemistry to control the setting of the hydration products. However, the compressive strength of the hydration products of $C_3S+CaCO_3$ has not been studied. C_3A hydration has been studied widely [3, 4]. On the other hand, some studies on the system $C_3A–CaO–CaCO_3–H_2O$ show that the following hydrates can be detected [5–8].

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* **Conventional nomenclature in cement chemistry: C:CaO; S:SiO_2; A:Al_2O_3; F:Fe_2O_3; H:H_2O**

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$C_3A{\cdot}0.5CaCO_3{\cdot}0.5Ca(OH)_2{\cdot}11.5H_2O$
$C_3A{\cdot}CaCO_3{\cdot}11H_2O$
$C_3A{\cdot}3CaCO_3{\cdot}32H_2O$

Longuet and Thuret [9] have proposed that the formation of carboaluminate hydrate can be used to measure the reactivity of $CaCO_3$ with C_3A.

This field is of great interest in Morocco, since a decrease in clinker production is the best manner to save energy and avoid pollution. However, much attention must be directed towards the performances of the corresponding pastes (the strength, for example).

The purpose of the present work is to try to understand the sequence of steps in the hydration of the system $C_3A+CaCO_3$. In our subsequent experiments we shall study the effects of $CaCO_3$ on the hydration of other cement compounds, alone or combined.

Experimental procedure

Materials

C_3A was synthesized from reagent grade $CaCO_3$ and Al_2O_3, by heating the mixture in the appropriate molar ratio at 1350°C in several consecutive burnings. The product obtained (surface area in the range 2500–3000 $cm^2\ g^{-1}$) was blended with reagent grade $CaCO_3$ (about 6 $m^2\ g^{-1}$), (Table 1). The samples were ground in a laboratory mill.

Distilled water was added to C_3A and $C_3A+CaCO_3$. The hydration at room temperature of pastes with a water/solid ratio of 0.5 was examined. At a definite time, the hydration was stopped by grinding the pastes with acetone. The pastes were dried at room temperature under vacuum.

Methods

X-ray diffraction

X-ray measurements were made on a fully automated Rigaku unit diffractometer operating at 40 kV and 20 mA, using copper K_α radiation ($\lambda=1.5418$ Å).

Thermal analysis

TG and DTG curves were obtained with a Setaram Thermoanalyseur G 70 at heating rate of 10°C min^{-1}. The temperature range was from room temperature to about 800°C. The sample mass was 200 mg.

Table 1 Percentage composition of mixture (by weight)

Mix	C_3A	$CaCO_3$
1	100	0
2	90	10
3	80	20

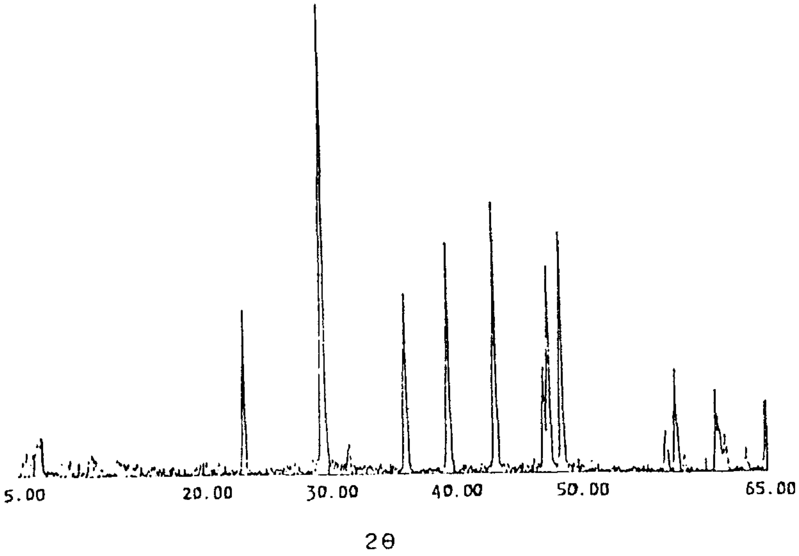

Fig. 1 XRD pattern of $CaCO_3$

Conduction calorimetry

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

Results and discussion

XRD measurements

The XRD pattern of $CaCO_3$ shows that it has the calcite structure (Fig. 1). Figure 2 depicts the XRD diagram of synthesized C_3A, which is in agreement with the literature [10]. The XRD pattern of C_3A hydrated for 15 min is illustrated in Fig. 3. The hydration products noted are C_2AH_8, C_4AH_{13} and C_3AH_6. Table 2 presents the results of XRD. The different quantities of compounds present were indicated semiquantitatively by the relative intensities of some characteristic lines in arbitrary units. The following lines were used:

