

## HIGH-TEMPERATURE SYNTHESIS OF CALCIUM SULPHOALUMINATE FROM PHOSPHOGYPSUM

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### ABSTRACT

The possibility of using phosphogypsum for the production of cements based on calcium sulphoaluminate ( $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ ), which is of interest in the fields of rapid-hardening, expansive and energy-saving hydraulic binders, has been examined.

Mixtures of  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$  and phospho- or pure gypsum have been fired at temperatures between 950 and 1350°C for 30 min to 10 h.

When compared to pure gypsum, phosphogypsum greatly reduces both the temperature and time required for completion of the synthesis, owing to the fluxing and mineralizing properties of its impurities.

The results show that an interesting method of disposal of phosphogypsum can be proposed.

### INTRODUCTION

Cements based on calcium sulphoaluminate,  $\text{C}_4\text{A}_3\bar{\text{S}}$ \*, have various applications [1–3]. Depending mainly on the rate of formation of ettringite and other hydrated phases, as well as on their relative amounts, a series of binders with different performances, such as rapid-hardening [4], shrinkage-compensating and self-stressing [5–7] cements, can be obtained. Furthermore,  $\text{C}_4\text{A}_3\bar{\text{S}}$ -bearing clinkers allow a substantial energy saving to be achieved in their manufacture, inasmuch as they are obtained at burning temperatures considerably lower than those required by ordinary Portland clinkers.

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\* Common cement chemistry nomenclature is used herein: C = CaO; S =  $\text{SiO}_2$ ; A =  $\text{Al}_2\text{O}_3$ ; F =  $\text{Fe}_2\text{O}_3$ ;  $\bar{\text{S}}$  =  $\text{SO}_3$ .

Ragozina first described in 1957 a ternary compound formed at 1200°C in the system CaO–Al<sub>2</sub>O<sub>3</sub>–SO<sub>3</sub> [8]. Later Klein and Troxell [5] prepared an expansive cement by firing a mixture of lime, gypsum and bauxite at 1350°C; X-ray diffraction showed that an unknown phase had been formed. Fukuda [9] first reported in 1961 the composition of the ternary product in the system CaO–Al<sub>2</sub>O<sub>3</sub>–SO<sub>3</sub> to be C<sub>4</sub>A<sub>3</sub>S̄.

In an important study [10] Halstead and Moore analysed the behaviour of mixtures of CaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub> at 1350°C for times ranging from 4 to 12 h. Other authors [11–13] used mixtures of CaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> or Al(OH)<sub>3</sub> and CaSO<sub>4</sub>·2H<sub>2</sub>O to make C<sub>4</sub>A<sub>3</sub>S̄ at temperatures of 1200 and 1350°C with reaction times ranging between 5.5 and 80 h.

Sudoh et al. [4] prepared clinkers containing mainly C<sub>4</sub>A<sub>3</sub>S̄ and C<sub>2</sub>S by means of mixtures of limestone, clay and a by-product gypsum. The reaction temperature and time were 1320–1380°C and 80 min, respectively. A mixture containing kaolin, CaCO<sub>3</sub> and CaSO<sub>4</sub>·2H<sub>2</sub>O was used by Mikhail et al. [14] to make a clinker containing C<sub>4</sub>A<sub>3</sub>S̄, 2(C<sub>2</sub>S)·C̄S, C<sub>4</sub>AF, C̄S and free lime by firing at 1150°C for 2 h.

The formation of C<sub>4</sub>A<sub>3</sub>S̄ and C<sub>2</sub>S has also been studied by Ikeda [15]. Mixtures of granulated blast-furnace slag, CaSO<sub>4</sub>·2H<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub> in different proportions were used to give Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratios ranging between 0.4 and 3.0. At 1200°C, clinkers were prepared by means of two 30-min burning cycles with intermediate grinding, while at 1300°C only a single 30-min burning was used. It is reported that reaction times are longer as the amount of charge increases, but no quantitative data are given.

