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Cement and Concrete Composites 21 (1999) 99–105

Cement & Concrete Composites

Influence of finely ground limestone on cement hydration

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Abstract

Some work has been carried out on the effect of calcium carbonate on cement paste, but there is no general agreement on the relative effects of different amounts of calcium carbonate on cement paste properties. The objective of the present work is to assess the effect of various amounts of calcium carbonate on the hydration of tricalcium silicate in order to explain the physico-chemical changes occurring during Portland cement hydration. It is shown that calcium carbonate has an accelerating effect on C_3S and cement hydration, and leads to the precipitation of some calcium carbosilicate hydrate. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium carbonate; Calorimetry; Carbosilicate; Cement; Hydration; Infrared spectroscopy; Microstructure; Strength

1. Introduction

For a long time, ground limestone has been considered as an inert filler. However, recent studies carried out in the 1980s have pointed out the following phenomena:

— calcium carboaluminate hydrates precipitate during the hydration of cements containing ground limestone [1–7]
— during the formation of ettringite, sulfate ions can be replaced by carbonate ions without modifying the sequences of the reaction [8–11]
— there is an interaction between calcium silicate (alite) and calcium carbonate; the latter accelerates the hydration of C_3S and modifies the Ca/Si ratio of C–S–H [12–14]

As the interactions of ground limestone and C_3A are well documented, we have, in the present paper, focused our attention on the reactions which occur during the hydration of C_3S in the presence of calcium carbonate. The behaviour of blended Portland cements containing up to 50% ground limestone has also been investigated.

2. Experimental

2.1. Materials

2.1.1. Calcium carbonate ($CaCO_3$)

The calcite studied was derived from marble and was very pure (98.6% $CaCO_3$). Its specific gravity was 2.75. It was ground to get the following characteristics:

— 100% particle below 20 μm,
— average diameter $D_{50} = 2.5$ μm,
— 35% particles below 1 μm.

For this product, the Blaine specific surface area was 680 $m^2\,kg^{-1}$ and the BET specific surface area was 3600 $m^2\,kg^{-1}$.

Calcium silicate (C_3S)

Calcium silicate was synthesized by reacting a well mixed stoichiometric blend mixture of pure calcium carbonate and reactive silica. The blend was wetted and pellets prepared. The temperature program was as follows:

— 20–700°C: 20°C min^{-1}
— 700–1000°C: 15°C min^{-1}
  - temperature maintained at 1000°C for 40 min.
— 1000–1450°C: 8°C min^{-1}
— 1450–1600°C: 5°C min^{-1}
  - temperature maintained at 1600°C for 120 min.

The residual lime (CaO) was measured by hydrochloric acid titration of a solution containing 250 mg C_3S and 100 mL ethyleneglycol, shaken at 70°C for 30 min. The calcination was considered good as the free CaO content was less than 2%. A well-crystallized triclinic C_3S was then obtained and ground in a laboratory ball-mill. Its particle size distribution was characterized by:

— 100% particles below 80 μm
— $D_{50} = 15$ μm
— 30% particles below 10 μm

2.1.2. Ordinary Portland cement (OPC)

The cement used in the present study was a CPA CEM I 52.5 according to the European prestandard

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PII: S0958-9465(98)00020-1

Table 1
Water to solid ratios of pastes

C_3S (w_t%)	100	90	80	70	60	50
$CaCO_3$ (w_t%)	0	10	20	30	40	50
W/S S = C_3S+$CaCO_3$	0.35	0.34	0.33	0.32	0.31	0.30
OPC (w_t%)	100	90	80	70	60	50
$CaCO_3$ (w_t%)	0	10	20	30	40	50
W/S S = OPC+$CaCO_3$	0.28	0.28	0.27	0.26	0.25	0.24

ENV 197-1 for common cements. Its Bogue potential composition was $C_3S = 67.9\%$; $C_2S = 4.8\%$; $C_3A = 10.4\%$; $C_4AF = 9.3\%$. Its Blaine and BET specific surface areas were $364\ m^2\ kg^{-1}$ and $1400\ m^2\ kg^{-1}$, respectively. The average value of the particle size distribution was $D_{50} = 16\ \mu m$.

