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HYDRATION OF GRANULATED BLAST-FURNACE SLAG IN THE PRESENCE OF PHOSPHOGYPSUM

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ABSTRACT

The behaviour of the system granulated blast-furnace slag–phosphogypsum–water has been studied in the presence of a small amount of hydrated lime and in the range of phosphogypsum/slag composition ratio up to 20/100.

When compared to pure gypsum, phosphogypsum appears to be a more efficacious activating agent with regard to the formation of the hydrated phases, specifically calcium silicate hydrate and calcium trisulphoaluminate hydrate.

The results are worthy of consideration as far as the disposal of phosphogypsum is concerned.

INTRODUCTION

One of the most serious problems that modern industry possesses is the disposal of solid by-products. Therefore, attention is being increasingly paid to the search for solutions which optimally meet requirements arising from the exploitation of natural resources, energy saving and environmental safeguard.

Blast-furnace slag and phosphogypsum are by-produced in large amounts in the production of pig iron and in the wet process for the manufacture of phosphoric acid. They have great potential in the light of the above considerations.

Possible applications for the disposal of these by-products are linked to the fact that blast-furnace slag is a source of CaO and SiO_2, while phosphogypsum, a calcium sulphate-rich residue, can be used as a substitute for natural gypsum [1–6].

It is well known that granulated blast-furnace slag exhibits hydraulic properties when activated by strong alkaline media, and that calcium sulphate enhances these properties.

The aim of this work is to investigate the behaviour of the system slag–phosphogypsum–water in the presence of a small amount of hydrated lime in view of the possible disposal of the above by-products.

For the sake of comparison the investigation has been extended to the system slag–pure gypsum–water, activated as before.

The chief experimental technique was differential scanning calorimetry (DSC).

EXPERIMENTAL

The phosphogypsum and granulated blast-furnace slag employed in the experimental runs were supplied by Montedison S.p.A. and Cementir S.p.A., respectively. Their chemical compositions are given in Table 1. Other reagents were analytical grade $CaSO_4 \cdot 2\ H_2O$ and $Ca(OH)_2$.

Blast-furnace slag was ground in a cross-beater mill; the resulting particle size distribution is given in Table 2. Phospho- and pure gypsum were much finer, as they passed the 325-mesh (45-μm) sieve in amounts of 68 and 100%, respectively.

Mixtures of phospho- or pure gypsum, slag, hydrated lime and CO_2-free water were cured in polyethylene bags at a constant temperature of 25°C. The compositions of the mixtures examined are given in Table 3. The weight ratios of compositions SG5, SG10 and SG20 are such as to ensure the same slag/calcium sulphate ratios as for compositions SP5, SP10 and SP20, respectively. The water/solid ratio was 0.5.

TABLE 1

Phosphogypsum and blast-furnace slag compositions (wt%)

	Phosphogypsum	Blast-furnace slag
Loss on ignition	22.9	3.0
CaO	34.3	42.7
SO_3	40.0	—
P_2O_5	1.8	—
SiO_2	1.4	34.6
Fe_2O_3	—	1.6
Mn_3O_4	—	0.6
Al_2O_3	—	11.8
MgO	—	4.3
S	—	1.0

TABLE 2

Blast-furnace slag size distribution

Size (μm)	wt%
> 250	0.3
125–250	33.0
63–125	29.8
45–63	27.1
20–45	8.5
< 20	1.3

TABLE 3

Compositions examined (wt. ratios)

	Slag	Phosphogypsum	Pure gypsum	$Ca(OH)_2$
S	100	—	—	0.5
SP5	100	5	—	0.5
SP10	100	10	—	0.5
SP20	100	20	—	0.5
SG5	100	—	4.3	0.5
SG10	100	—	8.6	0.5
SG20	100	—	17.2	0.5

