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ESTIMATION OF THE DEGREE OF HYDRATION IN MODIFIED ORDINARY PORTLAND CEMENT PASTES BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

As an essential preliminary to understanding the mechanism through which accelerators work, the effect of some admixtures on the early hydration of ordinary Portland-cement (OPC) paste has been investigated, mainly by means of X-ray diffraction and differential scanning calorimetry. The results show that by incorporating equal moles of calcium chloride, calcium nitrate or sodium thiocyanate, calcium hydroxide is formed and the total energy absorbed by the reaction products on heating up to 550 ° C are increased. After hydration for more than 12 h and 24 h, however, less calcium hydroxide and a lower total absorbed energy than in the neat OPC are detected, respectively, when the nitrate was the additive. Although the addition of sucrose is shown to inhibit the formation of calcium hydroxide, the results reveal that more ettringite was formed, especially during the first 6 h.

INTRODUCTION

Calcium hydroxide is one of the major phases formed in set Portland cements. The presence of calcium hydroxide in a hydrating ordinary Portland cement (OPC) produces an endothermic peak in the temperature range 420–510 ° C. Depending on the chemical composition of the cement and the method and time of hydration, up to 25% calcium hydroxide is formed [1]. The formation of calcium hydroxide in a hydrating OPC not only determines the degree of hydration of the cement, but may also influence its mechanical properties.

Many types of admixtures are used in concrete to obtain better workability, retardation or acceleration and improved mechanical properties [2,3]. These additives are capable of altering the hydration mechanism in a given cement paste, thereby resulting in varying contents of calcium hydroxide

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and varying total product formation. The quantitative estimation of calcium hydroxide or total reaction product is, therefore, useful in determining the degree of hydration upon the incorporation of any additives.

Various authors have shown thermal analysis techniques to be very reliable for estimating the calcium hydroxide content of set Portland cement [4–6]. Ramachandran [7] studied the role of chemical admixtures in hydrating cement using differential thermal analysis (DTA), while Bhatty et al. [8] used both thermogravimetry (TG) and DTA to estimate the calcium hydroxide content of OPC, pulverised fuel ash and polymer blends. In the present study, differential scanning calorimetry (DSC) has been employed to estimate the degree of hydration using both calcium hydroxide and the total amount of energy absorbed due to the dehydration and dehydroxylation reactions.

EXPERIMENTAL

Hydration procedure

The systems studied are summarised in Table 1. The components were weighed accurately and the admixture dissolved in water prior to mixing the cement. The admixtures used were all of AnalaR grade and the same OPC was used throughout. The chemical analysis of the cement is given in Table 2.

At the start of each hydration the cement was added to the deionized water/admixture or deionized water which had been decarbonated by boiling and then allowed to cool. The paste was mixed for 2 min using a

TABLE 1

Composition of the mixtures investigated

System	OPC (g)	Admixture	Dosage of admixture (anhydrous)		Water : cement ratio
			% of cement	mol kg^{-1} of cement	
OPC–H_2O	400	–	–	–	0.5
OPC–$CaCl_2$–H_2O	400	Calcium chloride ($CaCl_2 \cdot 2H_2O$)	1.0000	0.0901	0.5
OPC–$Ca(NO_3)_2$–H_2O	400	Calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$)	1.4785	0.0901	0.5
OPC–NaSCN–H_2O	400	Sodium thiocyanate (NaSCN)	0.7305	0.0901	0.5
OPC–sucrose–H_2O	400	Sucrose ($C_{12}H_{22}O_{11}$)	0.1000	0.0029	0.5

TABLE 2

Chemical 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

low-speed domestic food mixer and then quickly sampled into stoppered polythene tubes and tumble mixed at a very slow speed for as long as possible. To enhance the mixing, two stainless steel ball bearings were placed inside each of the polythene tubes. After setting, the remaining tubes were sealed in plastic bags and immersed in a water tank maintained at the same hydration temperature of 22° C.

Samples were taken after hydration had proceeded for 5 min, 1 h, 3 h, 6 h, 24 h and 3 days respectively. The hydration was quenched by grinding the crushed samples in an excess of acetone (AnalaR) and filtering. The residues were then dried in an oven at 22° C while continuously pumping air through silica gel and soda lime to maintain a moisture- and CO_2-free atmosphere. This method was found to be very effective for stopping the hydration reaction and giving a negligible carbonation level. The method has also been applied successfully to the hydration of the major phases present in OPC, aluminous cements and magnesia-phosphate cement [9]. The dried samples were then passed through a 200-μm nylon sieve, transferred into stoppered glass tubes and finally stored in a desiccator kept under vacuum.

