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ROLE OF PHOSPHOGYPSUM IN THE HYDRATION OF CALCIUM SULPHOALUMINATE

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ABSTRACT

In view of possible ways of disposal of phosphogypsum the hydration of a series of preparations of calcium sulphoaluminate, made from this by-product at 1000 and 1100 °C or from pure gypsum at 1200 and 1350 °C, has been studied in mixtures with phospho- or pure gypsum and $Ca(OH)_2$. The compositions of the mixtures to be hydrated were stoichiometric for the formation of calcium tri- and monosulphoaluminate hydrates.

The hydration properties of calcium sulphoaluminate are not significantly influenced by the nature of gypsum employed in the high temperature synthesis.

Phosphogypsum impurities act as catalysts in the formation of calcium trisulphoaluminate hydrate which is of major interest among the hydration products of a wide range of cements.

INTRODUCTION

Calcium sulphoaluminate $C_4A_3\bar{S}$ * is of interest in the fields of rapid-hardening, expansive and energy-saving cements [1–7]. In a recent paper [8] its high temperature synthesis was reported using mixtures of $CaCO_3$, Al_2O_3 and phospho- or pure gypsum. Evidence was found that phosphogypsum impurities have fluxing and mineralizing properties. Therefore the use of phosphogypsum in the raw mix allows the synthesis to be performed at temperatures and times considerably lower than those required when pure gypsum is employed.

In this paper the conversion of $C_4A_3\bar{S}$ into hydrated phases is studied using different preparations made from phosphogypsum at 1000 and 1100 °C or alternatively from pure gypsum at 1200 and 1350 °C. To achieve this the

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* Common cement chemistry nomenclature is used: $C = CaO$; $A = Al_2O_3$; $\bar{S} = SO_3$; $H = H_2O$.

samples of $C_4A_3\bar{S}$ were paste hydrated after mixing with phospho- or pure gypsum and $Ca(OH)_2$ in stoichiometric ratios to form calcium trisulphoaluminate hydrate $C_6A\bar{S}_3H_{32}$ and calcium monosulphoaluminate hydrate $C_4A\bar{S}H_{12}$, respectively.

The influence of phosphogypsum on the hydration of calcium sulphoaluminate was then examined from two points of view; on one hand as a component of the raw mix for $C_4A_3\bar{S}$ synthesis and on the other as a source of $CaSO_4 \cdot 2H_2O$ in the mixtures to be hydrated.

EXPERIMENTAL

Phosphogypsum was supplied by Montedison S.p.A. (Italy). Its chemical composition is shown in Table 1.

The samples of $C_4A_3\bar{S}$ were prepared as previously reported [8]. They were ground to pass the 325 mesh sieve. The other reagents used in the hydration experiments were analytical grade $CaSO_4 \cdot 2H_2O$, $Ca(OH)_2$ and CO_2-free water. The water/solid ratio was 1.0, the curing temperature 25 ° C. The ageing times were 1, 3, 6, 24, 72 and 168 h; at the end of each the reaction was stopped by grinding under acetone followed by washing with ether. The hydrated samples were then stored in a desiccator in the presence of P_2O_5.

The hydration products were qualitatively characterized by thermal analysis using a Netzsch STA 409 apparatus. Complementary data were obtained by X-ray analysis with a Philips diffractometer (a PW 1730/10 generator, a PW 1050/70 goniometer, a PW 1965/30 proportional counter and a PW 1390 channel control); Cu $K\alpha$ radiation was used.

Quantitative data were obtained by determining the amount of unreacted $Ca(OH)_2$ by the Franke method [9]. Non-evaporable water was determined by ignition at 1000 ° C.

TABLE 1

Chemical composition of phosphogypsum samples

	Wt%
Loss on ignition	22.9
CaO	34.3
SO_3	40.0
P_2O_5	1.8
SiO_2	1.4
F	1.2
Na	0.8

RESULTS AND DISCUSSION

The mixtures to be hydrated are identified by a code of the type X_tYZ where:

X can be P or G depending on whether phospho- or pure gypsum is used for the synthesis of $C_4A_3\bar{S}$, respectively;
t refers to the synthesis temperature and can be l (low) or h (high) meaning 1000 or 1100 °C, respectively, in the case of phosphogypsum, 1200 or 1350 °C, respectively, in the case of pure gypsum;
Y can be P or G depending on whether phospho- or pure gypsum is added to $C_4A_3\bar{S}$ in the hydration runs;
Z refers to the composition of the mixtures to be hydrated and can be T or M depending on whether the composition is stoichiometric for the formation of calcium tri- or monosulphoaluminate hydrate, respectively.

