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HYDRATION STUDIES OF MODIFIED OPC PASTES BY DIFFERENTIAL SCANNING CALORIMETRY AND THERMOGRAVIMETRY

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Thermal methods are used extensively in investigating cements and effects of additives on their hydration behaviour. Calcium chloride is the most effective and widely used accelerator for cement hydration, but the result is largely dependent on the rate at which it is added. In this study the influence of calcium chloride dosage on the hydration behaviour of OPC pastes aged for different periods has been investigated by means of differential scanning calorimetry (DSC), thermogravimetry (TG) and X-ray diffraction (XRD) methods. The results are discussed in relation to the relative amounts of calcium hydroxide and total reaction product formed. Chloroaluminate was a product of hydration in the samples dosed with greater than 1% calcium chloride. XRD was unable of itself to differentiate between monochloroaluminate and the calcium aluminate hydrate C_4AH_{13} when present in small amounts. Thermal methods proved effective in characterising the products of hydration in the presence of chloride.

Keywords: cement hydration, DSC, TG

Introduction

A large number of compounds, both organic and inorganic, have been used to accelerate the setting and/or strength development of cement, although in current practise only a few such compounds are used. Calcium chloride is the most effective but its use is now severely limited due to corrosion effects of chlorides on the reinforcing bars. Because of its wide use it has been the subject of most research on accelerators. Its effect is known to be dosage dependent but a great deal of uncertainty still exists as to how it works.

Various authors have shown thermal analysis techniques to be very useful in identifying and quantifying the hydration products in set Portland cement

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with or without admixtures. In a recent publication [1] it has been shown that the addition of 1% calcium chloride to OPC resulted in accelerating the degree of hydration. This was estimated using both calcium hydroxide and the total amount of energy absorbed due to the dehydration and dehydroxylation reactions using differential scanning calorimetry.

The objective of this study was to assess the influence of calcium chloride dosage on the hydration of OPC paste; determine whether chloroaluminates are formed and if so in what form and at what dosage. The analyses of the samples at intervals up to one week hydration was followed by means of TG, DSC and XRD.

Experimental

Calcium chloride was added at the rate of 1%, 3%, 5% and 10% by weight of cement. A control mix which contained no calcium chloride was also examined. The components for each batch were accurately weighed and the admixture when used was dissolved in water prior to mixing with the cement. Calcium chloride used was of the Analar grade and the same OPC with the oxide analysis shown in Table 1 was used throughout.

Table 1 Oxide analysis of OPC

Constituent	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	Free CaO
Weight/%	64.9	20.8	4.6	2.9	2.6	1.2	0.1	0.6	1.0

At the start of each hydration the cement was added to the deionised water or $CaCl_2$-water solution using a water : cement ratio of 0.5; then mixed for two minutes using a low speed domestic food mixer. Samples were taken after hydration had proceeded for 3h, 7h, 24h, 3 days and 7 days. The treatment of samples, methods of investigation and conditions used were the same as those described previously [1].

Results and discussions

Control mix

The relative intensities of the phases identified by XRD are summarised in Table 2 using a semi-quantitative approach. This approach is based upon

Table 2 Summary of XRD data for the OPC – H_2O and the OPC – $CaCl_2$ – H_2O systems investigated

XRD Phase	d / Å	Unhydrated	Control					1% $CaCl_2$					3% $CaCl_2$					5% $CaCl_2$					10% $CaCl_2$				
		OPC	3h	7h	1d	3d	1w	3h	7h	1d	3d	1w	3h	7h	1d	3d	1w	3h	7h	1d	3d	1w	3h	7h	1d	3d	1w
Alite	3.02	S	S	M	M	M	M	M	M	M	W	W	S	M	M	W	M	M	M	M	M	W	S	M	M	M	M
Anhydrite	3.49	W	W	W	T	–	–	W	W	W	W	–	W	W	W	W	W	–	–	–	–	–	T	W	–	–	–
Ettringite	9.73	–	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Calcium Hydroxide	4.90	–	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	S	VS	VS	VS	VS	S	S	VS	S	VS	W	W	M	S	S
Calcium Chloroaluminate	7.89	–	–	–	–	–	–	–	–	–	W	W	–	T	W	W	W	T	W	W	W	W	W	W	W	W	W
Aluminate Hydrate (C_4AH_{13})OR Solid solution Monosulphate $C_4A\bar{S}H_{12}$	8.92	–	–	–	–	W	W	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