Methods of investigation

The DSC curves were obtained using 4.9–5.1 mg samples in a Perkin-Elmer DSC4 differential scanning calorimeter which includes a microprocessor controller, model 3600 data station and a graphic plotter 2. The samples were heated at 20° C $\min^{-1}$ in nitrogen atmosphere with crimped aluminium crucibles as the reference material. The amount of energy absorbed by each endothermic reaction was computed for each run. The percentage of $Ca(OH)_2$ present in each sample was then calculated using the energy absorbed by the 480° C DSC peak and that of AnalaR calcium hydroxide. This energy and the total energy absorbed due to the dehydration and dehydroxylation were used as measures of the degree of hydration.

X-ray diffraction (XRD) traces were obtained using a Phillips PW-1050 diffractometer with Cu $K\alpha$ radiation, a nickel filter and a scanning rate of 1° 2θ $\min^{-1}$. Samples for electron microscopy were examined on a Camscan microscope, model 3/30 with a link system energy dispersive analysis by X-rays (EDAX) unit facility, operated at 20 kV.

RESULTS AND DISCUSSION

OPC-H_2O system

In the OPC-H_2O system (**I**) no admixture was used. The cement powder was added to deionized, decarbonated water only, as shown in Table 1. The water : cement ratio used was 0.5.

The phases identified by XRD are summarised in Table 3. Both C_3S and the anhydrite ($C\bar{S}$) decreased gradually throughout the hydration period. The latter, however, was detected in trace amounts only, after the first 24 h. Ettringite ($C_3A \cdot 3C\bar{S} \cdot 32H$) and calcium hydroxide (CH) were the main hydration products during the first hour. After 3 h, however, the latter gave increasingly intense XRD peaks throughout the subsequent hydration time. Typical DSC curves for this system are shown in Fig. 1.

The initial reaction products from 5 min to 3 h also contained a phase which gave an XRD peak at $d = 7.63$ Å and a DSC endotherm around 145 °C [Fig. 1A]. Gypsum and $C_3A \cdot C\bar{C} \cdot 12H$ have been reported to give an XRD peak at $d = 7.63$ Å and, therefore, it is likely that either may be the phase responsible for these peaks. Upon examining the XRD trace of the anhydrous cement, it was clear that the calcium sulphate was present in the anhydrite form ($CaSO_4$) apart from trace amounts of the hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$). This was also confirmed by DSC which exhibited a very

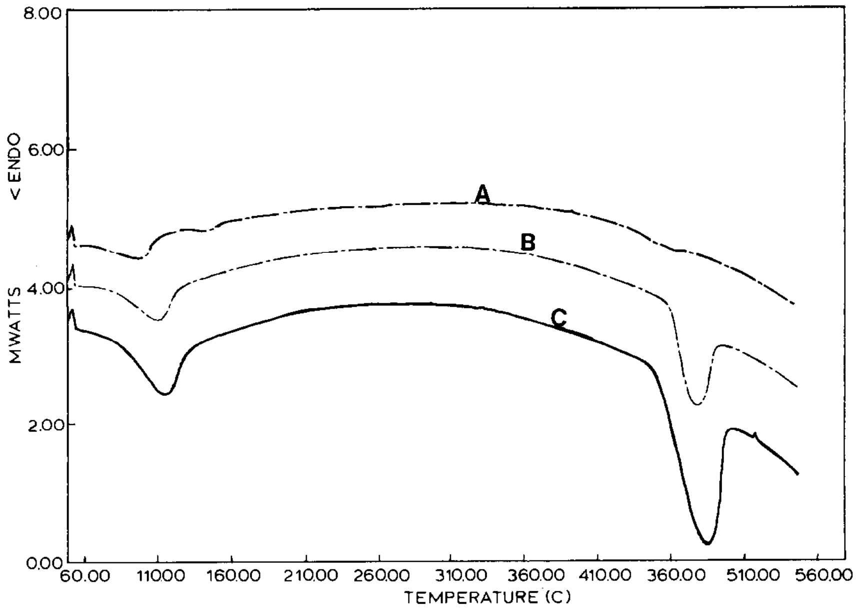


Fig. 1. DSC curves of the samples hydrated in the OPC–H_2O system. A, 1 h; B, 6 h; C, 3 days.

TABLE 3

Summary of XRD data for the systems investigated

System	XRD phase					
	C_3S ($d = 3.028$ Å)	$C\bar{S}$ ($d = 3.48$ Å)	$C_3A\cdot 3C\bar{S}\cdot 32H$ ($d = 9.72$ Å)	CH ($d = 4.9$ Å)	$C\bar{S}\cdot 2H$ ($d = 7.63$ Å)	Others
I OPC–H_2O	XXX	X	XX	XXXX	tr.	–
II OPC–$CaCl_2$–H_2O	XXX	X	XX	XXXX	tr.	C_4AH_{13}–chloroaluminate solid solution
III OPC–$Ca(NO_3)_2$–H_2O	XXX	X	XX	XXXX	tr.	C_4AH_{13}–monosulphate solid solution
IV OPC–NaSCN–H_2O	XXX	X	XX	XXXX	tr.	Monosulphate
V OPC–sucrose–H_2O	XXX	X	XX	XXXX	tr.	–

XXXX, Main phase increasing throughout the hydration period; XXX, main phase decreasing throughout the hydration period; XX, present throughout the hydration period; X, present for at least part of the hydration period; tr., present in trace amounts for part of the hydration period.

