Thermochimica Acta, 106 (1986) 273–282
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL ANALYSIS OF THE $3CaO \cdot Al_2O_3$–$CaSO_4 \cdot 2H_2O$–$CaCO_3$–H_2O SYSTEM

V.S. RAMACHANDRAN and ZHANG CHUN-MEI *

Division of Building Research, National Research Council of Canada, Ottawa, K1A 0R6 (Canada)

(Received 4 March 1986)

ABSTRACT

Hydration products formed at different periods in mixtures containing C_3A with either or both $CaSO_4 \cdot 2H_2O$ (0, 12.5, 25%) and $CaCO_3$ (0, 12.5, 25%) were followed by differential scanning calorimetry and thermogravimetry. Depending on the length of hydration, different products were formed. Calcium carbonate retards or suppresses formation of the cubic aluminate hydrate in the hydration of C_3A, but it accelerates the formation of ettringite and its conversion to the monosulfoaluminate phase in the hydration of C_3A + gypsum.

INTRODUCTION

Calcium carbonate added to portland cement, as a partial replacement for cement, modifies early setting and hardening characteristics by influencing hydration of the C_3A phase. $CaCO_3$ is known to form complexes with C_3A, as does gypsum. Attempts have also been made, therefore, to substitute part of gypsum by $CaCO_3$. Only limited data are available, however, pertaining to the role of $CaCO_3$ in fresh concrete [1,2]. It was the objective of the present work to follow the hydration characteristics of C_3A and C_3A + gypsum in the presence of different amounts of finely divided $CaCO_3$.

EXPERIMENTAL

Equipment

DSC and TGA curves were obtained using the Du Pont 1090 thermal analysis system. In each DSC experiment a 20-mg sample was heated in a

---

* Visiting Scientist, Nanjing Institute of Technology, Nanjing, The People's Republic of China.

continuous flow of nitrogen gas from room temperature to 600 °C at 20 °C min^{-1}. The TGA experiment was carried out by heating the samples to 1000 °C. X-ray photographs were obtained by a Norelco unit using a Debye–Scherrer camera. The relative intensities of the lines were obtained by densitometer traces of the X-ray films.

Materials

Tricalcium aluminate was supplied by the Tetratech Co.; gypsum and calcium carbonate (N_2 surface area 6.5 m^2 g^{-1}), both of reagent quality, were supplied by Fisher Scientific Co. and by Anachemia Chemical Co., respectively.

Sample preparation

In all, eight mixes were prepared: (1) C_3A containing no gypsum, (2) $C_3A + 12.5\%$ gypsum, (3) $C_3A + 25\%$ gypsum, (4) $C_3A + 12.5\%$ $CaCO_3$, (5) $C_3A + 25\%$ $CaCO_3$, (6) $C_3A + 12.5\%$ gypsum + 12.5% $CaCO_3$, (7) C_3A + 25% gypsum + 12.5% $CaCO_3$ and (8) $C_3A + 25\%$ gypsum + 25% $CaCO_3$. The percentage of additive was based on the weight of C_3A.

The dry powders were transferred to capped vials and glass beads were mixed into them using a Spex mixer for 3 min. Double-distilled water was added gradually and the mix was stirred at a water/C_3A ratio of 4. At specified intervals (5, 10, 20, 30 min; 1, 2, 4, 7 h; and 1, 2, 3 days) the samples were removed for examination. Cold methanol was used to stop hydration at different intervals. The pastes were dried at room temperature under vacuum or at 50 °C under vacuum.

RESULTS AND DISCUSSION

Hydration of $3CaO \cdot Al_2O_3$

Figure 1 shows DSC thermograms of C_3A hydrated for periods varying from 5 min to 2 days. Even at 5 min, endothermal effects signifying the presence of hydration products are evident. Peaks at about 145–150 and 265–280 °C represent the presence of a metastable hexagonal phase. As hydration progresses, the endothermal peak at about 150 °C increases for up to 4 h, and that at about 265–300 °C continues to increase up to 2 days. The large peak at about 300 °C (4 h to 2 d) is due mainly to the presence of the cubic phase (C_3AH_6). The exact time of conversion of the hexagonal phase to the cubic phase is not easy to determine because the two co-exist. XRD results confirm the DSC results (Table 1).