Peaks VS – Very Strong (> 100), S-Strong (100–50)
M – Medium (49–25) W-Weak (25–5)
T – Traces (< 5)

estimates of the intensities of chosen XRD peaks for the various components. the intensities were assigned arbitrary units from very strong (indicating an off scale peak) to very weak or traces. The data for this mix show that both alite and the anhydride decreased with passing hydration time. Anhydrite, however, was present in trace amounts after 24 hours and was totally consumed after 3 days hydration, the time at which monosulphate was detected. Ettringite and calcium hydroxide were present throughout the hydration period and their trends are best shown by thermal analysis. Typical DSC curves are presented in Fig. 1, which are of the samples hydrated for 3h, 24h, and 7 days. The three curves are very similar showing an endothermic peak around 105°C, due to ettringite and C–S–H gel, and another in the temperature range 440°–480°C, due to calcium hydroxide. The reaction products after 3 hours (curve A) also contained gypsum ($C\bar{S}.2H$) which gave an XRD peak at d = 7.63 Å and DSC endotherm around 145°C. Gypsum was not detected in the unhydrated OPC.

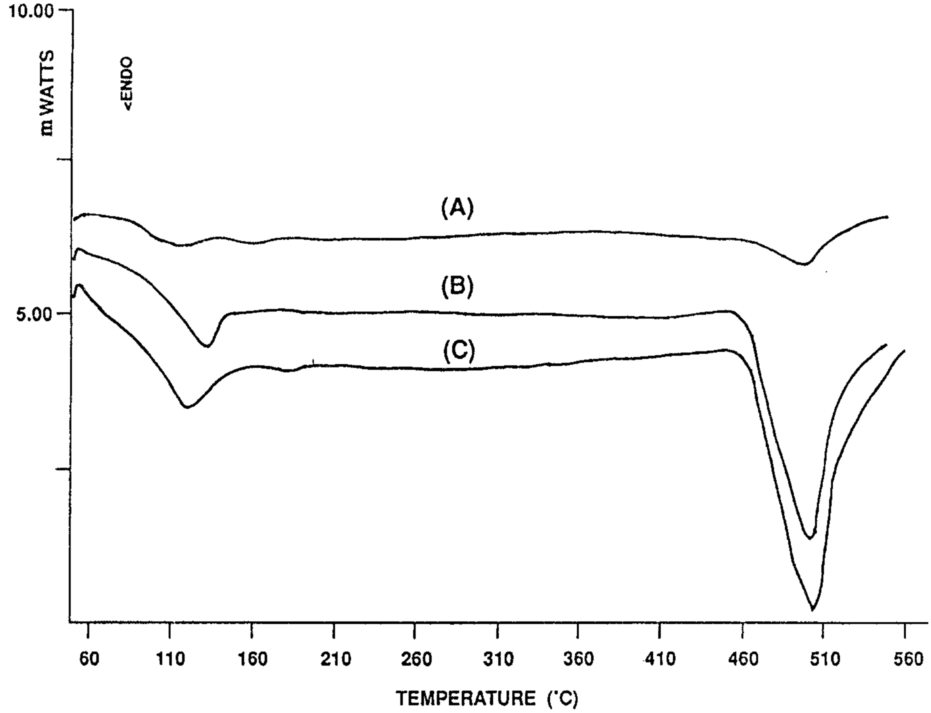

Fig. 1 DSC curves of the samples hydrated for 3 hours (A), 24 hours (B), and 7 days (C) in the control mix