2.2. Methods used for investigation

Isothermal calorimetry was used to study the interactions between C_3S (or OPC) and $CaCO_3$. C_3S (or OPC) was mixed with $CaCO_3$ in the weight ratio 1:1. The mixture (300 mg) was then hydrated in presence of the same quantity of water (300 mg). The total heat developed during the reaction was recorded. The length of the experiment was 15 h.

The morphology of these hardened pastes was investigated by means of scanning electron microscopy (SEM), and the hydrates formed were identified, using infrared spectrometry (IRS), X-ray diffraction (XRD) and differential thermal analysis (DTA).

Pastes of pure C_3S (or OPC) and $CaCO_3$ were prepared at equivalent consistency. The water to solid ratios are shown in Table 1.

From Table 1, it is clear that the presence of $CaCO_3$ has a plasticizing effect on the paste: the higher the $CaCO_3$ content, the lower the amount of mixing water.

Minicylinders of paste were cast ($\varnothing = 20$ mm, $h = 40$ mm), demoulded after 2 days of hydration, and kept at 20°C and relative humidity 95% until mechanical testing, which occurred after 7, 28 and 60 days of age.

3. Results and discussion

3.1. Reactions between C_3S and $CaCO_3$

3.1.1. Isothermal calorimetry

The isothermal calorimetry curves showing the rate of heat development of 300 mg C_3S and (150 mg C_3S+150 mg $CaCO_3$) during hydration, up to 15 h, are given in Fig. 1. The values recorded for the blend (C_3S+$CaCO_3$) were always higher than those of hydrated C_3S.

The total heat resulting from pure C_3S hydration was 145 joules, whilst that of the mixture (50% C_3S+50% $CaCO_3$) reached 260 joules. These results are in good agreement with those obtained by Ramachandran [14]. They indicate that $CaCO_3$ cannot be considered as an inert addition towards C_3S hydration.

3.1.2. SEM examination

As shown in Fig. 2, the pastes presented about the same texture after 7 days of hydration; namely platlets of calcium hydroxide and fibrils of C–S–H. After 60 days of hydration, the morphology of the pastes is different, as presented in Fig. 3. In pure C_3S, platlets of calcium hydroxide and C–S–H type II are present according to Taylor [15]. In 'C_3S+$CaCO_3$' paste, granules of C–S–H are formed.

3.1.3. Infrared spectrometry

The IR spectra of hydrated C_3S at different ages are shown in Fig. 4. Those of the 'C_3S+$CaCO_3$' paste are shown in Fig. 5. The wavenumbers present in each product hydrated either for one day or 28 days are reported in Table 2. The vibrations associated with each wavenumber are also presented in Table 2.

In hydrated C_3S, all the Si–O–Si stretching bands were reorganized between 1 and 28 days. The structure of tobermorite gel was reached [16], as shown by the emboldened wavenumbers.

In the blend 'C_3S+$CaCO_3$' the characteristic bands of the CO_3 ion appeared. Some SiO_4 bands were shifted after one day of hydration, demonstrating the accelerating effect of $CaCO_3$ on C_3S hydration. Those