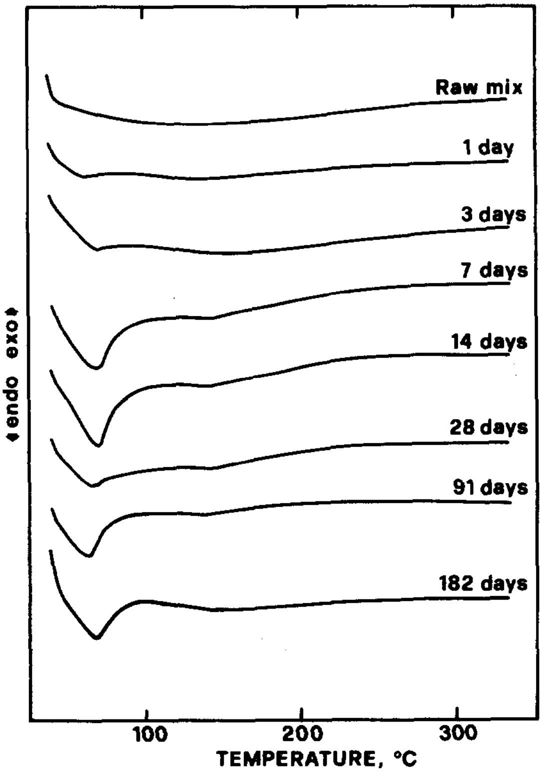

Fig. 1. Thermograms of samples of composition S.

At the end of fixed ageing times (i.e., 1, 3, 7, 14, 28, 91 and 182 days) samples were taken and the reaction stopped by grinding in acetone followed by washing with ether. The samples were then stored in a desiccator in the presence of P_2O_5.

Non-evaporable, chemically-combined water was determined by ignition at 850°C; unreacted slag and free gypsum were determined following the extraction procedures reported by Kondo and Ohsawa [7].

Thermal analysis was performed with a Perkin-Elmer DSC-2 calorimeter; complementary data were obtained by X-ray analysis with a Philips diffractometer composed of a PW 1730/10 generator, a PW 1050/70 goniometer, a PW 1965/30 proportional counter and a PW 1390 channel control. Cu K_α radiation was used.

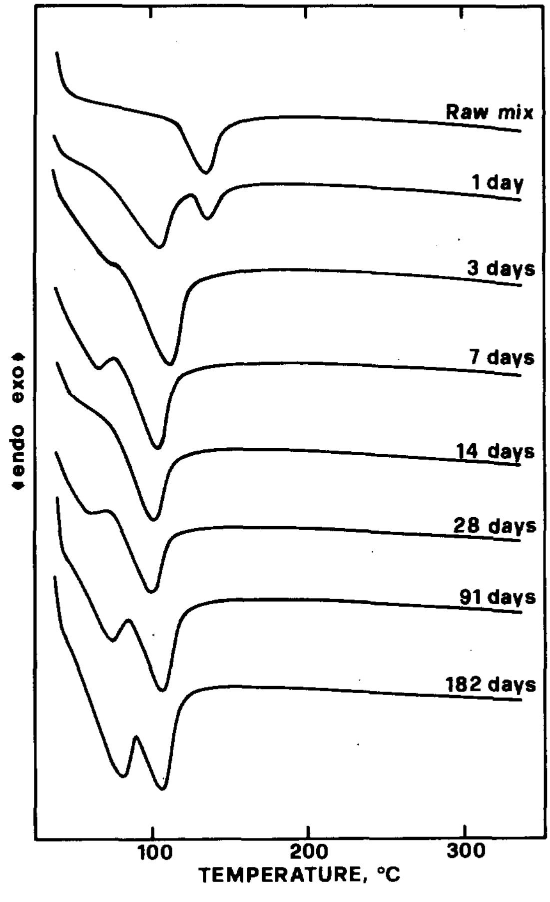

Fig. 2. Thermograms of samples of composition SP5.

RESULTS AND DISCUSSION

Qualitative analysis

Figures 1 to 7 show the results of thermal analysis for all the systems tested.

The identification of unconverted gypsum and neo-formed hydration products has been made on the basis of literature data [8]. In particular the thermograms show endotherms at 72 ± 12, 108 ± 10 and 138 ± 10°C due to the presence of calcium silicate hydrate (CSH), calcium trisulphoaluminate hydrate, $3\ CaO \cdot Al_2O_3 \cdot 3\ CaSO_4 \cdot 32\ H_2O$(TSH) and gypsum, respectively.