As an example, G_hPT means that $C_4A_3\bar{S}$ is made from pure gypsum at 1350 °C and phosphogypsum is used in the mixture to be hydrated, whose composition is stoichiometric for the formation of calcium trisulphoaluminate hydrate.

The identification of reaction products by differential thermal analysis was made using data available in the literature on calcium aluminate hydrates and related phases [10,11].

Figure 1 shows the thermograms of samples of type P_hPT. The endothermic effects at 166 ± 11 °C and 472 ± 12 °C are related to the reagents $CaSO_4 \cdot 2H_2O$ and $Ca(OH)_2$, respectively, and decrease in intensity as ageing time increases. The endothermic effect at 140 ± 15 °C reveals the presence of a single reaction product ($C_6A\bar{S}_3H_{32}$). Its amount is considerable as early as after 1 h and rapidly increases with the ageing time. Similar qualitative results have been obtained by differential thermal analysis for the systems of type P_lPT, G_lGT and G_hGT.

Figure 2 shows the amount of unreacted $Ca(OH)_2$, in terms of percentage of the initial quantity in the mixtures to be hydrated, as a function of ageing time for the systems P_lPT and P_hPT. No difference in reactivity is observed. In a previous paper [8] it was shown that the calcium sulphoaluminates made from phosphogypsum at 1000 and 1100 °C differed only by the content of $C_{12}A_7$. This was present besides the main product $C_4A_3\bar{S}$ as minor phase, in higher concentration at the lower temperature. Data from Fig. 2 indicate that this difference as well as others eventually induced by the reaction temperature have no effect on the overall reactivity of the synthesis products in the hydrating mixtures.

Figure 3 shows the amount of unreacted $Ca(OH)_2$ as a function of ageing time for the systems G_lGT and G_hGT. In this case the sulphoaluminate reactivity decreases from 1200 to 1350 °C. This may be due to the growth of

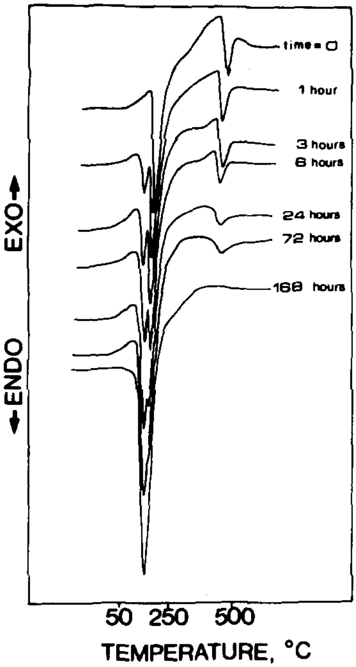

Fig. 1. Thermograms of samples of type P_hPT.

crystallites process which takes place to a greater extent at higher temperature, with a negative effect on reactivity.

Figure 4 shows the thermograms of samples of type G_1GM. $C_6A\bar{S}_3H_{32}$ is the product formed most rapidly. After 1 h of hydration its amount is so large that the corresponding endothermic effect widely overlaps that of

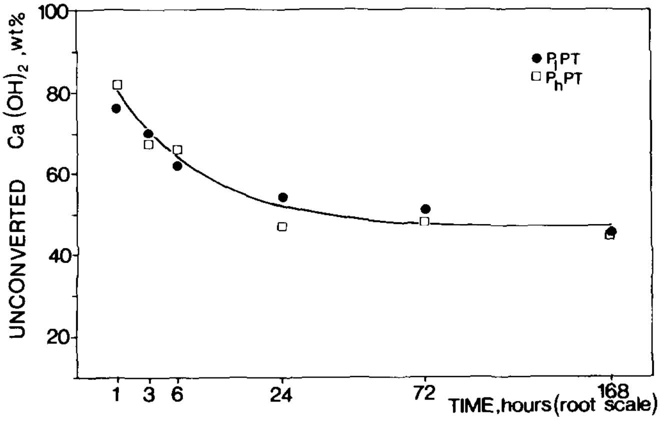

Fig. 2. Unreacted $Ca(OH)_2$ vs. time for systems P_lPT and P_hPT.