In this paper the behaviour of mixtures containing CaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub>·2H<sub>2</sub>O in stoichiometric ratio to form C<sub>4</sub>A<sub>3</sub>S̄ is systematically studied in order to investigate the influence of temperature and time of reaction on the conversion of the reactants to C<sub>4</sub>A<sub>3</sub>S̄.

Two different sources of CaSO<sub>4</sub>·2H<sub>2</sub>O have been used: analytical grade gypsum and phosphogypsum. The latter has shown to have mineralizing properties when added to the raw mix for Portland cement manufacture [16], inasmuch as it allows the clinker to be made at a substantially reduced temperature. The effect of the phosphogypsum impurities on the synthesis of C<sub>4</sub>A<sub>3</sub>S̄ is then investigated in order to assess the possibility of disposing of this by-product in the field of C<sub>4</sub>A<sub>3</sub>S̄-based cements.

## EXPERIMENTAL

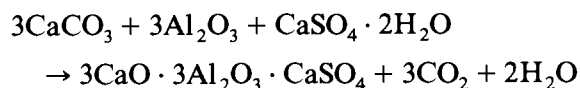
The phosphogypsum used in the experiments has been supplied by Montedison S.p.A. (Italy). Its chemical composition is shown in Table 1. Other reagents were analytical grade CaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub>·2H<sub>2</sub>O. Pure gypsum was finer than phosphogypsum, since the residues on the 325 mesh sieve were 0 and 32%, respectively.

TABLE 1

Chemical composition of the phosphogypsum used (wt.-%)

Loss on ignition	22.9
CaO	34.3
SO <sub>3</sub>	40.0
P <sub>2</sub> O <sub>5</sub>	1.8
SiO <sub>2</sub>	1.4
F	1.2
Na	0.8

The synthesis of  $C_4A_3\bar{S}$  was carried out by firing mixtures (5 and 100 g in weight) of phospho- or pure gypsum,  $Al_2O_3$  and  $CaCO_3$  in a muffle furnace in stoichiometric ratio for the reaction:



Firing temperatures ranged from 950 to 1350°C and reaction times from 30 min to 10 h. In the case of the mixtures containing pure gypsum, the synthesis was performed by means of burning cycles with intermediate grindings to pass the 325 mesh sieve.

The fractional conversion has been found by determining the unconverted lime concentration according to the Franke method [17]. X-ray diffraction analysis has been employed in order to identify the phases present in the products obtained under different synthesis conditions.

## RESULTS AND DISCUSSION

Figure 1 shows the amount of unconverted lime, in terms of percentage of the initial quantity in the raw mix, as a function of time, for the mixtures containing phosphogypsum. The data refer to 5-g samples, but no significant difference was observed when 100-g samples were used.

The high-temperature sensitivity of the reaction rate is clear. The synthesis goes to completion within times that decrease from 90 to 30 min when the temperature increases from 1000 to 1100°C.

Figure 2 and 3 show the conversion data for 5- and 100-g samples, respectively, for mixtures containing pure gypsum. It is evident that when pure gypsum is used in the raw mix the synthesis is performed at temperatures and times considerably higher than those required in the case of phosphogypsum. The acceleration of the synthesis due to the presence of phosphogypsum is more marked than that which can be deduced by a direct comparison between the results of Fig. 1 on one side and those of Figs. 2 and 3 on the other, inasmuch as the following considerations must be taken

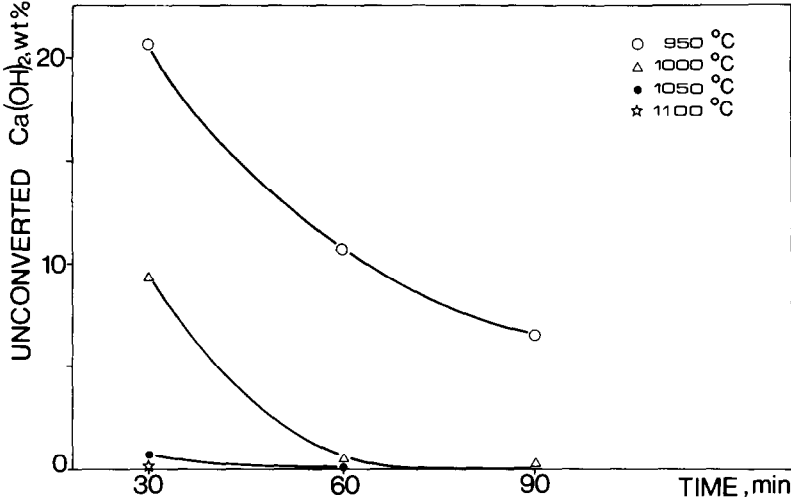


Fig. 1. Unconverted  $\text{Ca(OH)}_2$  vs. time for systems containing phosphogypsum.