The thermograms of samples of composition S are shown in Fig. 1. A

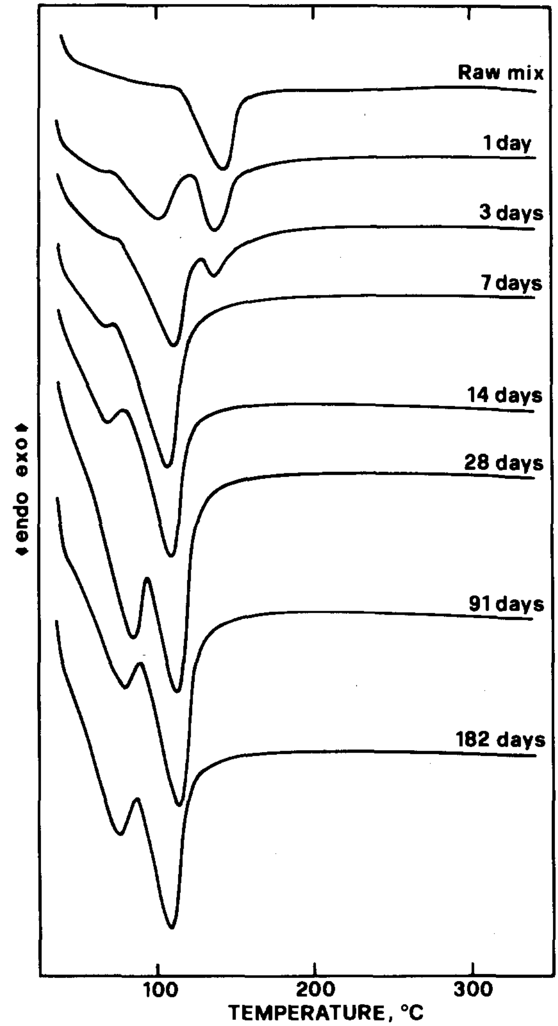

Fig. 3. Thermograms of samples of composition SP10.

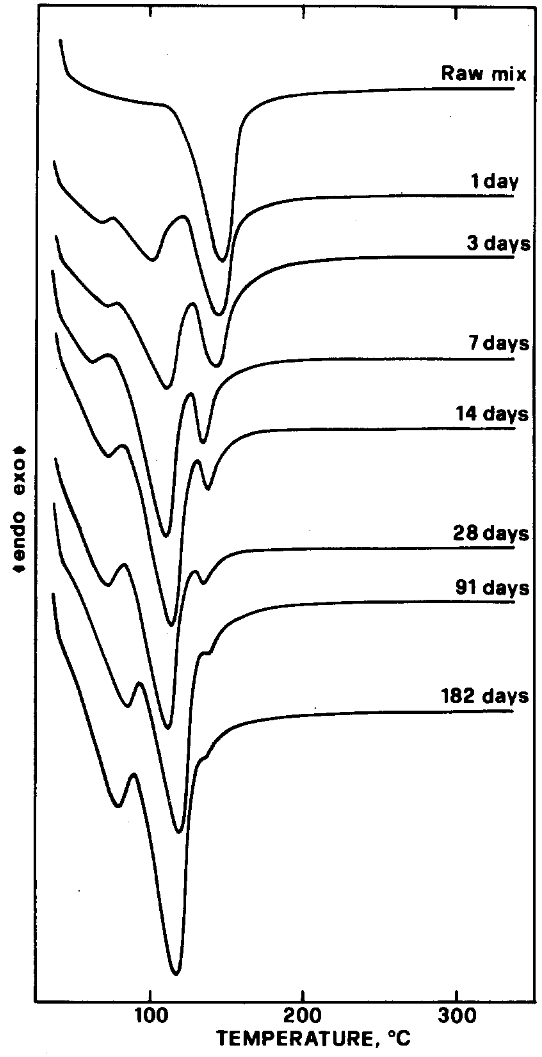

Fig. 4. Thermograms of samples of composition SP20.

single endothermic effect related to the presence of neo-formed CSH is observed. It appears as early as after 1 day and its intensity increases with the ageing time.

Figure 2 shows the thermograms of samples of composition SP5. The phosphogypsum in the raw mixture is rapidly converted to TSH. The reaction seems to go to completeness in as much as phosphogypsum is no longer detected after 3 days and starting from this time the intensity of the TSH peak does not change appreciably. The low-temperature endotherm is related to the presence of CSH, and the extent to which this phase is produced is greater than for composition S, due to the well-known stimulating effect of gypsum on slag hydration.