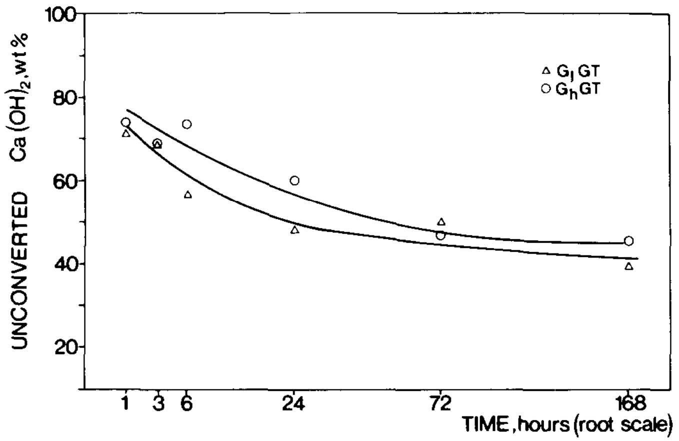

Fig. 3. Unreacted $Ca(OH)_2$ vs. time for systems G_lGT and G_hGT.

unreacted $CaSO_4 \cdot 2H_2O$. As ageing time increases $C_4A\bar{S}H_{12}$ and C_3AH_6 are formed also, as indicated by the endothermic effects at 212 ± 8 °C and 298 ± 6 °C, respectively. The reduction in intensity of the peak related to $C_6A\bar{S}_3H_{32}$ and the occurrence of the effect due to $CaSO_4 \cdot 2H_2O$ at the longest ageing times indicate that decomposition of $C_6A\bar{S}_3H_{32}$ takes place.

A comparison with the thermograms of Fig. 1 shows that the reaction of formation of $C_6A\bar{S}_3H_{32}$ is much faster in the system under consideration.

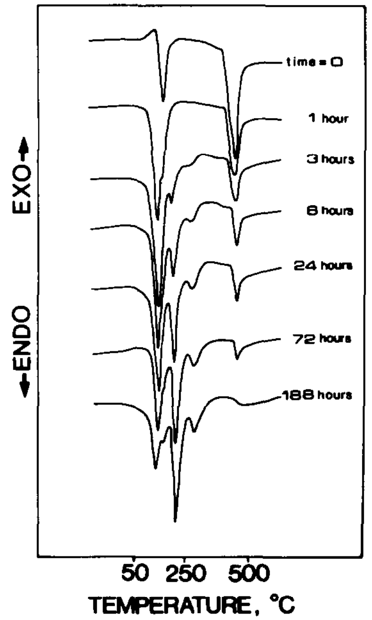

Fig. 4. Thermograms of samples of type G_lGM.

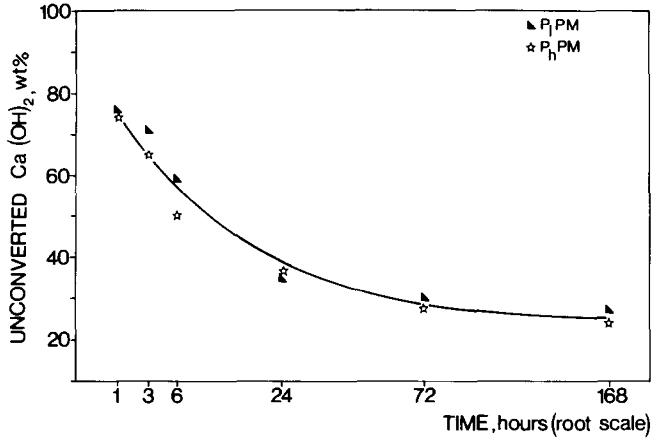

Fig. 5. Unreacted $Ca(OH)_2$ vs. time for systems P_lPM and P_hPM.

This means that the apparent order of the reaction of formation of $C_6A\bar{S}H_{32}$ with regard to $CaSO_4 \cdot 2H_2O$ is lower than that for the other reagents, because the molar ratios between the reactants $C_4A_3\bar{S}$, $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ are 3 : 6 : 8 and 3 : 6 : 2 in the systems stoichiometric for the formation of $C_6A\bar{S}_3H_{32}$ and $C_4A\bar{S}H_{12}$ respectively. This agrees with a previous finding for the system phosphogypsum–CaO–$Al(OH)_3$–H_2O [12]. Results similar to those shown in Fig. 4 were obtained by thermal analysis for the systems of type G_hGM, P_lPM and P_hPM.

Figures 5 and 6 show the amount of unreacted $Ca(OH)_2$ vs. time for the systems containing phosphogypsum (P_lPM and P_hPM) and those containing pure gypsum (G_lGM and G_hGM), respectively. As in the systems stoichio-

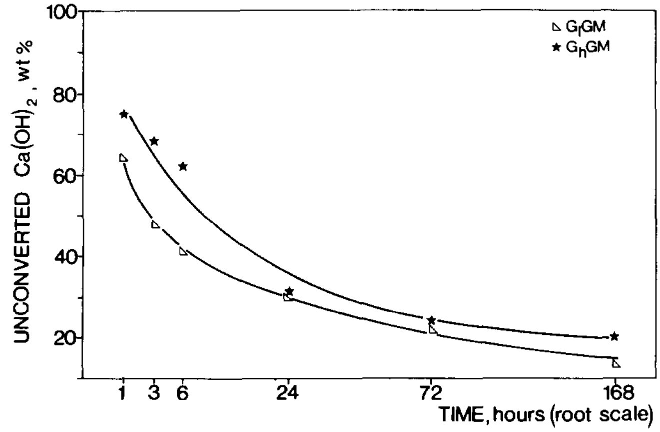

Fig. 6. Unreacted $Ca(OH)_2$ vs. time for systems G_lGM and G_hGM.