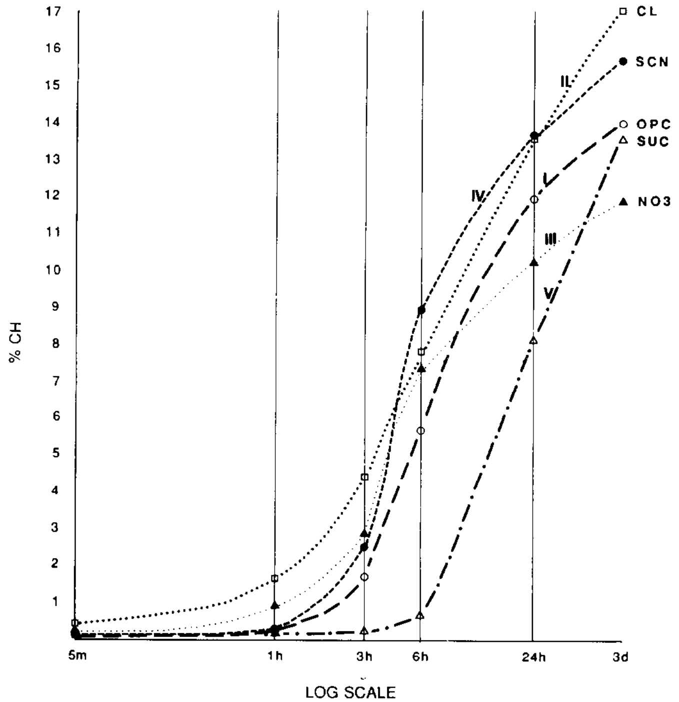


Fig. 2. The percentage of calcium hydroxide formed versus log time for systems I–V.

small endotherm around 110 °C. The same XRD peak ($d = 7.63$ Å) and DSC endotherm (ca. 145 °C) were detected when further hydrations were carried out under nitrogen atmosphere using freshly decarbonated, deionized water. In addition, the solution chemistry of the aqueous phase showed that the calcium and sulphate ion concentrations decreased during the first hour only. It is, therefore, concluded that gypsum was the phase formed.

Figure 1A also indicates the presence of a small endotherm around 260 °C; this was also observed in the samples hydrated for 5 min and 3h. The exact cause of this endotherm is not fully understood, but it may be due to AH_3 formed from the hydration of the very reactive $C_{12}A_7$ [10], which may be present in the cement in trace amounts. Assignment of the remaining DSC peaks observed in Fig. 1 could be made in accordance with the XRD results. The endothermic peak around 105 °C is attributed to ettringite and C–S–H gel, while the strong endotherm in the temperature range 440–480 °C is due to calcium hydroxide.

Curves I in Figs. 2 and 3 present the changes in the relative amounts of calcium hydroxide formed and the total energy absorbed throughout the hydration period for this system versus log time, respectively. It is clear that the trend was of increasing calcium hydroxide and total reaction-product formation especially during the first 24 h. In Figs. 2 and 3, it is particularly

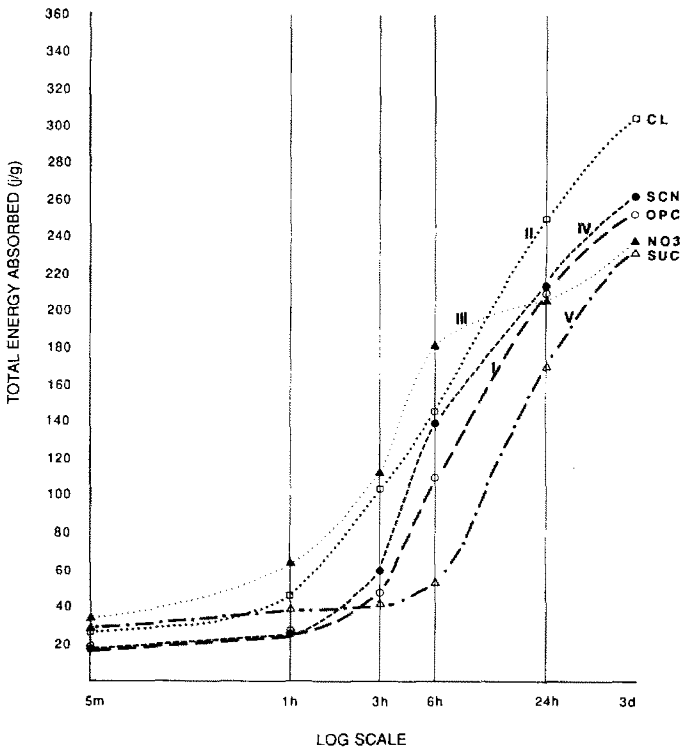


Fig. 3. Total energy absorbed versus log time for systems I–V.

interesting to note the slow rate of hydration during the first hours which is indicative of the dormant period.