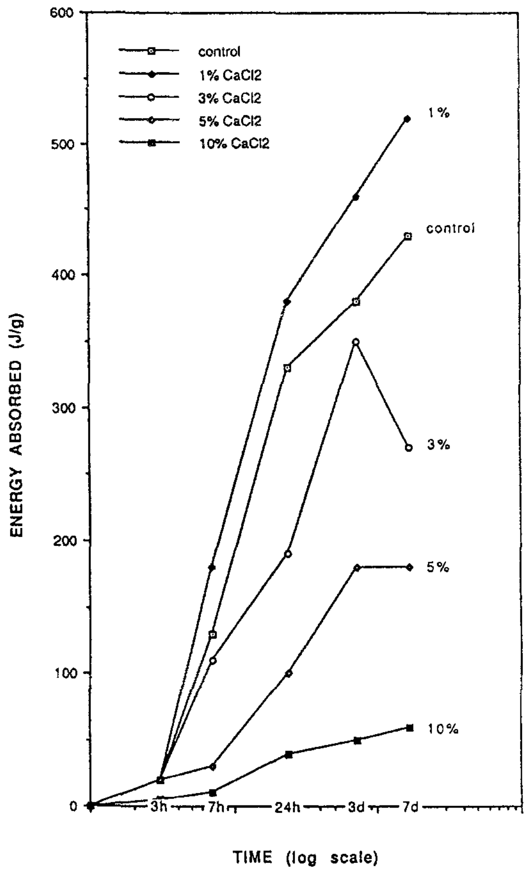

Fig. 2 Energy absorbed due to Calcium Hydroxide formed at different chloride dosage *vs.* log time

Changes in the relative amounts of calcium hydroxide formed, estimated by DSC, using the energy absorbed by the dehydroxylation reaction are plotted in Fig. 2. Figure 3, shows the % weight loss due to the total products formed, determined from TG curves. It is clear that the trend was of increasing calcium hydroxide and total hydration product, throughout the hydration period.

Calcium chloride dosed mixes

These mixes differed from the control only in that calcium chloride was dissolved in water prior to the addition of cement; 1%, 3%, 5% and 10%

calcium chloride by weight of cement were added in each case. Table 2 also summarises the XRD data of the hydrated pastes up to 7 days.

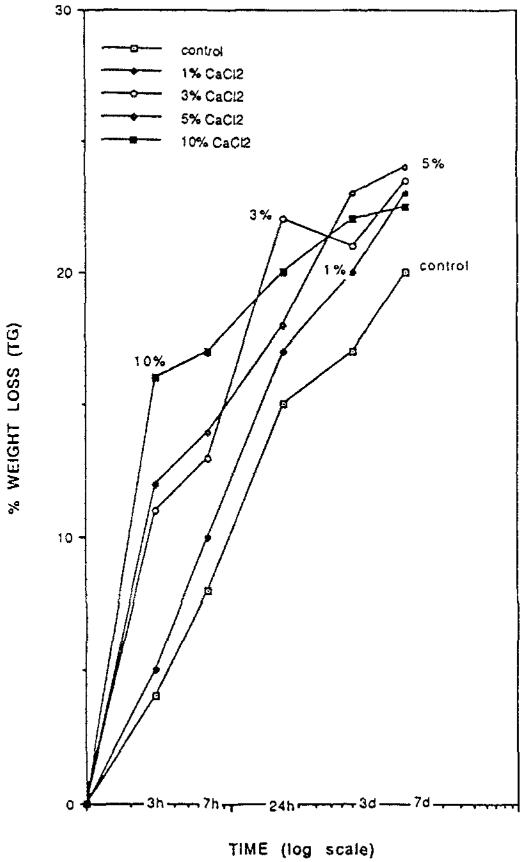

Fig. 3 Weight loss % due to total hydration products formed at different chloride dosage *vs.* log time