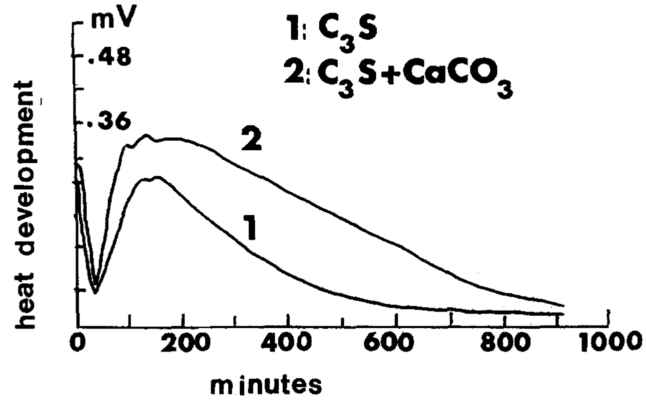


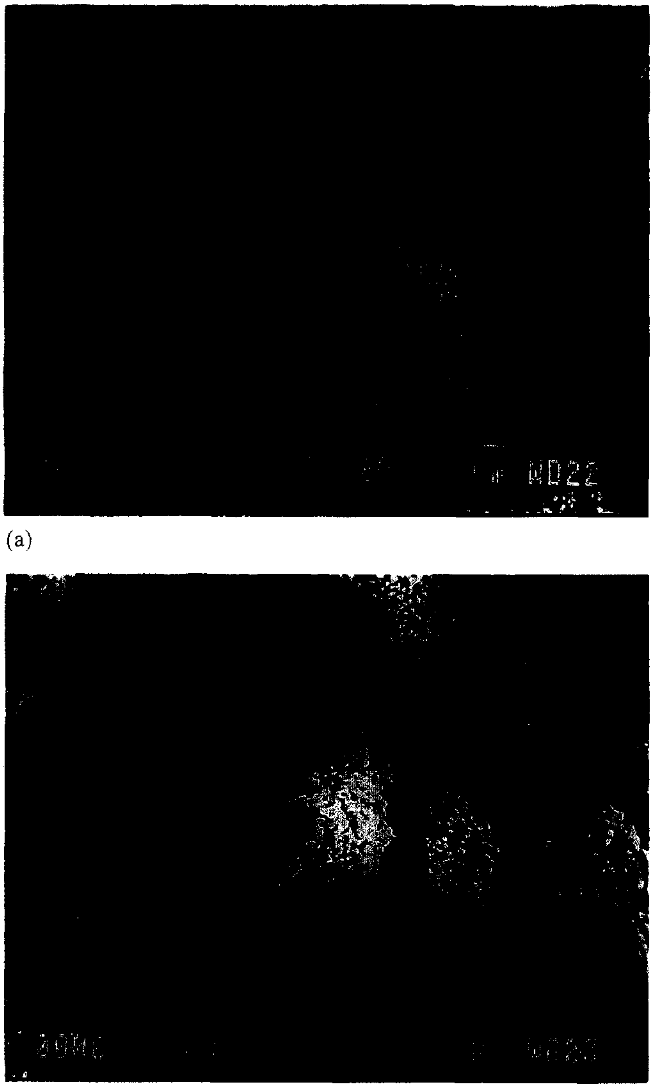
Fig. 1. Isothermal calorimetry data: C_3S and C_3S+$CaCO_3$.

results were also obtained using the diffuse reflectance method, as shown in Fig. 6.

The results of XRD investigations are given in Fig. 7, after 60 days of hydration. The following conclusions can be drawn from these analyses:

- calcium hydroxide is present in all compositions;
- the intensity of the C_3S peak decreases when the amount of $CaCO_3$ increases such that in the blend containing 50% $CaCO_3$ these peaks have almost disappeared;
- the intensity of the peak at $2\theta = 14.9°$ increases with the $CaCO_3$ content and is due to the formation of some hydrated carbosilicate.