OPC–$CaCl_2$–H_2O system

In the OPC–$CaCl_2$–H_2O system (II) the cement was added to the calcium chloride/water solution in the amounts shown in Table 1. As in the previous system the water : cement ratio was 0.5.

The DSC curves of the samples hydrated for 1 h, 6 h and 3 days are shown in Fig. 4, curves A, B and C respectively. The endothermic peaks around 100 °C, 145 °C and 480 °C are all similar to those in the OPC–H_2O system and in accordance with the XRD results (Table 3).

The reaction products after hydration for 3 days, however, were found to contain a phase which gives an XRD peak at $d = 7.9$ Å and a DSC endotherm around 166 °C [Fig. 4C]. After hydration for 1 year, the SEM micrographs (Fig. 5) showed hexagonal plates grown on the surface of the hydrated cement particles. These plates were not observed in the sample hydrated for 3 days. The EDAX analysis of these plates (Fig. 6) shows a strong calcium peak with weak aluminium and chloride peaks as the second

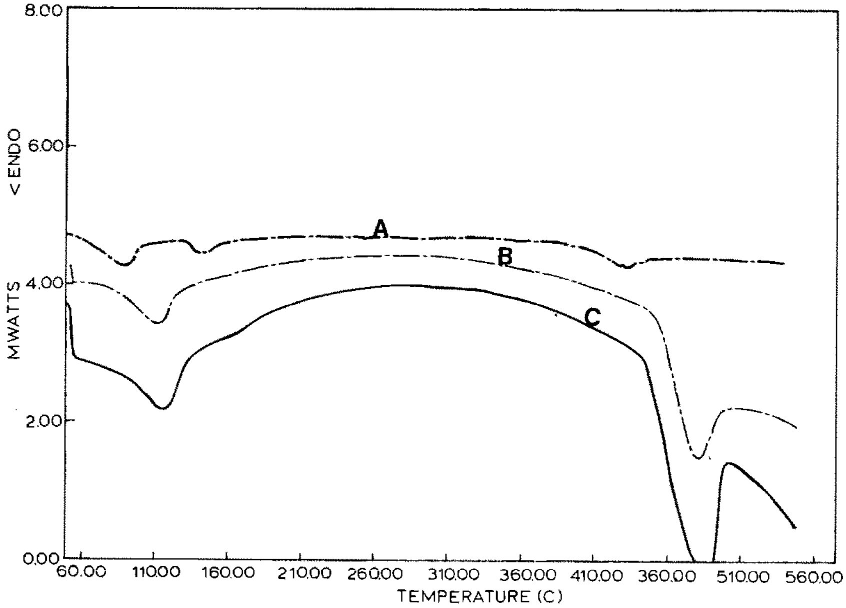


Fig. 4. DSC curves of the samples hydrated in the OPC–$CaCl_2$–H_2O system. A, 1 h; B, 6 h; C, 3 days.

and third peaks respectively. At the same time, the intensities of the XRD peak at $d = 7.9$ Å and the DSC endotherm around 166 °C were markedly increased after hydration for 1 year, but no extra peaks were detected. It seems, therefore, that the same phase is responsible for the platelets, XRD peak and DSC endotherm. Monochloroaluminate gave DSC endotherms around 170 °C and 335 °C (Fig. 7), with the latter being more intense than the former. This was also confirmed by differential gravimetry in a different study on the influence of cement chemistry on chloride attack of concrete [11]. Hence it is concluded that the extra phase formed after 3 days was a C_4AH_{13}–chloroaluminate solid solution.

The DSC data for system II, given in Figs. 2 and 3, show that more calcium hydroxide as well as total reaction product had formed than in the neat OPC paste (I). Moreover, the trend was of increasing $Ca(OH)_2$ and total reaction-product formation even after the first 3 days. It must be noted, however, that in another study on the influence of calcium chloride dosage on the formation of calcium hydroxide it was found that less $Ca(OH)_2$ had formed than in the neat OPC paste as the chloride added was increased to three times the level used in the present investigation [12]. This indicates that the addition of calcium chloride above a certain level results in the formation of less calcium hydroxide. Ramachandran showed that at $CaCl_2$ contents higher than 2%, the C–S–H formed has a high calcium : silica ratio [7]. It seems, therefore, that the formation of less $Ca(OH)_2$ is associated with the larger than normal calcium : silica ratio gel.