C_3A (2.18 and 1.55 Å)
$CaCO_3$ (3.04 Å)
C_2AH_8 (11.12 Å)
C_4AH_{13} (7.9 Å)
C_3AH_6 (3.26 Å)
$C_3A{\cdot}CaCO_3{\cdot}H_{11}$ (7.57 Å): carboaluminate hydrate.

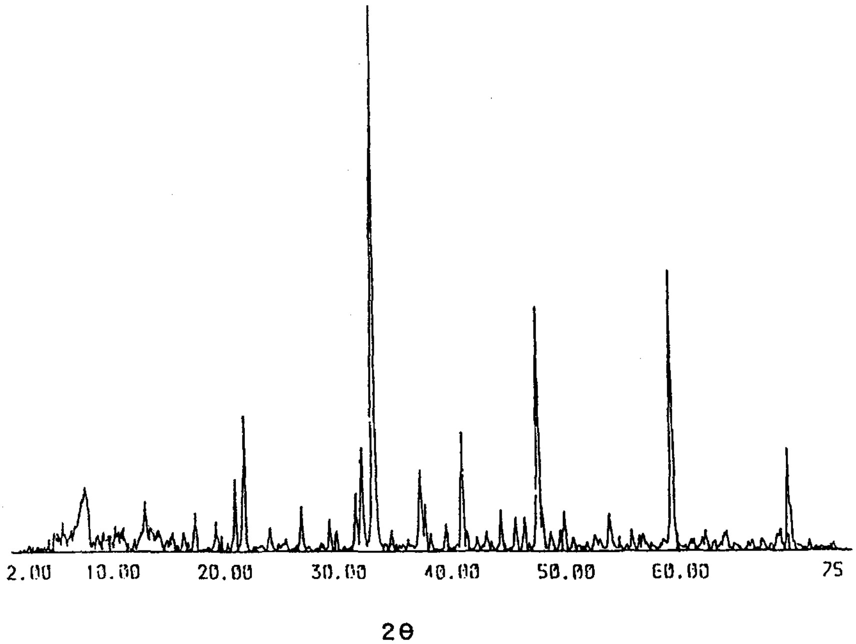

Fig. 2 XRD pattern of C_3A

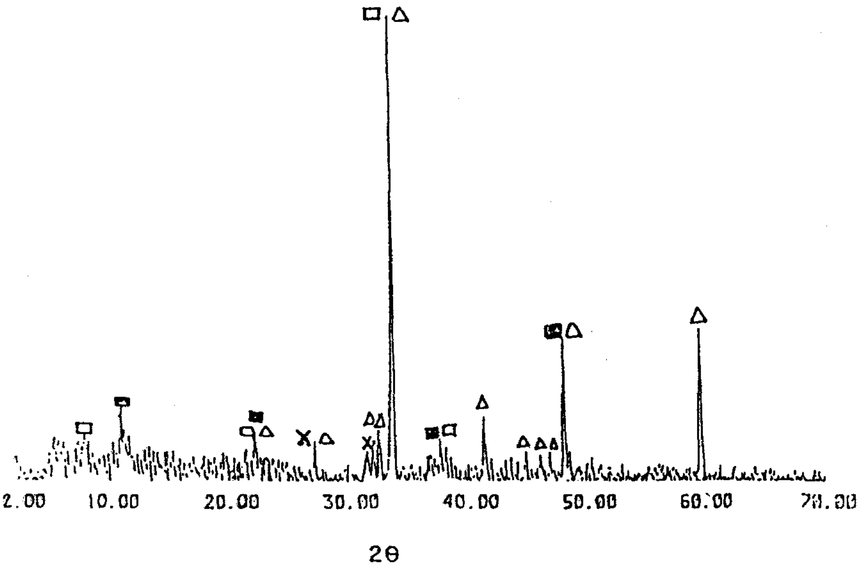

Fig. 3 XRD pattern of C_3A hydrated for 15 min; △ C_3A; □ C_2AH_8; ■ C_4AH_{13}; × C_3AH_6