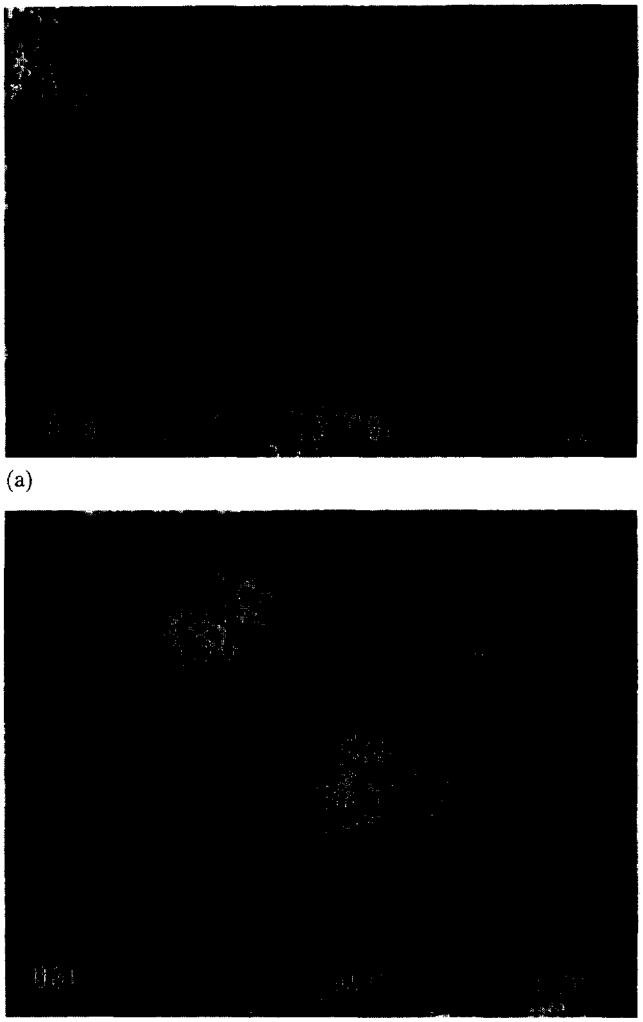
The consumption of $CaCO_3$ was studied by means of DTA. The area of the decomposition peak of $CaCO_3$ decreased with the hydration time and the temperature corresponding to the maximum of this peak shifted towards smaller values as shown in Fig. 8. Such results



(a)

(b)

Fig. 2. SEM micrographs after 7 days of hydration.


(a)

(b)

Fig. 3. SEM micrographs after 60 days of hydration.

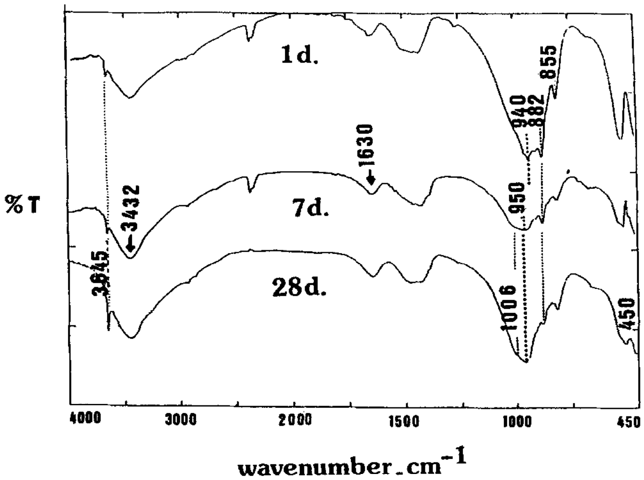


Fig. 4. Infrared spectra of hydrated C_3S.

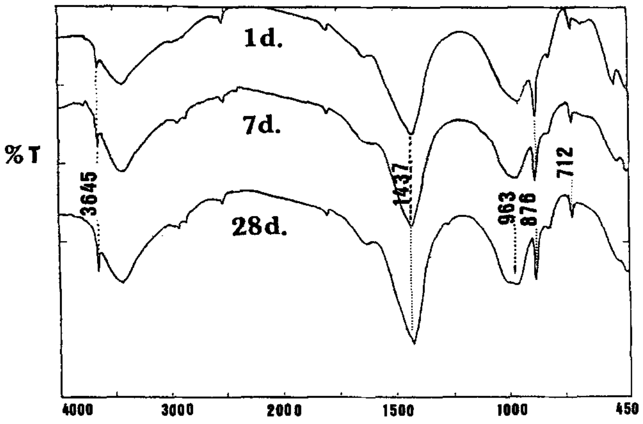


Fig. 5. Infrared spectra of hydrated (C_3S+$CaCO_3$).

were previously observed by Henning [6] in the case of precipitation of carbonate hydrates.

