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CALORIMETRIC STUDIES OF SPECIAL CEMENTS

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Abstract

The kinetics and even the mechanism of cement reaction with water can be successfully investigated by use of microcalorimetry. In this study this method was applied to follow the hydration of the new family of portland cements containing $C_{12}A_7$* and $C_{11}A_7{\cdot}CaF_2$ addition as well as special cement with C_3A replacement by calcium sulphoaluminate. It has been found that $C_{11}A_7{\cdot}CaF_2$ acted as hydration retarder. The heat evolution curves for $C_{12}A_7$ containing samples without CaF_2 are very similar to those for the reference portland cement samples. XRD and SEM studies confirm the results described above, relating to the retardation of alite hydration. The process is positively modified by the addition of anhydrite. In the presence of calcium sulphoaluminate ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$) the hydration at early stage occurs with the rapid formation of large amount of the ettringite phase. The calcium fluoride acts as a set retarder. The full compatibility of calorimetry with SEM and XRD results should be underlined.

Keywords: calcium aluminate, calcium fluoride, calorimetry, heat of hydration, rapid hardening cements

Introduction

The calorimetric measurements are used not only in the heat output evaluation during the hydration of cement but also in the studies of the hydration mechanism. The rate of heat evolution *vs.* time plot show the occurrence of two maxima with the so-called induction period between them. The length of this induction period is influenced by the additives accelerating or retarding the hydration, and consequently, the setting and hardening process.

The rapid hardening portland cements can be produced by several methods on the basis of normal portland cement clinker; among them the addition of $12CaO{\cdot}7Al_2O_3$ or $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$ to portland cement can be applied [1]. The latter aluminate-fluoride phase is synthesized at lower temperatures, at the presence of CaF_2 in the initial batch for the portland cement clinker, and ap-

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* In cement chemistry the following notation is used: C = CaO, A = Al_2O_3, S = SiO_2, H = H_2O etc. for the main oxide constituents of portland cement clinker and hydrates.

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pears as a tricalcium aluminate replacement. The calcium aluminate can be accompanied in cement by the increased calcium sulphate content, usually added in the form of anhydrite. At the insufficient sulphate ions concentration in the liquid phase, the aluminate ions adsorb on the silicate grains thus retarding the hydration process [2]. The $C_{12}A_7$ containing cements reveal a very high early strength, as a consequence of the rapid calcium aluminate hydration, but sometimes their behaviour is surprising – they do not fulfil the standard requirements. There is no data on the $C_{12}A_7$ – portland cement system hydration mechanism. Another way of the rapid hardening cement production consists in the addition of calcium sulphoaluminate (so-called Klein's compound – $4CaO{\cdot}Al_2O_3{\cdot}SO_3$) to the batch for the normal cement clinker [3]. This clinker, due to the mineralizing action of $CaSO_4$, can be also produced at lower temperature. The Klein's compound containing cements also exhibit a significant strength development. Their hydration process has not been investigated in details yet. Therefore the studies on the hydration of cements by an addition of calcium aluminate or sulphoaluminate have been carried out with aim to get the informations about their properties and furthermore, to develop the technology of special cement.

Experimental

Materials

The nine cement samples were used in the investigations. The four cement clinkers with calcium sulphoaluminate were synthesized from the analytically pure compounds (Table 1). These clinkers were ground together with gypsum to obtain cements (4% SO_3 in cement).

Table 1 Composition of sulphoaluminate cements

Component	Percentage in			
	C I	*C* II	*C* III	*C* IV
$3CaO{\cdot}SiO_2$	55	55	70	70
$2CaO{\cdot}SiO_2$	15	15	0	0
$4CaO{\cdot}3Al_2O_3{\cdot}Fe_2O_3$	15	15	15	15
$4CaO{\cdot}3Al_2O_3{\cdot}SO_3$	15	15	15	15
CaF_2*	0.5	2	0.5	2

*Added before clinker burning

The commercial portland cement class 45 (denoted as *PC* 45) was used in the second series of samples. The following calcium aluminates to be added to this cement were produced by sintering of the batches prepared from the analytically pure components:

$12CaO\cdot 7Al_2O_3$ (1300°C)
$11CaO\cdot 7Al_2O_3\cdot CaF_2$ (1280°C)

These aluminates were ground together with the commercial portland cement clinker. The next four cements have been thus produced (Table 2).

Table 2 Composition of cements with aluminate addition

Component	Percentage in			
	C V	*C* VI	*C* VII	*C* VIII
PC 45	90	80	90	80
$11CaO\cdot 7Al_2O_3\cdot CaF_2$	10	20	–	–
$12CaO\cdot 7Al_2O_3$	–	–	10	20

Finally, the two samples composed of the portland cement mentioned above and calcium aluminates were mixed with the ground anhydrite. These cements have been prepared with aim to investigate the effect of sulphate on the aluminate and silicate phase hydration (Table 3).