TABLE 1

XRD lines of products formed at different times in the C_3A–$CaCO_3$–$CaSO_4 \cdot 2H_2O$–H_2O system

Material	Hydration period	Components detected							
		C_3A	Gypsum	$CaCO_3$	Hexagonal aluminate hydrate	Cubic aluminate hydrate	Ettringite	Monosulfo-aluminate hydrate	Carbo-aluminate hydrate
C_3A	10 min	1	–	–	3	–	–	–	–
	1 h	2	–	–	2	4	–	–	–
	7 h	2	–	–	4	2	–	–	–
	2 d	4	–	–	–	1	–	–	–
C_3A + 12.5% $CaCO_3$	10 min	1	–	2	–	–	–	–	2
	2 d	4	–	5	–	2	–	–	1
C_3A + 12.5% gypsum	30 min	1	4	–	–	–	4	–	–
	1 h	1	–	–	–	–	–	3	–
	7 h	3	–	–	4	4	–	2	–
	3 d	5	–	–	–	4	–	2	–
C_3A + 12.5% gypsum + 12.5% $CaCO_3$	10 min	1	4	2	–	–	2	–	5
	20 min	1	–	2	–	–	–	4	5
	1 h	2	–	4	–	–	–	4	4
	7 h	2	–	5	–	–	–	4	2
	3 d	5	–	–	–	–	–	3	2

Numbers refer to the relative intensities of peaks: 1, very strong; 2, strong; 3, medium strong; 4, weak; 5, very weak.

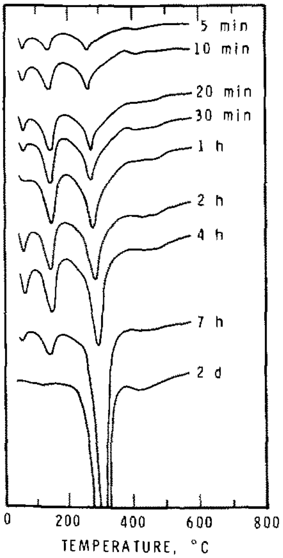

Fig. 1. DSC curves of C_3A hydrated for different periods.

Hydration of $3CaO \cdot Al_2O_3$–$CaCO_3$ mixture

DSC curves of the products of hydration of C_3A–$CaCO_3$ are different from those obtained with hydration of C_3A (Fig. 1–3). In the early periods endothermal peaks form at 150–160 and 235–245°C in the C_3A–$CaCO_3$

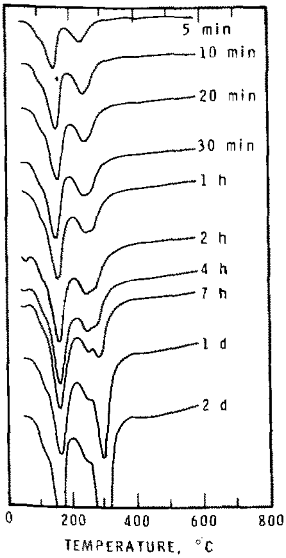

Fig. 2. DSC curves of C_3A hydrated for different periods in the presence of 12.5% $CaCO_3$.

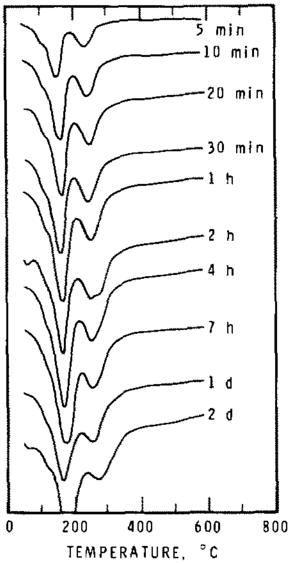

Fig. 3. DSC curves of C_3A hydrated for different periods in the presence of 25% $CaCO_3$.

mixture containing 12.5% $CaCO_3$. They may also be observed during the hydration of C_3A without $CaCO_3$ (Fig. 1). The peaks, however, represent calcium carboaluminate (or a solid solution $C_3A \cdot Ca(OH)_2 \cdot XH_2O$–$C_3A$–$CaCO_3 \cdot XH_2O$) [3]. XRD reveals no hexagonal phase (C_2AH_x or C_4AH_x) in this system (Table 1). The formation of a small amount of cubic aluminate hydrate (peak at about 260–280°C) at 2 h and intensifying at 2 d is also evident (Fig. 2). In the presence of 12.5% $CaCO_3$ carboaluminate (solid solution) and cubic phases seem to co-exist at 2 d. The addition of $CaCO_3$ to C_3A seems to retard the formation of the cubic phase [4]. XRD results also suggest that in the presence of 12.5% $CaCO_3$ the main phases at 2 d are carboaluminate and cubic hydrates.