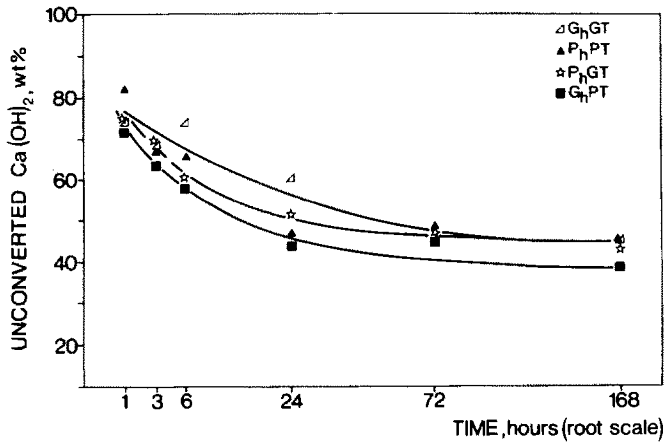

Fig. 7. Unreacted $Ca(OH)_2$ vs. time for systems G_hPT, P_hGT, G_hGT and P_hPT.

metric for the formation of $C_6A\bar{S}_3H_{32}$ (Figs. 2 and 3) the reactivity of the sulphoaluminate made from phosphogypsum does not depend on the synthesis temperature, while in the case of pure gypsum the reactivity decreases as the synthesis temperature increases.

Because the sulphoaluminates used in the hydration runs were made over two different temperature ranges (1000–1100 °C for phosphogypsum and 1200–1350 °C for pure gypsum) the effect of the nature of gypsum employed in the synthesis at constant temperature on the hydration properties of $C_4A_3\bar{S}$ cannot be deduced from the experimental data related to the systems so far examined. In order to investigate how hydration is influenced by the type of gypsum added to $C_4A_3\bar{S}$ of given origin and synthesis temperature, the behaviour of the systems G_hPT and P_hGT has been studied and compared with that of the systems G_hGT and P_hPT (Fig. 7).

The system G_hPT hydrates more rapidly than G_hGT, due to catalytic activity of phosphogypsum impurities. The observed enhancement of $C_6A\bar{S}_3H_{32}$ formation agrees with previous findings on different systems. In fact it has been reported [13] that the impurities present in phosphogypsum accelerate $C_6A\bar{S}_3H_{32}$ formation in the early stages of Portland cement hydration. Similarly, when compared with pure gypsum, phosphogypsum appears to be a more efficacious activating agent of granulated blast-furnace slag with regard to $C_6A\bar{S}_3H_{32}$ formation [14]. As the enhancing effect has been observed in systems very different from each other, the catalytic activity is an intrinsic property of phosphogypsum impurities.

The comparison between the systems P_hPT and P_hGT does not show significant differences. Evidently the role played by the impurities, present either in the synthesized product or in the source of added $CaSO_4 \cdot 2H_2O$, is constant within their concentration limits relative to the two systems above.

The last part of this study has been limited to the systems stoichiometric for $C_6A\bar{S}_3H_{32}$ formation, but, from the results previously discussed, it can be expected that those stoichiometric for $C_4A\bar{S}H_{12}$ formation would behave similarly. On the other hand, $C_6A\bar{S}_3H_{32}$ is of major interest in the hydration products of the cements detailed in the Introduction because of its excellent expansive and fast-hardening properties.

CONCLUSIONS

Phosphogypsum, when employed as a component of the raw mix for the formation of calcium sulphoaluminate $C_4A_3\bar{S}$, not only allows the synthesis to be performed at temperatures and times considerably lower than those required in the case of pure gypsum, but also allows the hydration properties of the product to remain unaltered. Moreover the reactivity of $C_4A_3\bar{S}$ made from phosphogypsum does not depend on the synthesis temperature in the range 1000–1100 °C, while that of $C_4A_3\bar{S}$ made from pure gypsum decreases as the synthesis temperature increases from 1200 to 1350 °C.

Phosphogypsum, as a source of $CaSO_4 \cdot 2H_2O$ instead of pure gypsum in hydrating mixtures with $C_4A_3\bar{S}$ and $Ca(OH)_2$, exhibits a catalytic activity in the formation of $C_6A\bar{S}_3H_{32}$ which is an intrinsic property of its impurities.

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