Table 3 Composition of aluminate and anhydrite doped cements

Component	Percentage in	
	C IX	*C* X
PC 45	80	80
$11CaO\cdot 7Al_2O_3\cdot CaF_2$	10	–
$12CaO\cdot 7Al_2O_3$	–	10
$CaSO_4$	10	10

Methods

The heat evolution occurring on cement hydration was followed by microcalorimetry (BMR differential microcalorimeter constructed in the Institute of Physical Chemistry, Polish Academy of Science) on the pastes prepared at water to solid ratio 0.5. The XRD was used to control the phase composition of synthesized materials and to identify the hydration products. The components of hydrated pastes were also observed under the scanning electron microscope.

Results

The sets of calorimetric curves are shown in Figs 1–5. The heat evolution curve for the commercial cement (*PC* 45) is plotted as a reference. The same sample notations are used as in the Tables 1–3 (*C* I, *C* II, *C* III etc.). The heat evolved values are presented in Table 4.

Table 4 Heat evolved during the hydration of cements

Sample	Heat evolved after 24 h hydration / $kJ \cdot kg^{-1}$
PC 45	283
C I	240
C II	129
C III	202
C IV	196
C V	129
C VI	128
C VII	288
C VIII	269
C IX	216
C X	277

Discussion

As it results from the calorimetric studies, the sulphoaluminate components modify significantly the hydration kinetics and mechanism in the case of the lower alite content (see Fig. 1). The first broad and high exothermic peak can be attributed to the sulphoaluminate hydration, with the formation of ettringite ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32H_2O$). The delaying effect of fluoride ions on the calcium silicate hydration is clearly seen as an induction period elongation. The hydration of high alite content cements (Fig. 2) is less affected by the addition of sulphoaluminate and in the presence of fluoride in the clinker but the heat evolution decrease is observed also. The hydration of cement – $C_{11}A_7 \cdot CaF_2$ blends (Fig. 3) also proceeds very slowly, as a consequence of the fluoride ions actions.

The maximum of the main effect corresponding to the calcium silicates hydration is observed after almost 50 h. In turn, the $C_{12}A_7$ phase brings about a significant acceleration of the heat evolution process (Fig. 4), due to the formation of the hydrated calcium aluminates, but the total heat evolved values are not higher than for the reference portland cement. The data for the cement – aluminate samples doped with anhydrite (Fig. 5) confirm the set controlling influence of calcium sulphate. The heat evolution curves become similar to that for the reference sample. However, the heat evolved values are lower than for pure cement, as it would result from the delaying influence of the calcium aluminates admixtured to cement on alite hydration.

The hydration products in all the samples were identified by XRD and SEM. The formation of the substantial amount of ettringite in the presence of calcium sulphoaluminate was thus confirmed. A low degree of hydration in the presence of fluoride was also evidenced as well as the occurrence of hexagonal calcium

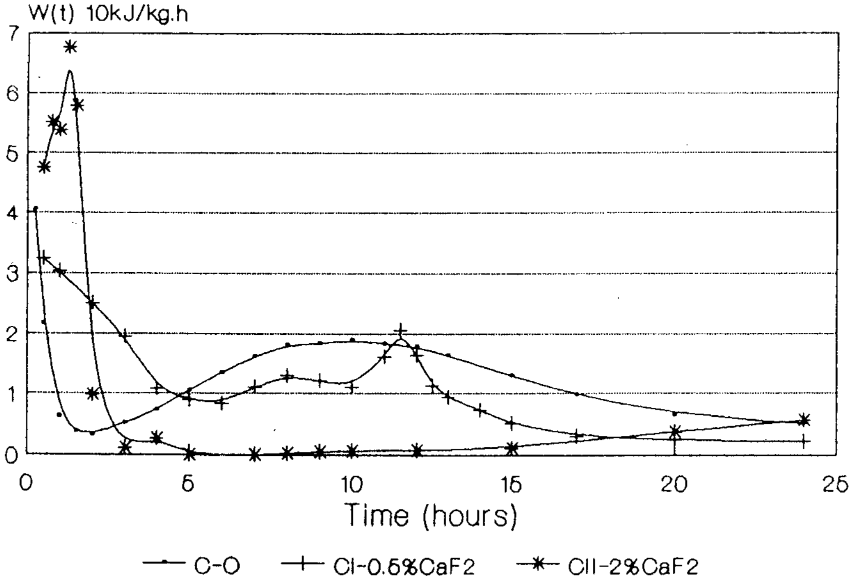

Fig. 1 Calorimetric curves of sulphoaluminate cements (55% C_3S)