Differential thermogravimetric results are in agreement with those of DSC and XRD (Fig. 4). In the mixtures containing 12.5% $CaCO_3$, two peaks appear below 250°C at 10 min, caused by the carboaluminate. Two additional peaks occur at 700–750°C (due to decomposition of $CaCO_3$) and at 850–900°C (due to decomposition of the carboaluminate) [5]. The presence of cubic aluminate is indicated at 7 h and 2 d by peaks at about 300–315°C. The combined $CaCO_3$ in the carboaluminate in the samples was determined by the peak areas occurring at 850–900°C. The amounts were 1.5, 6.0 and 8.2% at hydration periods of 10 min, 7 h and 2 d, respectively, signifying a steady increase in the amount of carboaluminate as hydration progresses.

In the C_3A–$CaCO_3$–H_2O system containing 25% $CaCO_3$, larger amounts of carboaluminate are formed than in that containing 12.5% $CaCO_3$, and there is no evidence of cubic aluminate hydrate for up to 2 days (Fig. 3). The formation of the cubic phase may possibly be retarded or suppressed by the

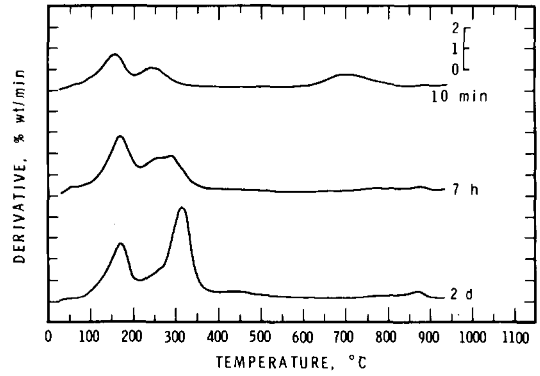

Fig. 4. Differential thermogravimetric curves of $C_3A + 12.5\%$ $CaCO_3$ hydrated for different periods.

solid solution of carbonate. In the C_3A–lignosulfonate–H_2O system a complex forms that is known to retard or suppress the conversion of the hexagonal to the cubic phase [6].

Hydration of $3CaO \cdot Al_2O_3$–$CaSO_4 \cdot 2H_2O$ mixtures

In the system containing 12.5% gypsum, the gypsum is almost consumed at 30 min, as is evident by the decreasing intensity of the endothermal peak at 130°C (Fig. 5). XRD results indicate formation of the ettringite at 30

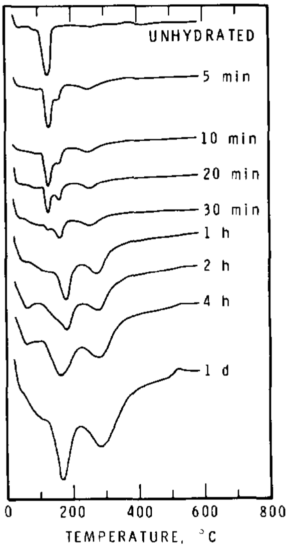

Fig. 5. DSC curves of C_3A hydrated for different periods in the presence of 12.5% gypsum.

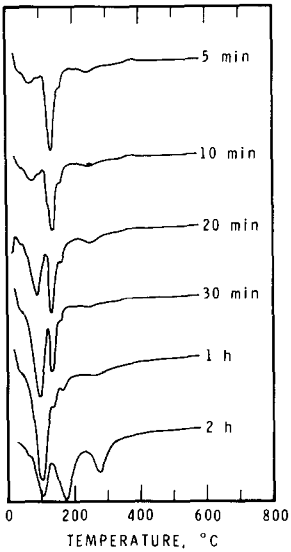

Fig. 6. DSC curves of C_3A hydrated for different periods in the presence of 25% gypsum.

min, after which the intensity of the endothermal peak at 165–180°C increases substantially. This peak represents monosulfoaluminate hydrate. XRD data confirm the presence of monosulfoaluminate hydrate at 1 h and after. From 7 h to 3 days monosulfoaluminate and some cubic phases are present (Table 1).

With 25% gypsum, ettringite can be detected even at 5 min (Fig. 6), the amount increasing with the time until between 1 and 2 h there is a sharp decrease. Gypsum is mostly consumed within 1 h, but at 12.5% gypsum it is consumed within 30 min.

Hydration of $3CaO \cdot Al_2O_3$–$CaSO_4 \cdot 2H_2O$–$CaCO_3$ mixtures

In the system containing 12.5% gypsum and 12.5% $CaCO_3$, the rate of disappearance of gypsum seems to be accelerated by $CaCO_3$ (Figs. 5 and 7). XRD results confirm that in the presence of $CaCO_3$ gypsum is consumed within 20 min (Table 1). Comparison of the DSC curves for mixtures of $C_3A + 25\%$ gypsum and $C_3A + 25\%$ gypsum + 12.5% $CaCO_3$ shows that gypsum is consumed more rapidly in the mixture containing $CaCO_3$ (Figs. 6 and 8).