into account: (a) pure gypsum is finer than phosphogypsum and (b) the samples containing pure gypsum were ground before the subsequent firing.

The experimental data show that the weight of charges, which has no effect on the overall conversion in the case of phosphogypsum, plays an important role when pure gypsum is employed, in agreement with previous findings [15]. A comparison between the results of Figs. 2 and 3 shows that the weight effect is large at 1200 and 1250 °C, greatly decreases at 1300 °C and vanishes at 1350 °C.

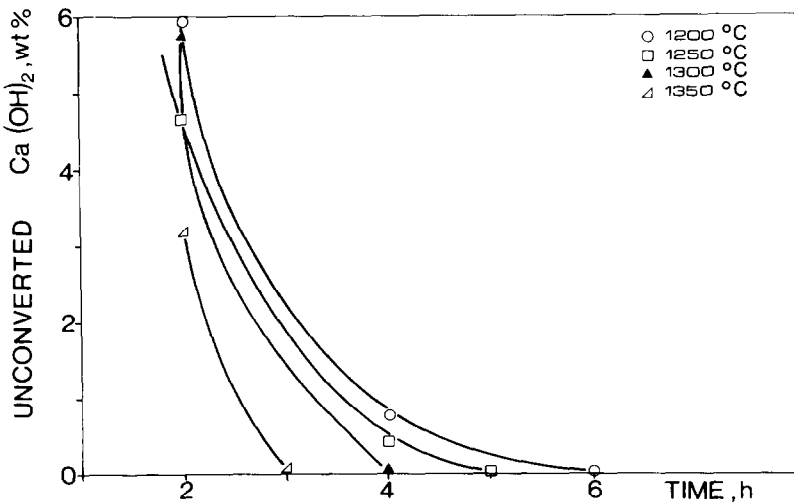


Fig. 2. Unconverted  $\text{Ca(OH)}_2$  vs. time for systems containing pure gypsum (5-g samples).

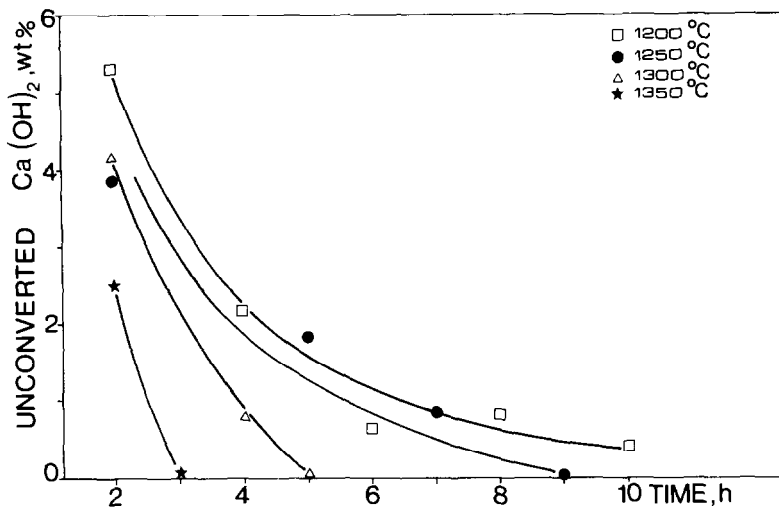


Fig. 3. Unconverted  $\text{Ca}(\text{OH})_2$  vs. time for systems containing pure gypsum (100-g samples).