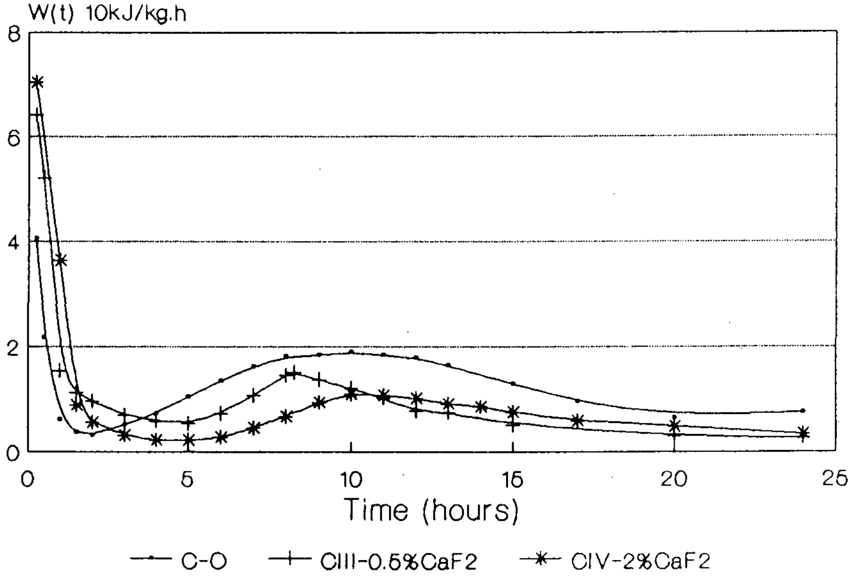

Fig. 2 Calorimetric curves of sulphoaluminate cements (70% C_3S)

aluminate hydrates produced from the $C_{12}A_7$ phase. In turn, the addition of anhydrite resulted in the ettringite formation and even the so-called secondary gypsum was found.