Formation of ettringite (peak at about 100°C) is accelerated by the addition of 12.5% $CaCO_3$ to the mixture containing 12.5% gypsum. In the presence of $CaCO_3$, even at 10 min intense XRD lines of ettringite are evident (Table 1). DSC results also demonstrate that ettringite peaks occur within 5 min in the presence of $CaCO_3$, but not in the sample with only gypsum (Fig. 7). Examination of thermograms in Figs. 6 and 8 shows that

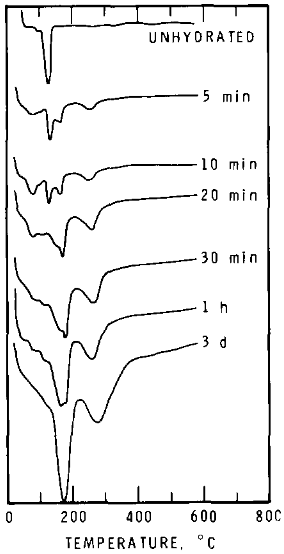

Fig. 7. DSC curves of C_3A hydrated for different periods in the presence of 12.5% gypsum + 12.5% $CaCO_3$.

the formation of ettringite is also accelerated by the addition of 12.5% $CaCO_3$ to C_3A + 25% gypsum mixtures.

Conversion of ettringite to monosulfoaluminate is also accelerated by incorporation of $CaCO_3$. XRD results confirm this. Ettringite, which is

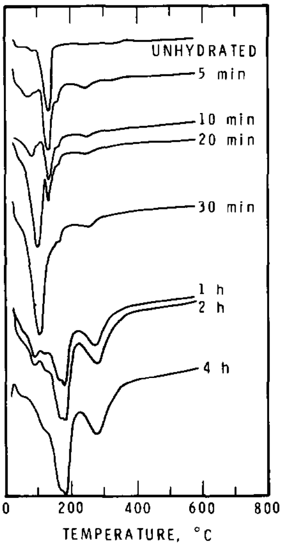

Fig. 8. DSC curves of C_3A hydrated for different periods in the presence of 25% gypsum + 12.5% $CaCO_3$.

detected at 30 min in the C_3A–gypsum mixtures, disappears within 20 min in the presence of $CaCO_3$ (Table 1).

In the system with 25% gypsum and 12.5% $CaCO_3$, DSC thermograms indicate that most conversion occurs in the first 2 h, whereas with $CaCO_3$ it occurs in about an hour. The conversion of ettringite to monosulfoaluminate is accelerated further at higher $CaCO_3$ contents.

Role of $CaCO_3$

In the C_3A–gypsum–$CaCO_3$ mixture the $CaCO_3$ particles (6.5 $m^2\ g^{-1}$) are much finer than either the C_3A or gypsum particles (approximately 0.5 $m^2\ g^{-1}$). The $CaCO_3$ particles surround the C_3A and on contact with water the two react to form carboaluminate on the surface of the C_3A. This layer may be less compact and more permeable to water than ettringite, and will interfere with the formation of a more rigid layer of ettringite. It is known that the conversion of ettringite to monosulfoaluminate hydrate takes place after gypsum has been exhausted in the system. Calcium carboaluminate hydrate enhances the rate of consumption of gypsum and hence facilitates early conversion of ettringite to monosulfoaluminate.

CONCLUSIONS

(1) In C_3A–H_2O mixtures, conversion to C_3AH_6 is either suppressed or retarded by addition of $CaCO_3$.
(2) The reaction between C_3A and gypsum to form ettringite is accelerated by the addition of $CaCO_3$.
(3) Conversion of ettringite to monosulfoaluminate hydrate is accelerated by $CaCO_3$.
(4) It is possible for ettringite, monosulfate, and carboaluminate to co-exist.

ACKNOWLEDGEMENT

The authors are grateful to J. Clark, G.M. Polomark and P.J. Lefebvre for experimental assistance. This paper is a contribution from the Division of Building Research, National Research Council of Canada.

REFERENCES

1 J. Bensted, World Cem. Technol., 11 (1980) 395.
2 J. Bensted, World Cem. Technol., 14 (1983) 383.

3 V.S. Ramachandran, Application of Differential Thermal Analysis in Cement Chemistry, Chemical Publishing Co., Inc., New York, 1969, 308 pp.

4 J. Jambor, 7th Int. Congr. Chem. Cem., Vol. IV, Paris, 1980, pp. 487–492.

5 M. Collepardi, S. Monosi, G. Moriconi and M. Pauri, J. Am. Ceram. Soc., 68 (1985) 126.

6 V.S. Ramachandran and R.F. Feldman, Mater. Struct., 5 (1972) 67.