Table 2 XRD data

% $CaCO_3$	Hydration time	C_3A	$CaCO_3$	Hexagonal hydrates	Cubic hydrate	Carboaluminate hydrate
0	15 min	++++	–	+++	+++	–
	8 h	+++	–	+	++++	–
	24 h	+	–	+	++++	–
10	15 min	++++	++++	0	0	++++
	24 h	+	+	0	+++	++++
20	15 min	++++	++++	0	0	++++
	8 h	+++	+	0	+	++++
	24 h	+	0	0	+	++++

++++ abundant; +++ moderate; ++ little; + traces; 0 not detected

These *d*(Å) values are completely different from each other. Thus, we can suppose that only the corresponding compound contributes to its characteristic line. The content of C_3A decreases as the hydration proceeds. The hexagonal and cubic hydrates exist at 15 min. No hexagonal and cubic hydrates are formed at 15 min in the presence of 10% $CaCO_3$. At 24 h, practically only cubic and carboaluminate hydrates are detected.

In the presence of 20% $CaCO_3$, merely traces of the cubic hydrate are detected with the carboaluminate hydrate up to 24 h. In both mixes 2 and 3, no hexagonal hydrates are formed up to 24 h. The XRD peaks of calcium carboaluminate are in agreement with those published [12].

TG and DTG

Figure 4 shows the TG and DTG curves of C_3A hydrated for 15 min without $CaCO_3$. 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 the dehydration of the hexagonal hydrates. The shoulder corresponds to calcium hydroxide,

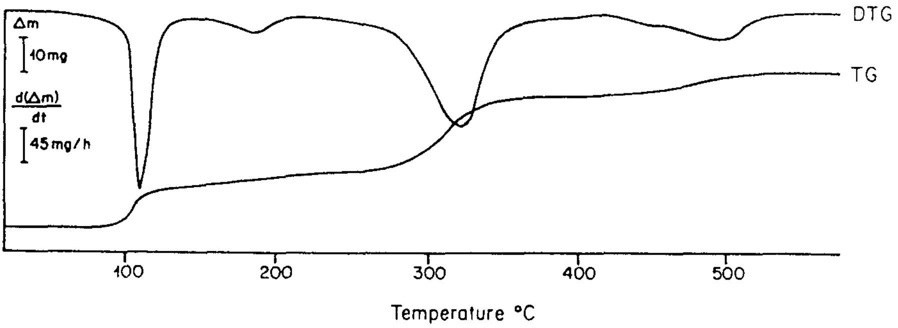

Fig. 4 TG and DTG curves of C_3A hydrated for 15 min

$Ca(OH)_2$. The dehydration of pure $Ca(OH)_2$ is seen in Fig. 5, with a DTG peak at about 480°C. The peaks at 320 and 500°C correspond to the cubic hydrate C_3AH_6. The peak at 100°C corresponds to the desorption of water [11]. Figure 6 depicts the DTG curves of mix 2. Two peaks are observed, at about 150 and 240°C. These peaks represent the dehydration of calcium carboaluminate hydrate. The curves reveal no peaks corresponding to the hexagonal and cubic hydrates. A peak (not represented) corresponding to the decomposition of $CaCO_3$ also appears at 750°C. At 24 h, a peak is observed at about 300°C. It is attributed to cubic aluminate hydrate. The small peak at about 100°C corresponds to the desorption of water adsorbed on this hydrate. This confirms the previous hypothesis: Water adsorption occurs on