3.1.4. Compressive strength of pastes

The compressive strength of the different pastes is presented in Fig. 9. The presence of $CaCO_3$ at levels higher than 30% has a beneficial effect on the strength, whatever the hydration time may be.

It is possible to compute the $K(t)$ value for each paste using Feret's formula:

$$R(t) = K(t)(V_s/V_t)^2$$

where $R(t)$ is the strength after t days of hydration, $K(t)$ is the coefficient of reactivity of the binder, V_s is the volume of binder, and V_t the sum of the following three volumes: binder, water and entrained air. In the present study, the volume of air was measured at 1.5–1.6%. Table 3 shows the $K(7)$ and $K(60)$ values obtained for the different pastes. After 7 days hydration, all blended pastes develop higher $K(7)$ values than pure C_3S, which proves that $CaCO_3$ reacts chemically. After 60 days hydration, only pastes containing more than 30% $CaCO_3$ develop higher $K(60)$ values.

Table 2
Infrared results of hydrated C_3S and (C_3S+$CaCO_3$)

C_3S			C_3S+$CaCO_3$		
Wavenumber (cm^{-1})		Vibration	Wavenumber (cm^{-1})		Vibration
1 day	28 days		1 day	28 days	
1635	**1630**	ν_2H_2O	1635	1635	ν_2H_2O
1480	1450	ν_3CO_3	1437	1437	ν_3CO_3
938	**960**	ν_3SiO_4	1161	1161	ν_1CO_3
905		ν_3SiO_4	954	963	ν_3SiO_4
882	882	ν_3SiO_4	876	876	ν_2CO_3
855	**855**	ν_3SiO_4	849		ν_3SiO_4
660	665	ν_4SiO_4	712	712	ν_4CO_3
	640	ν_4SiO_4	660	660	ν_4SiO_4
518		ν_4SiO_4	506	486	ν_4SiO_4
450	450	ν_2SiO_4	452	462	ν_2SiO_4

3.2. Reactions between OPC and $CaCO_3$

3.2.1. Isothermal calorimetry

Figure 10 shows that the same type of curve is observed with OPC and pure C_3S. The heat produced by the reaction between 50% OPC and 50% $CaCO_3$ is about double that issued from plain OPC hydration.

3.2.2. Hydrates formed

As shown by XRD (Fig. 11), carboaluminate and carbosilicate have been precipitated after 60 days of hydration.

The presence of calcium carboaluminate hydrate was also observed by infrared spectrometry (bands at 3670 and 3530 cm^{-1}). IR spectroscopy also pointed out differences in AF_m and AF_t phases (Fig. 12). In the paste containing pure OPC, both monosulphate (bands at 100 and 1170 cm^{-1}) and ettringite (band at 1120 cm^{-1}) are present. In the paste containing 50% $CaCO_3$, monosulphate almost disappeared and the band at 1120 cm^{-1} was reinforced, so some SO_4 ions in