Compared with the control mix, no monosulphate was detected at any time in these mixes. As with the control mix the sample hydrated for 3 hours using 1% calcium chloride also contained small amounts of gypsum. Monochloroaluminate, (C_3A, $CaCl_2$, $10H_2O$), C_4AH_{13} and/or their solid solution was detected in the chloride dosed mixes. Thermal analysis was found useful in distinguishing between monochloroaluminate and calcium aluminate hydrate especially when present in such small amounts. In a previous publication [1] it has been shown that pure monochloroaluminate gives DSC endothermic peaks around 170°C and 335°C, with the latter being more intense than the former. However when chloroaluminate is present together with other hydrates these peaks on the DSC curves are not as predominant. A typical DSC curve of a sample containing some chloroaluminate (5% $CaCl_2$, hydrated for 3 days) is shown in Fig. 4. The second peak around 335°C, is not produced by the aluminate hydrate phase alone. Using this criterion the energy absorbed by the decomposition reactions in each sample was computed by DSC and used as an estimate of the chloroaluminate formation. The results are plotted as a histogram in Fig. 5. At 3% chloride addition chloroaluminate was produced after hydration for 24 hours and found to increase up to 3 days hydration, but not subsequently. As the chloride dosage was increased to 5% and 10%, chloroaluminate formation was detected after shorter hydration times of 7 hours and 3 hours, respectively. The result in Fig. 5 indicate that chloroaluminate production increased as the chloride dosage was increased and this occurred at short time intervals. Clearly no chloroaluminate formation was detected in the control or on adding 1% calcium chloride. Whereas monosulphate was identified after 3 days in the former, a C_4AH_{13} – chloroaluminate solid solution was the phase responsible for the DSC endotherm around 170°C and XRD peak at $d = 7.89$ A°, after 3 days, in the latter [1].