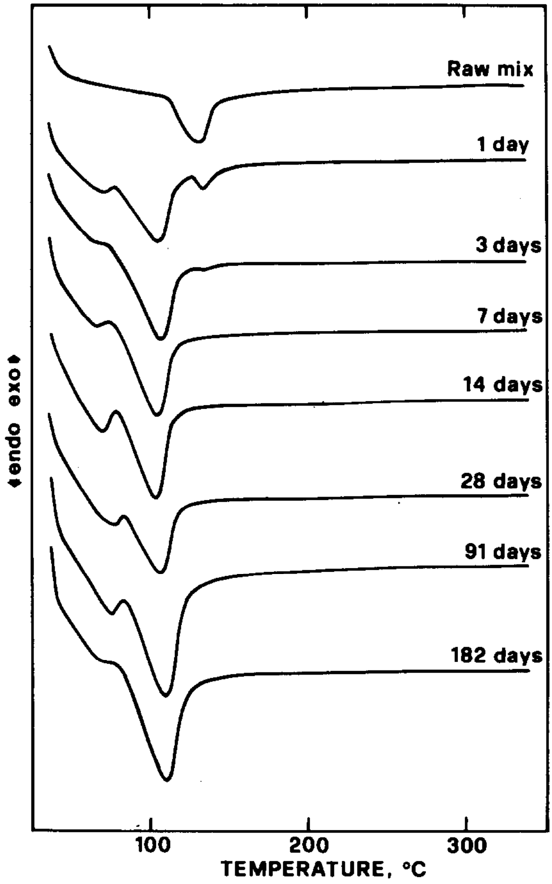

Fig. 5. Thermograms of samples of composition SG5.

A similar behaviour is observed when the ratio phosphogypsum/slag is increased, as shown by the thermograms of Figs. 3 and 4, of compositions SP10 and SP20, respectively. Differences related to an increase of the amount of phosphogypsum initially present are clearly evident at longer ageing times, where the amounts of both CSH and TSH formed increase. Furthermore, composition SP20 shows the presence of residual phosphogypsum up to 182 days.

The thermograms relative to systems of compositions SG5, SG10 and SG20 are shown in Figs. 5, 6 and 7, respectively. A comparison between the systems containing phospho- and pure gypsum, at constant gypsum/slag ratio, leads to the following conclusions:

(a) the nature of neo-formed phases is unaffected by the type of gypsum;

(b) pure gypsum is less reactive than phosphogypsum, despite its superior fineness;

(c) the amount of CSH formed at longer hydration times is greater when

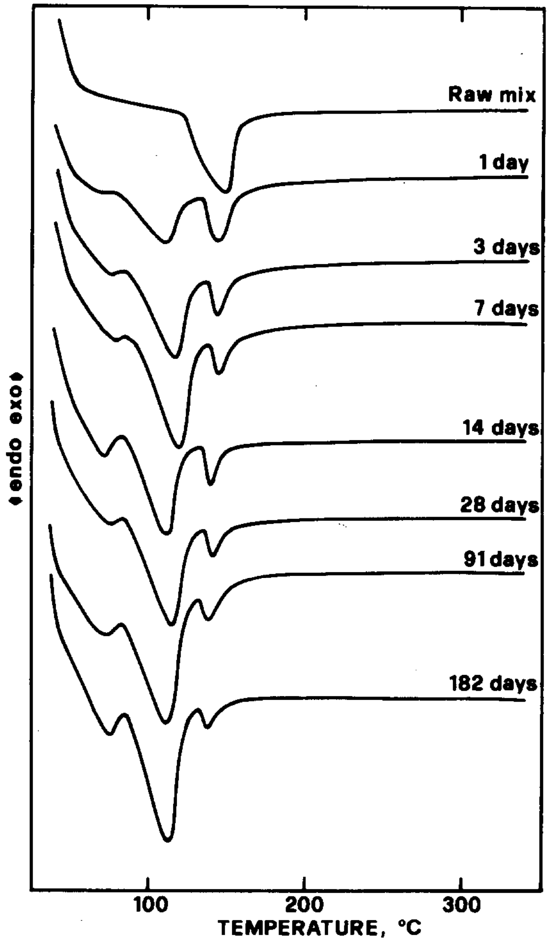

Fig. 6. Thermograms of samples of composition SG10.

phosphogypsum is used;

(d) the above differences increase as the ratio gypsum/slag increases.

Quantitative analysis

Figure 8 shows the amount of non-evaporable water as a function of ageing time. The hydration kinetics are clearly favoured by an increase in concentration of both phospho- and pure gypsum, the former being most efficient. A similar conclusion is drawn when the amount of converted slag is taken into account, as shown in Fig. 9.

The greater reactivity of the systems containing phosphogypsum, with regard to both TSH and CSH formation, is confirmed by the results shown in Figs. 10 and 11, where the amounts of reacted gypsum and slag converted to CSH are, respectively, reported vs. ageing time.