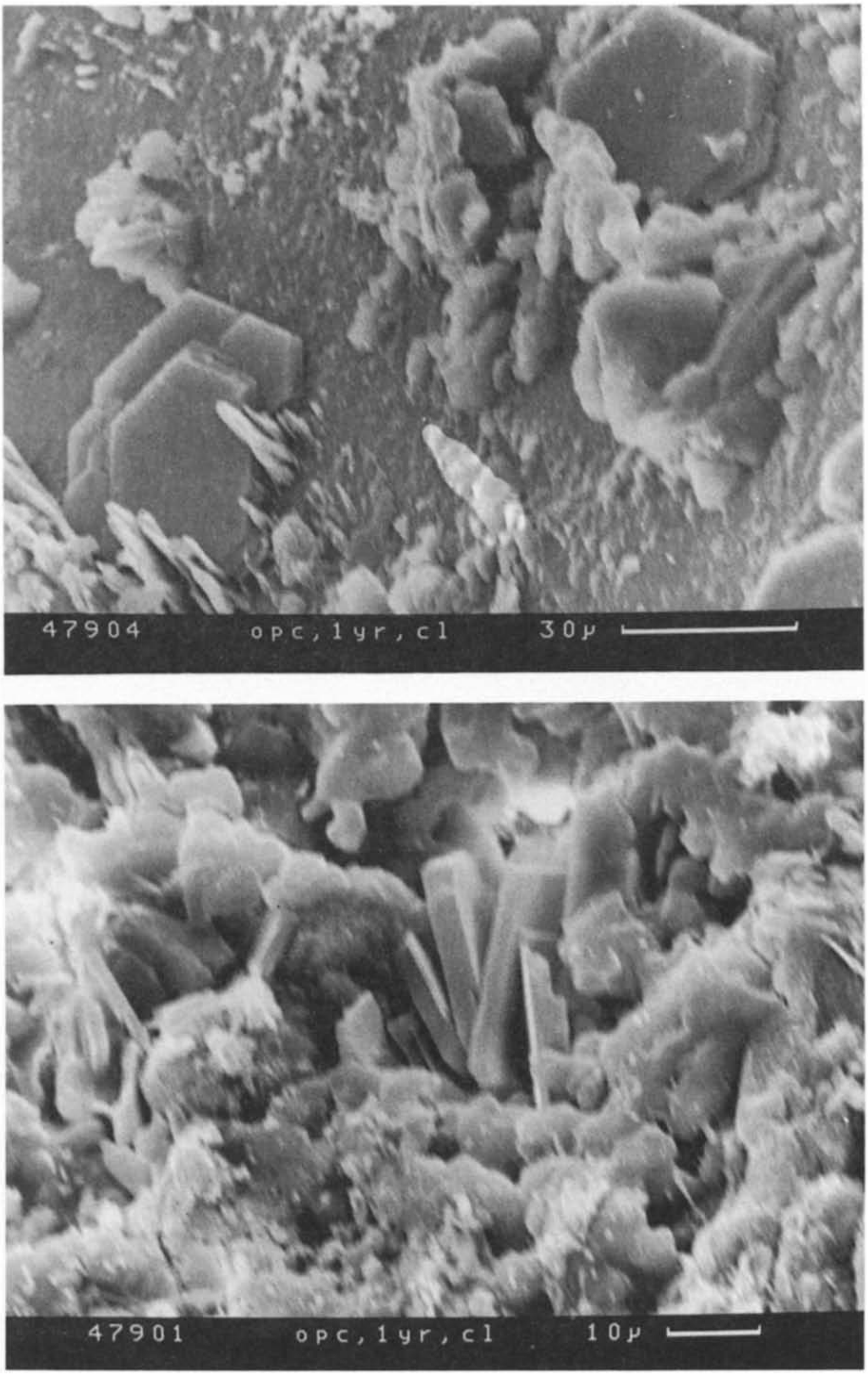
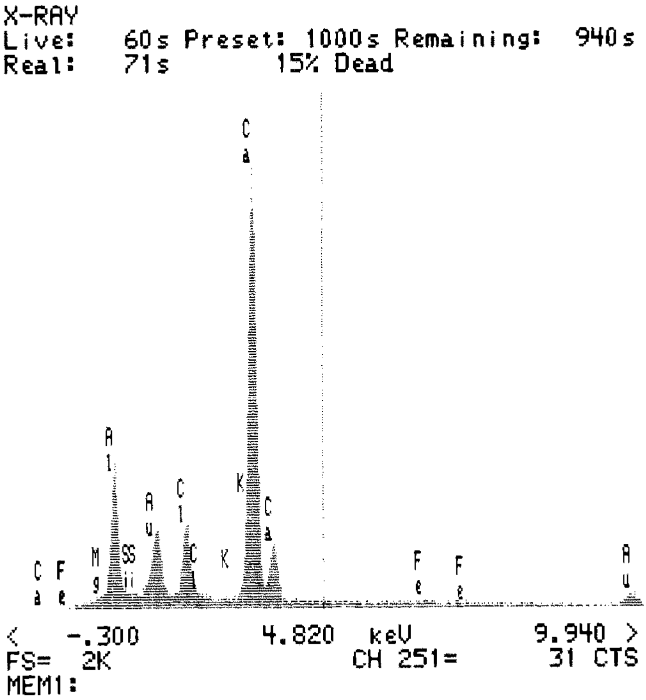