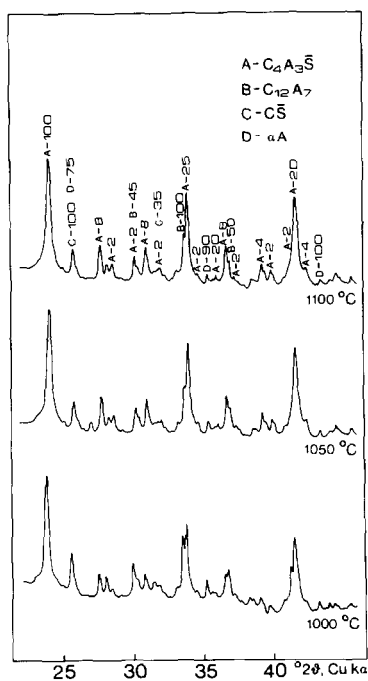


Fig. 4. X-ray diffraction patterns of burned samples containing phosphogypsum (figures after the letters indicate percentages of the maximum peak intensity).

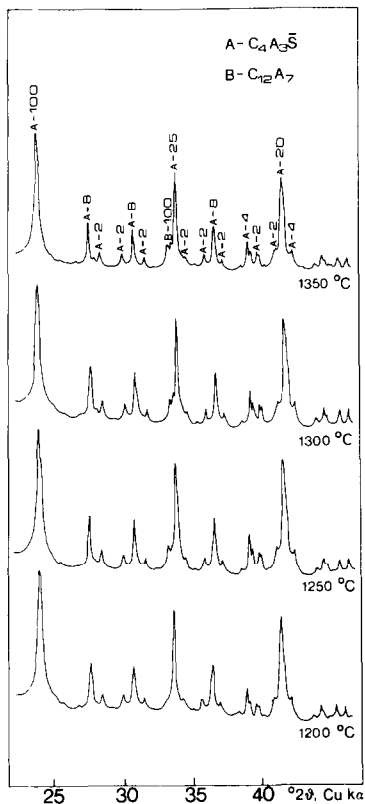


Fig. 5. X-ray diffraction patterns of burned samples containing pure gypsum (figures after the letters indicate percentages of the maximum peak intensity).

The absence of the weight effect in the case of phosphogypsum and its reduction with temperature in the case of pure gypsum are consistent with the hypothesis of the formation of a liquid phase which considerably increases the thermal diffusivity of the reacting mixtures. Then the impurities of phosphogypsum have a strong fluxing action in the system under investigation. Moreover, the mineralizing properties of phosphogypsum, already observed by Mehta and Brady [16] in the raw mix for the manufacture of Portland cement, extend to the field of  $C_4A_3\bar{S}$ -based cements.

Figures 4 and 5 show the X-ray diffraction patterns of the samples with total CaO conversion in the cases of phospho- and pure gypsum, respectively.  $C_4A_3\bar{S}$  is the prevailing phase under any of the conditions tested, as proved by the presence of weak reflections of this product.  $C_{12}A_7$  also forms, but in a larger amount in the case of phosphogypsum, as indicated by the stronger intensity of its peaks and by the presence of reflections due to unconverted  $Al_2O_3$  and  $CaSO_4$ . It should be pointed out that the amount of  $C_{12}A_7$  formed in the mixtures containing phosphogypsum decreases as the synthesis temperature increases.

The characteristics of the products, as determined by X-ray diffraction, are independent of the weight of charge.

## CONCLUSIONS

Studying the high-temperature synthesis of calcium sulphoaluminate,  $C_4A_3\bar{S}$ , in systems containing CaO,  $Al_2O_3$  and phospho- or pure gypsum has shown that the reaction rate is very temperature-sensitive, especially when phosphogypsum is used. Moreover, this by-product gypsum allows considerable reductions in the temperature and time required for the synthesis of  $C_4A_3\bar{S}$ , owing to its fluxing and mineralizing properties.

In the range of conditions tested, the weight of raw mix charge has no effect on the overall conversion when phosphogypsum is used, while it plays a significant role in the case of pure gypsum.

Only  $C_{12}A_7$  has been detected as minor reaction product; its yield is greater in the case of phosphogypsum.

## ACKNOWLEDGEMENT

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