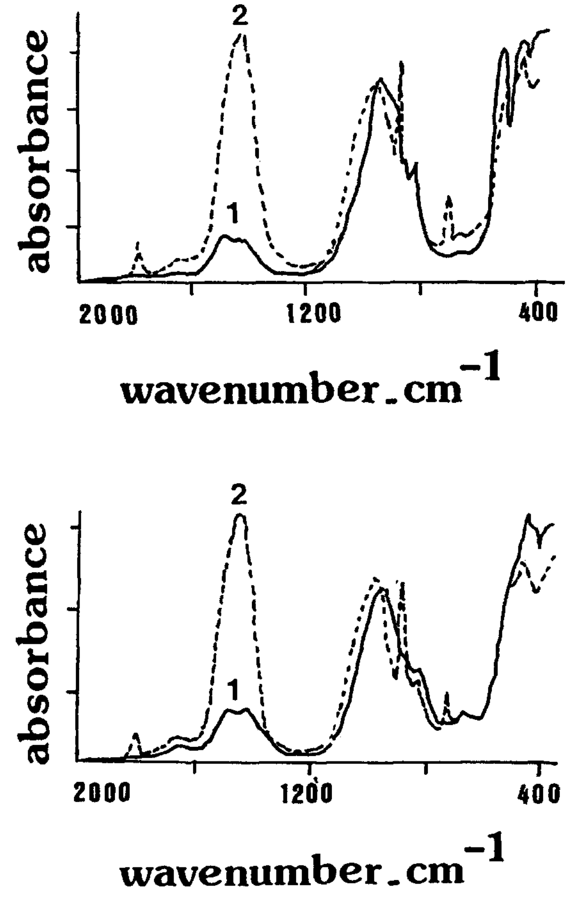


Fig. 6. IR spectra obtained from the diffuse-reflectance method.

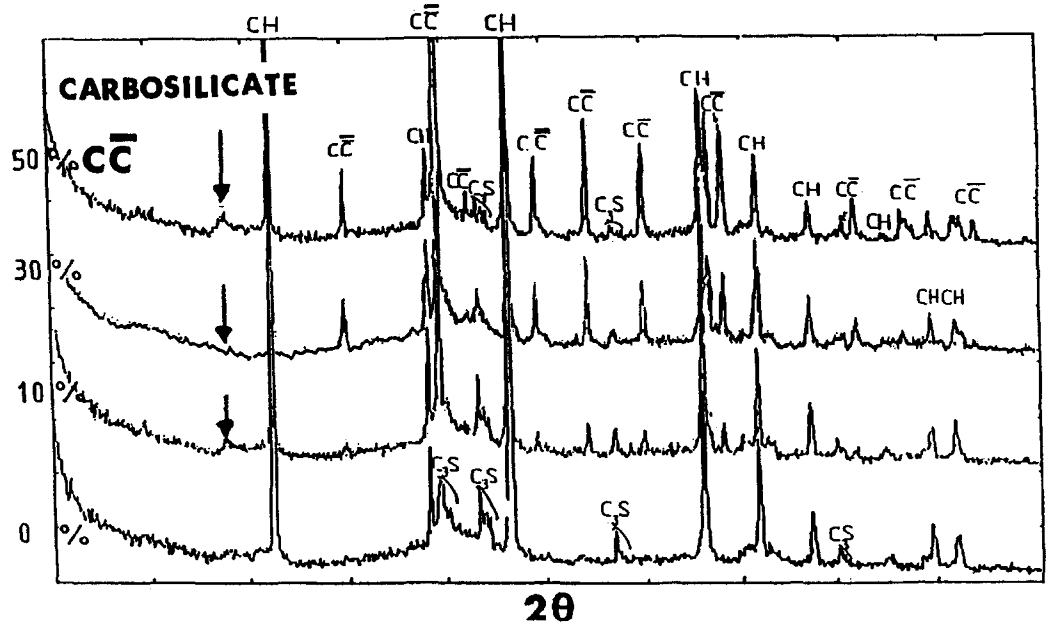


Fig. 7. XRD patterns of the different pastes after 60 days of hydration.

ettringite were probably replaced by CO_3 ions. The band assigned to the v_3 SiO_4 vibration at 970 cm^{-1} was also slightly modified and that of carbonate at 875 cm^{-1} amplified.

3.2.3. Compressive strength of pastes

The compressive strength of pastes is presented in Fig. 13. The strength is maintained or even increased in pastes containing 10% $CaCO_3$. Lower strengths are obtained with higher $CaCO_3$ levels. These results mean that the development of strength is not similar in C_3S and OPC pastes containing $CaCO_3$. In OPC, interactions occur between C_3A and $CaCO_3$, leading to the production of calcium carboaluminate hydrate and the modification of ettringite, whereas in blended C_3S pastes, only calcium carbosilicate hydrate is obtained.

Nevertheless, the level of strength remains acceptable for a 50% level of OPC substitution: it is 81% that of OPC alone. This result proves that chemical reactions occur, but in a smaller extent than in C_3S pastes and more $CaCO_3$ remains as an inert filler.