Fig. 5. SEM micrographs of the sample hydrated for 1 year in the OPC–$CaCl_2$–H_2O system.



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X-RAY
Live:    60s Preset:  1000s Remaining:   940s
Real:    71s          15% Dead
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<    -.300          4.820   keV           9.940 >
FS=  2K                CH 251=             31 CTS
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Fig. 6. EDAX analysis of the hexagonal plates shown in the micrographs of Fig. 5.

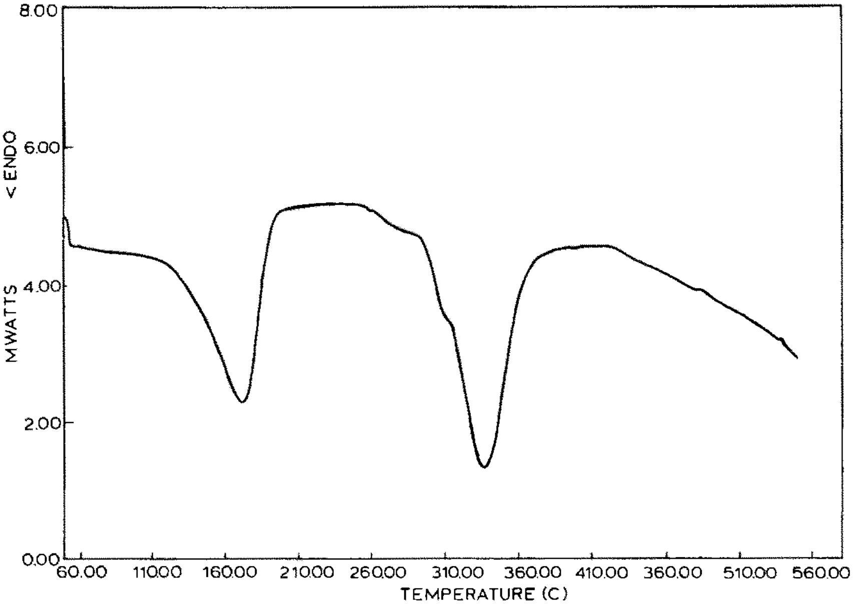

Fig. 7. DSC curve of synthesized monochloroaluminate.

OPC–$Ca(NO_3)_2$–H_2O system

The additive used in the OPC–$Ca(NO_3)_2$–H_2O system (**III**) was calcium nitrate at a dosage of 1.4785% (Table 1). This is equivalent to 0.0901 mol of anhydrous calcium nitrate [$Ca(NO_3)_2$] per kg of cement. It is, therefore, the same molar amount as that used in the OPC–$CaCl_2$–H_2O system, except for the replacement of calcium chloride by calcium nitrate.

The XRD data for this system, summarised in Table 3, show that the general hydration behaviour using the chloride or nitrate was very similar except for the formation of a C_4AH_{13}–monosulphate solid solution (diffuse peak at $d = 8.59$ Å) after 3 days and that gypsum was not detected after 3 h in the latter.

The DSC curves of the hydrated samples can be interpreted in line with the XRD results. DSC curves of the samples hydrated for 1 h, 6 h and 3 days are shown in Fig. 8, curves A, B and C respectively. The different hydration products can be detected by DSC as well as XRD. The well-developed endotherms in the temperature range 110–130 °C are due to ettringite and C–S–H gel. Calcium hydroxide is responsible for the endothermic peak around 460 °C. The small endotherm around 145 °C in Fig. 8(A) is attributed to gypsum while the shoulder around 180 °C [Fig. 8(C)] is due to the solid solution mentioned above. The presence of calcium nitrate is reported to promote the formation of the cubic phase, C_3AH_6 [7], but in our view the