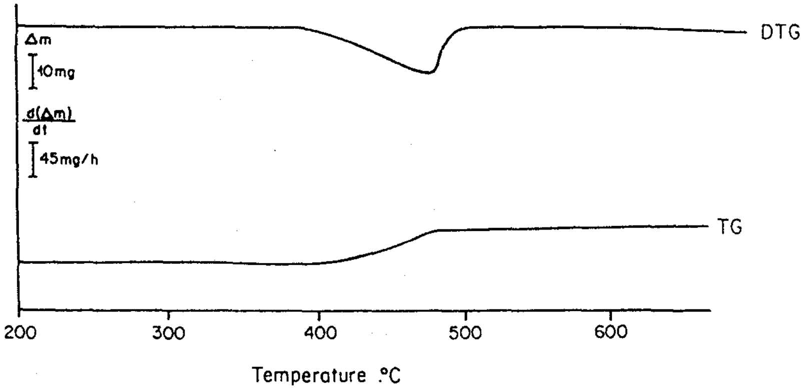

Fig. 5 TG and DTG curves of $Ca(OH)_2$

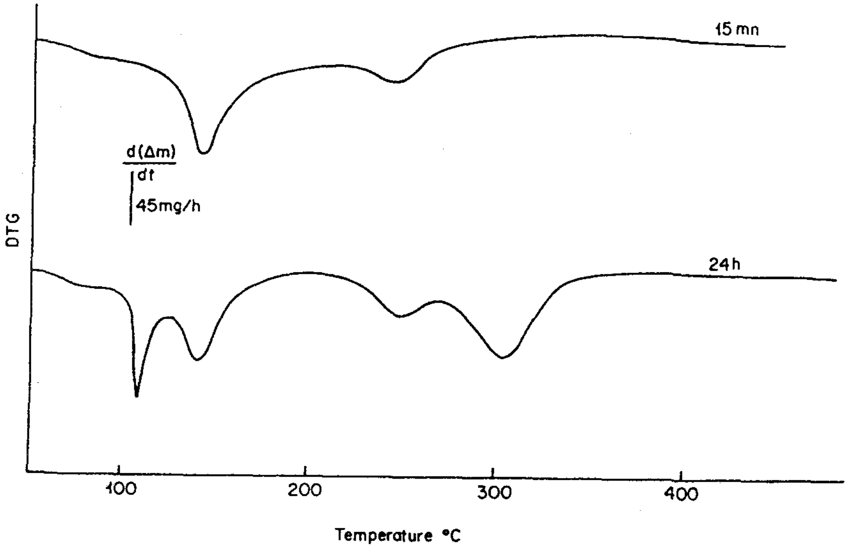

Fig. 6 DTG curves of $C_3A+10\%$ $CaCO_3$, hydrated for different times

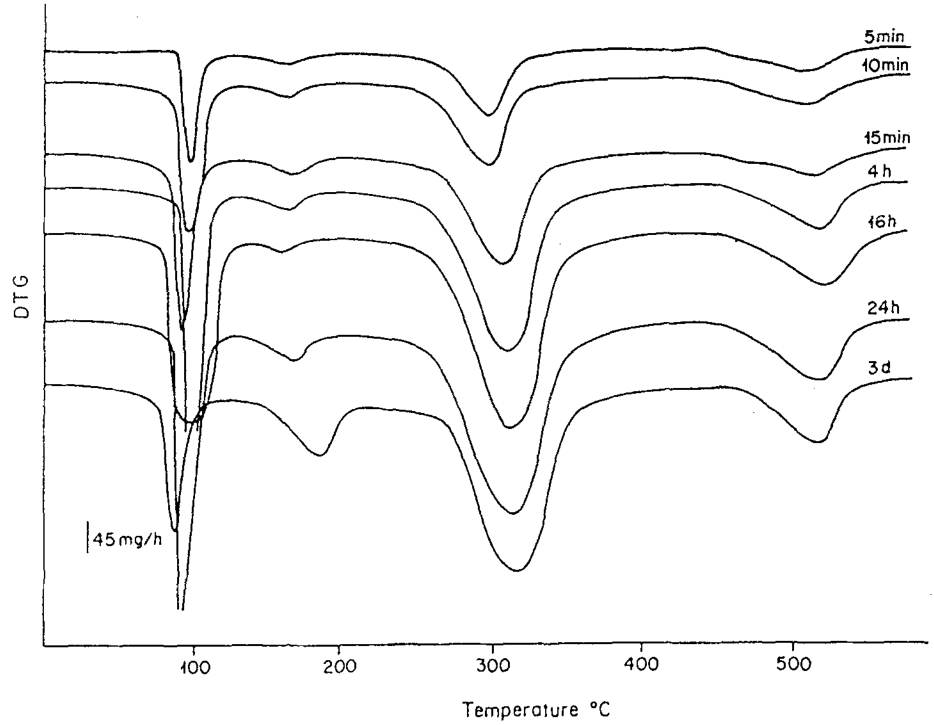

Fig. 7 DTG curves of C_3A hydrated for different times

both hexagonal and cubic hydrates [11]. The absence of the peak at 750°C indicates that $CaCO_3$ is completely consumed at 24 h. When C_3A was hydrated alone, we observed C_3AH_6 even at 5 min and the hexagonal hydrates were observed for up to 3 days (Fig. 7). It is evident that $CaCO_3$ retards formation of the cubic hydrate. These results suggest that calcium carboaluminate hydrate is formed in a reaction between the hexagonal hydrate and $CaCO_3$. This transformation blocks formation of the cubic hydrate. In mix 3, larger amounts of calcium carboaluminate hydrate are detected than in mix 2. The absence of the peak at 100°C means that calcium carboaluminate does not adsorb water.