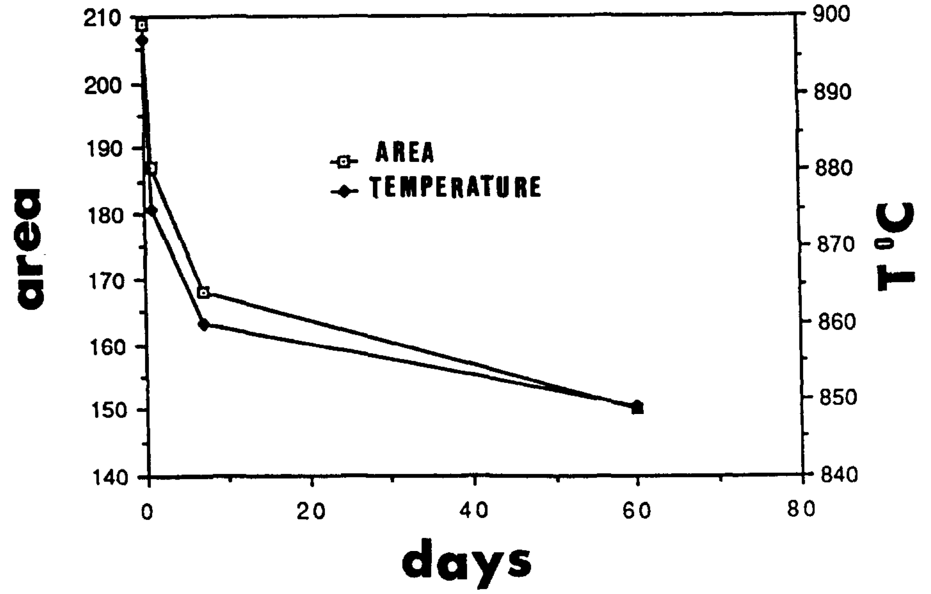


Fig. 8. Evolution of the area and the temperature of $CaCO_3$ decarbonation.

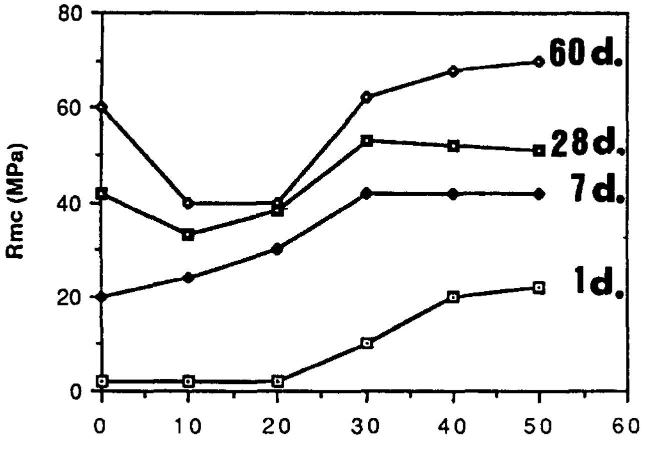


Fig. 9. Influence of $CaCO_3$ on the compressive strength of pastes.

Table 3
Reactivity of the different binders

C_3S	100	90	80	70	60	50
$CaCO_3$(%)	0	10	20	30	40	50
K(7)	100	107	129	179	164	157
K(60)	225	125	130	300	375	410

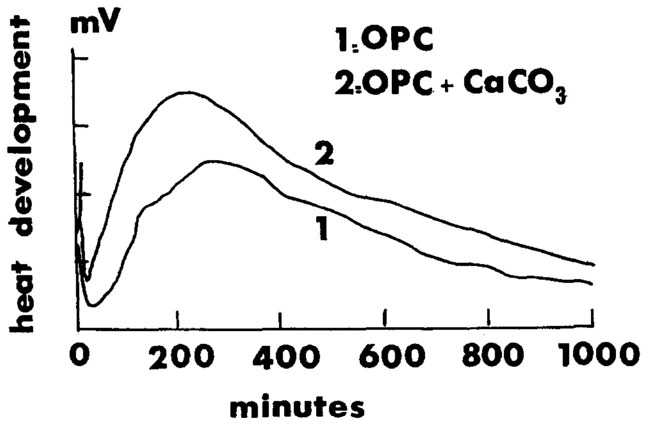


Fig. 10. Isothermal calorimetry curves: OPC and OPC+$CaCO_3$.