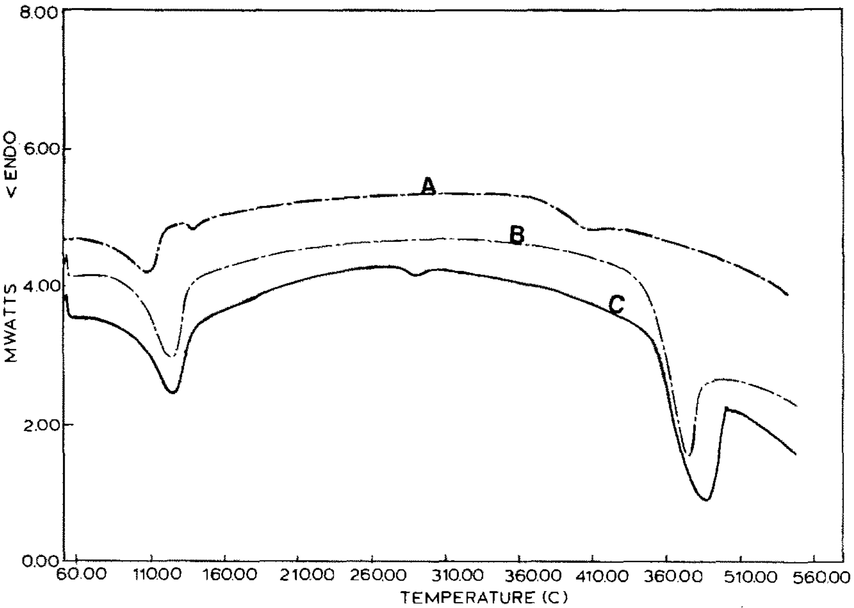

Fig. 8. DSC curves of the samples hydrated in the OPC–$Ca(NO_3)_2$–H_2O system. A, 1 h; B, 6 h, C, 3 days.

290 °C endotherm seen in Fig. 8(C) may be associated with the solid solution identified by XRD to be present in this sample only.

The percentage calcium hydroxide formed and the total energy absorbed versus log time are shown in curves **III** of Figs. 2 and 3, respectively. Although the percentage of calcium hydroxide formed was clearly more in system **II** using the chloride than in system **III** at any time during the hydration period, the total amount of hydration product was less during the first 12 h. This indicates that more ettringite and less C–S–H had formed during the first 12 h of hydration when calcium nitrate was the additive. In comparison to the neat OPC paste, the results show that less calcium hydroxide and total reaction products had formed after hydration for longer than 12 and 24 h, respectively, in the presence of the nitrate. It is therefore evident that the nitrate acts as a retarder after hydration for more than 12 h.

OPC–NaSCN–H_2O system

In the OPC–NaSCN–H_2O system (**IV**), as in the previous systems, 0.0901 mol of NaSCN per kg of cement were used (Table 1). This was done so that the performance of sodium thiocyanate with that of calcium chloride in system **II** and calcium nitrate in the previous system could be compared on an equal molar basis.

The relative intensities of the phases identified by XRD for this system are summarised in Table 3. It can be seen from the data that monosulphate was the phase identified to be present after hydration for 3 days. This was confirmed by DSC which showed a shoulder around 180 °C [Fig. 9C]. Once again and like the neat OPC paste a small endotherm around 260 °C is present in the DSC curve of the sample hydrated for 1 h [Fig. 9A]. This endotherm, which may be due to gibbsite, was not detected in systems **II** or **III** using the chloride and nitrate, respectively, perhaps because of the dilution effect due to the formation of more hydration products in these systems.

Curves **IV** in Figs. 2 and 3 present the variation in the amount of calcium hydroxide and total reaction products formed, respectively. Using these curves as a measure of the degree of hydration clearly indicates that there was always less total reaction product and calcium hydroxide at any time in this system than in system **II**, using the chloride except between 6 h and 18 h in Fig. 2. In comparison to the nitrate, sodium thiocyanate is shown to be more effective after hydration for longer than 6 h on the basis of the amounts of calcium hydroxide formed, but after hydration for longer than 12 h using the total amount of energy absorbed as a measure of the degree of hydration.

It must be emphasised, however, that the total amounts of calcium hydroxide estimated in Fig. 2 may be slightly exaggerated, especially in the samples hydrated for 5 min and 1 h. This is because of the presence of an