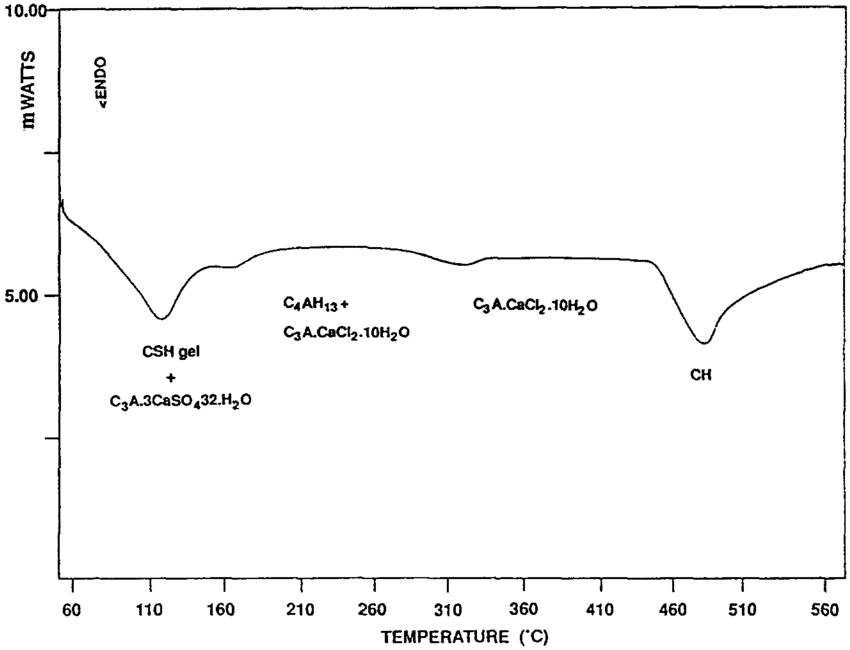

Fig. 4 DSC curve of the sample hydrated for 3 days using 5% $CaCl_2$

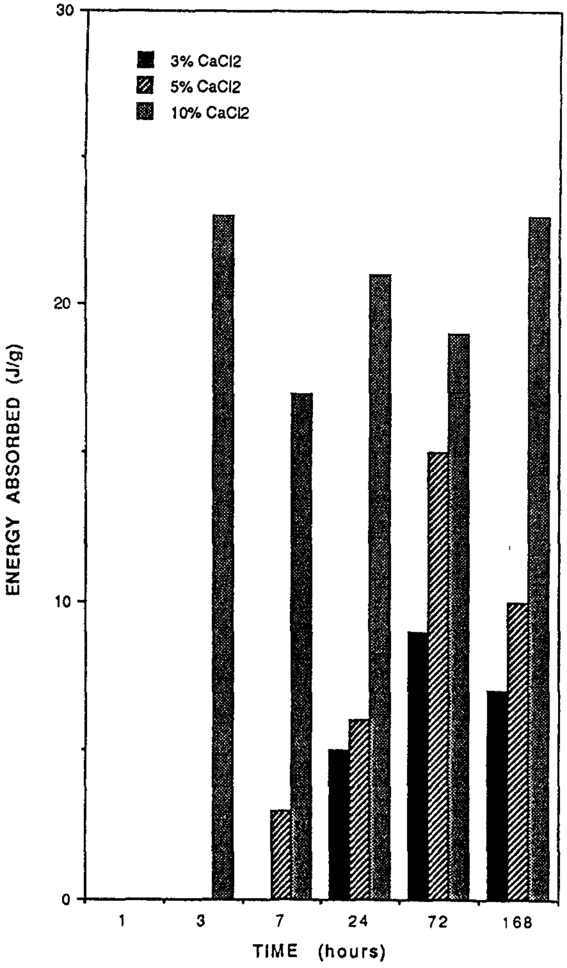

Fig. 5 Energy absorbed due to chloroaluminate formation at different chloride dosage *vs.* time

The XRD data for the control mix (Table 2), showed the monosulphate to form only after the anhydrite was completely exhausted. On adding 1% calcium chloride, the formation of the solid solution was also found to coincide with, at least, the partial disappearance of the anhydrite. When the chloride dosage was increased beyond 1%, however, the chloroaluminate was detected even though substantial amounts of the anhydrite were still present. It can be suggested therefore that the formation of chloroaluminate is predominantly dependent on the chloride dosage and not on the complete consumption of the anhydrite.

To assess the influence of calcium chloride dosage in the degree of hydration the relative changes in the amounts of calcium hydroxide formed estimated using the energy absorbed by the dehydroxylation peak are shown in Fig. 2. Figure 3, however, shows the influence of the chloride dosage on the total hydration product formed, estimated by TG. Although the trend within each system was the same, the amounts of calcium hydroxide and total products formed did differ from one mix to another. The following observations and remarks can be made upon examining the Figs together with the XRD data in Table 2.

(a) The formation of calcium hydroxide was increased by the addition of 1% calcium chloride in comparison to the control mix. However, systematically less calcium hydroxide was produced as the chloride dosage was increased.

(b) More total hydration product than in the control mix was formed throughout the hydration period on adding 1% calcium chloride. On further chloride additions, however, the trend was of increased total product formation with increased chloride dosage up to the first 7 hours. Between 24 hours and 7 days the difference between the mixes was less pronounced and at 7 days there was very little significant difference, in the amounts of the total products formed at different chloride dosage.

(c) A given addition of calcium chloride is required to accelerate both calcium hydroxide and the total product formation and will differ for different Portland cements especially those with different C_3A and sulphate contents.

(d) Thermal analysis methods are very useful major supporting techniques to XRD and can be used for the quantitative estimation, identification of hydration products and to distinguish between products with similar XRD patterns especially those present in small amounts.

References

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Zusammenfassung — Bei der Untersuchung von Zement und des Einflusses von Additiven auf das Hydratationsverhalten von Zement finden thermoanalytische Methoden eine breite Anwendung. Der effektivste und meistbenutzte Beschleuniger für die Hydratation von Zement ist Calciumchlorid, aber die Ergebnisse hängen stark von der Dosiergeschwindigkeit ab. In vorliegender Studie wird mittels DSC-, TG- und Röntgendiffraktionsmethoden der Einfluß der Dosierung von Calciumchlorid auf das Hydratationsverhalten von verschieden

alten OPC-Zementbreiproben untersucht. Die Ergebnisse wurden in Bezug auf die relativen Mengen Calciumhydroxid und das gebildete Gesamtreaktionsprodukt gewertet.
Bei Dosen von mehr als 1% Calciumchlorid konnte als Hydratationsprodukt Chloraluminat festgestellt werden. Sind Monochloraluminat und das Calciumaluminathydrat C_4AH_{13} in geringen Mengen vorhanden, kann man zwischen den beiden mittels Röntgendiffraktion nicht unterscheiden. Thermoanalytische Methoden erwiesen sich als effektives Hilfsmittel bei der Charakterisierung der Produkte der Hydratation in Gegenwart von Chlorid.