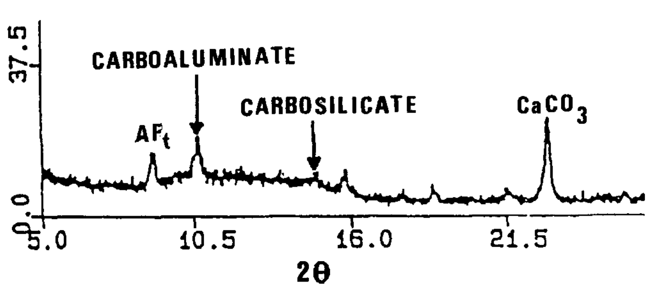


Fig. 11. XRD spectrum of hydrated paste (OPC/$CaCO_3$ = 1).

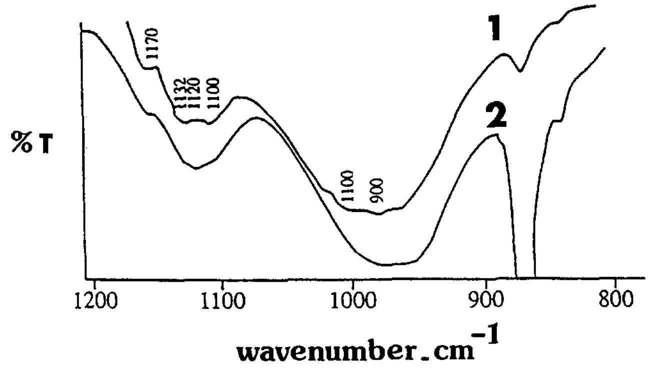


Fig. 12. Modification of AF_m and AF_t phases in the paste containing 50% OPC and 50% $CaCO_3$ after 60 days of hydration.

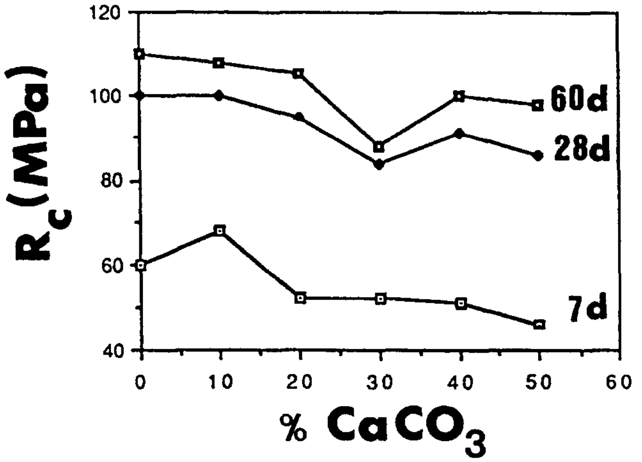


Fig. 13. Compressive strength of cement pastes containing different amounts of $CaCO_3$.

4. Conclusion

As shown by isothermal calorimetry, more total heat is developed in C_3S or cement containing up to 50% calcium carbonate than in the absence of $CaCO_3$ under comparable conditions signifying the accelerating effect of $CaCO_3$. Hydration of C_3S in the presence of $CaCO_3$ results in the production of some calcium carbosilicate hydrate and good mechanical performance for amounts of $CaCO_3$ higher than 30%.

In cement paste, calcium carbonate modifies the AF_m and AF_t phases, and produces calcium carbosilicate and carboaluminate hydrates but does not lead to the same strength development as in C_3S paste.

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