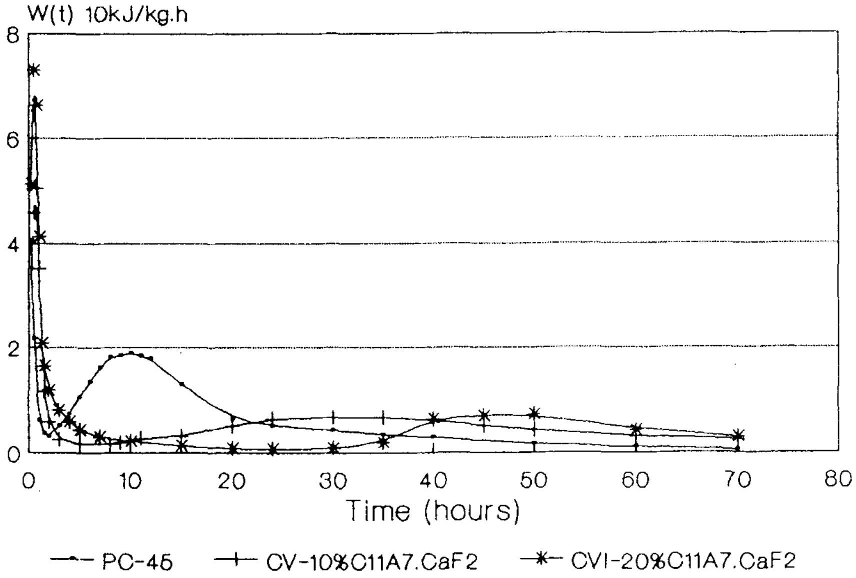

Fig. 3 Calorimetric curves of cements with $C_{11}A_7$·CaF_2 addition

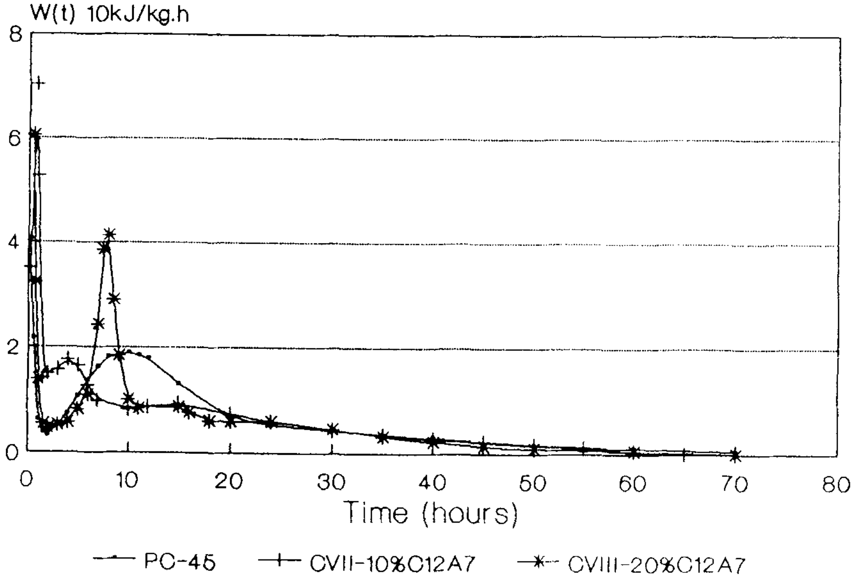

Fig. 4 Calorimetric curves of cements with $C_{12}A_7$ additon

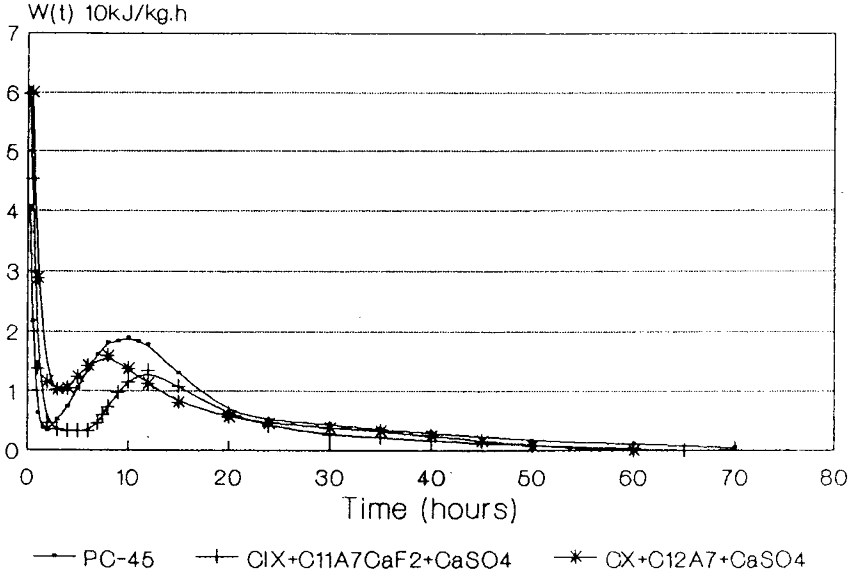

Fig. 5 Calorimetric curves of cements with aluminate + anhydrite addition

Summarizing the data thus obtained one can point out a quite different effect of the calcium aluminate, calcium fluoroaluminate and calcium sulphoaluminate on cement hydration.

Conclusions

1) The calorimetry is very helpful in the studies of early hydration, in evaluation of retarding effect of some compounds on the hydration of particular cement constituents and in determination of the optimum gypsum content. The full compatibility of calorimetry with SEM and XRD results should be also underlined.

2) The calcium sulphoaluminate itself transforms rapidly to ettringite during cement hydration and does not affect the hydration of calcium silicates.

3) The alite hydration is badly affected by the calcium aluminates: $C_{12}A_7$ and $C_{11}A_7{\cdot}CaF_2$. A suitable amount of calcium sulphate is necessary to ensure the formation of ettringite and to prevent the secondary gypsum precipitation.

4) The presence of fluoride in the clinker hinders significantly the hydration of alite.

References

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2 B. Cottin and C. Vibert, Cement-Wapno-Gips, 7 (1976) 196 (in Polish)
3 I. Odler, The possibilities of increasing SO_3 content in cement, in: Advances in Cement Manufacture and Use, ed. E. Gartner, Engineering Foundation, New York, 1989, p. 303.

Zusammenfassung — Mittels Mikrokalorimetrie kann die Kinetik und selbst der Mechanismus der Zementreaktion mit Wasser erfolgreich untersucht werden. Vorliegend wurde diese Methode zur Verfolgung der Hydratation einer neuen Reihe von Portlandzements mit Gehalt an $C_{12}A_7$- und $C_{11}A_7CaF_2$-Zusatz sowie von Spezialzement mit C_3A-Ersatz durch Calciumsulfoaluminat angewendet. Man fand, daß $C_{11}A_7CaF_2$ als Hydratationsbremsmittel wirkt. Die Kurven für die Wärmefreisetzung für $C_{12}A_7$-haltige Proben ohne CaF_2 ähneln sehr denen für die als Bezugssubstanz verwendeten Portlandzements. Röntgendiffraktions- und SEM-Untersuchungen bestätigen die obenbeschriebenen Ergebnisse bezüglich der Verzögerung der Alithydratation. Durch Zusatz von Anhydrit wird der Prozeß positiv modifiziert. In Gegenwart von Calciumsulfoaluminat ($4CaO\cdot 3Al_2O_3\cdot SO_3$) erfolgt die Hydratation in frühen Schritten unter schneller Bildung einer großen Menge Ettringitphase. Calciumfluorid wirkt als Verzögerungsmittel. Die volle Übereinstimmung von Kalorimetrie mit SEM- und Röntgendiffraktionsuntersuchungen wird betont.