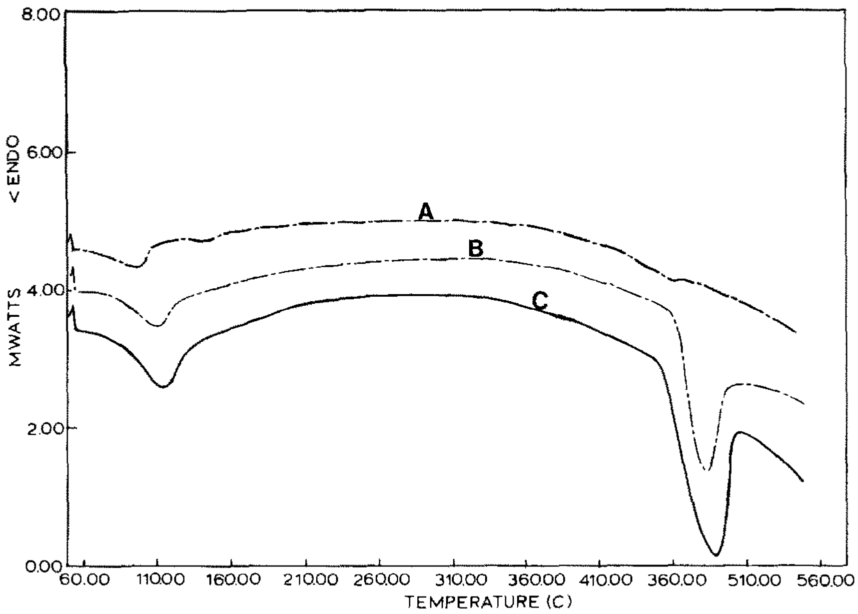

Fig. 9. DSC curves of the samples hydrated in the OPC–NaSCN–H_2O system. A, 1 h; B, 6 h; C, 3 days.

endothermic peak around 445°C in the DSC curve of the anhydrous cement, which may overlap with that due to calcium hydroxide in the hydrated samples.

There is clear evidence in our results to confirm the presence of a double endotherm in some of the samples hydrated for up to 1 h [e.g. Fig. 9A]. At the moment, it is not known to what extent the first endotherm relates to that observed in the anhydrous cement or the real cause of the latter, but the decomposition of amorphous calcium hydroxide which may be present during the early ages of hydration could also be responsible for the double endotherm.

OPC–sucrose–H_2O system

In the OPC–sucrose–H_2O system (V) sucrose was used as the additive. A dosage of 0.1 % by weight of cement was dissolved in water prior to hydration. The objective of this system was to check the trends observed in the previous ones with respect to the neat OPC.

The phases identified by XRD as well as DSC in Figs. 2 and 3 showed that much less hydration took place during the first 24 h in this system than in the previous ones. The DSC curves of the samples hydrated for 1 h and 6 h [Figs. 10A and 10B], indicate that very little hydration had occurred during the first 6 h in line with the XRD results. After hydration for 3 days,

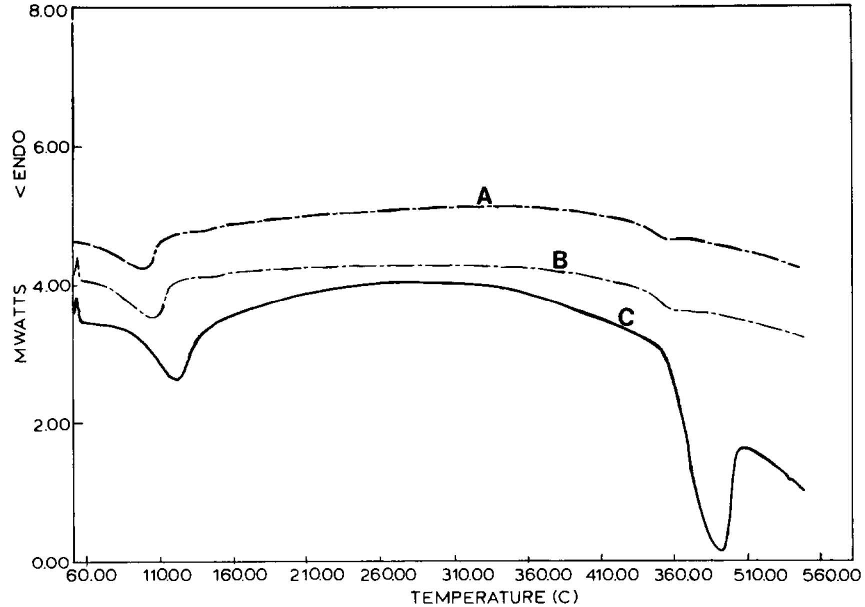

Fig. 10. DSC curves of the samples hydrated in the OPC–sucrose–H_2O system. A, 1; B, 6 h, C, 3 days.

however, the increased degree of hydration was indicated by DSC as well as XRD. On the basis of the total energy absorbed as a measure of the degree of hydration, sucrose was shown to be an effective retarder throughout the hydration period [Fig. 3V]. Initially, however, the total reaction product formed is shown to be comparable to that in the nitrate system (III). On the other hand, using the formation of calcium hydroxide as a measure of the degree of hydration, sucrose is confirmed as a retarder during the first 3 days.

After hydration for more than 2 days, however, calcium hydroxide formed was found to exceed that formed in system **III**, using the nitrate. It seems, therefore, that sucrose does not reduce the amounts of ettringite formed and its retardation effect is mainly through controlling the hydration of the silicate minerals.

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