Calorimetry measurements

In Fig. 8, the heat evolution rate is shown as a function of time. For C_3A, a large heat evolution peak is recorded during the first half hour. The C_3A hydration rate reaches a maximum at about 8 min, after which the hydration decreases. For the mixtures $C_3A+CaCO_3$, the intensities of the peaks increase with the amount of $CaCO_3$. This means that C_3A hydration is accelerated in the presence of $CaCO_3$. Thus, larger amounts of calcium carboaluminate hydrate are formed.

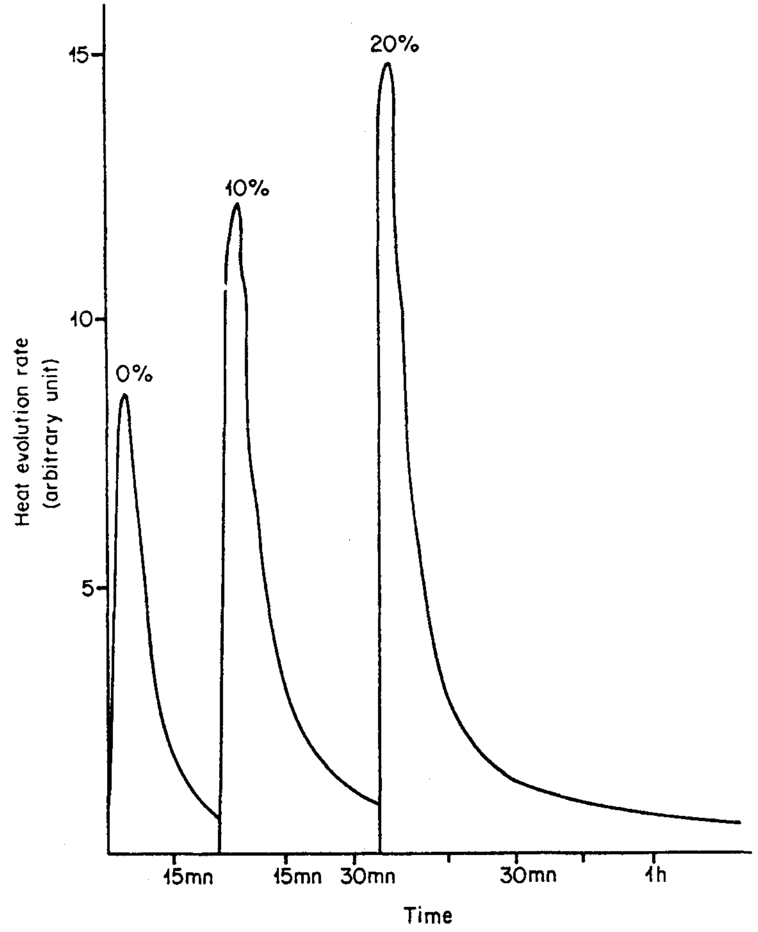

Fig. 8 Heat evolution rate

Conclusions

The following conclusions can be drawn:

C_3A hydration

Aluminate cubic and hexagonal hydrates appear almost simultaneously, although ESCA studies show only the presence of the hexagonal hydrates within a few milliseconds.

$C_3A+CaCO_3$ hydration

The formation of calcium carboaluminate hydrate retards formation of the cubic hydrate. the later appears when $CaCO_3$ is completely consumed.

Calcium carboaluminate hydrate is probably formed in a reaction between hexagonal hydrates and $CaCO_3$, as follows:

$$C_3A + H_2O \rightarrow \text{hexagonal hydrates} + CaCO_3 \rightarrow \text{carboaluminate hydrate.}$$

Although these results must be taken with caution, because C_3A in cement differs in composition from that of the pure compound, it is necessary to compare the respective developed strengths.

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