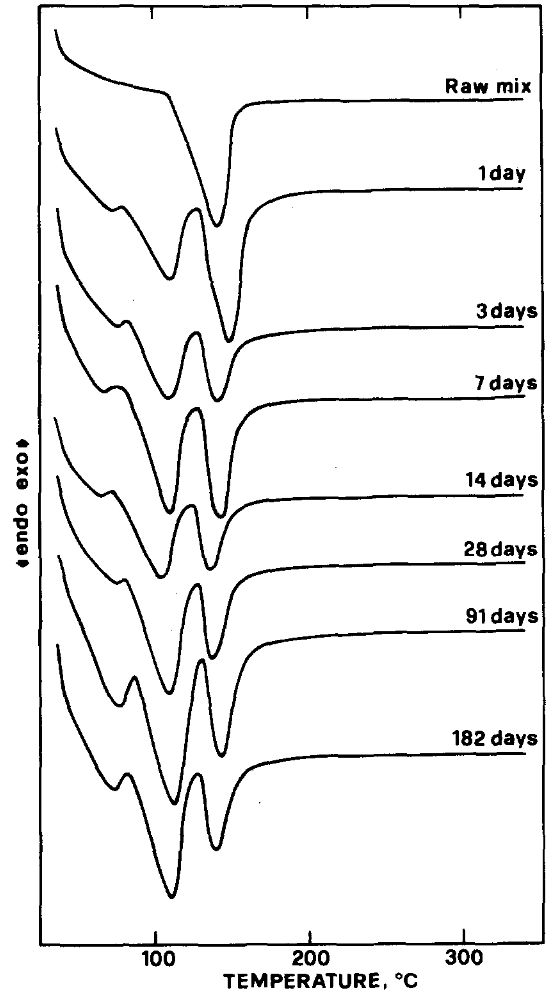

Fig. 7. Thermograms of samples of composition SG20.

It is evident from Fig. 10 that the phosphogypsum impurities not only have the effect of increasing the rate of TSH formation, but also of influencing the reaction mechanism. In fact, the apparent order of reaction with regard to gypsum is 1 for systems containing phosphogypsum, and < 1 for those containing pure gypsum.

It is to be noted that Bensted [9–11] found that the impurities present in phosphogypsum, as well as in other chemical by-product gypsums, enhance the formation of TSH in the early stages of Portland-cement hydration. The fact that in our system the source of calcium and aluminium oxides available for TSH formation is blast-furnace slag instead of tricalcium aluminate, as in Portland cement, proves that the enhancing effect is an intrinsic property of the impurities, mainly PO_4^{3-} ions in the case under consideration.

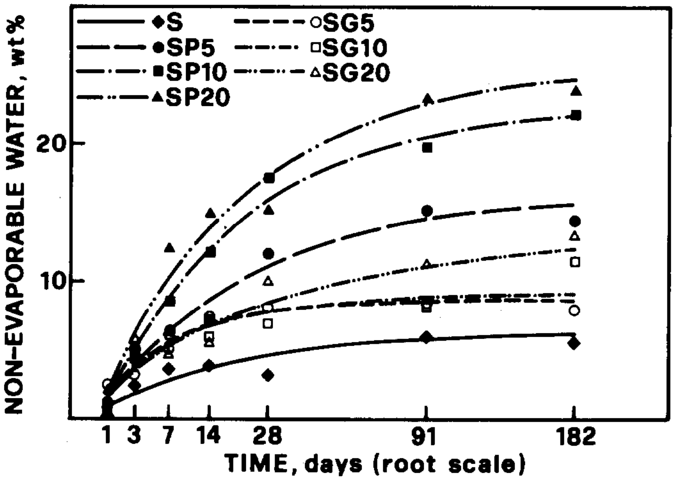

Fig. 8. Effect of composition on the amount of water chemically combined.

It is well known that in cements based on slag–calcium sulphate mixtures the development of mechanical strength is primarily due to TSH and CSH formation at early and later ages, respectively. Therefore, the more favourable kinetics of formation of both the hydrated phases referred to above, observed when phosphogypsum is employed, makes the use of this by-product attractive from an applicative point of view. This consideration may find support from the results reported by Metha and Brady [5] showing a favourable effect of phosphogypsum, when compared to pure gypsum, on the development of Portland cement mechanical strength.

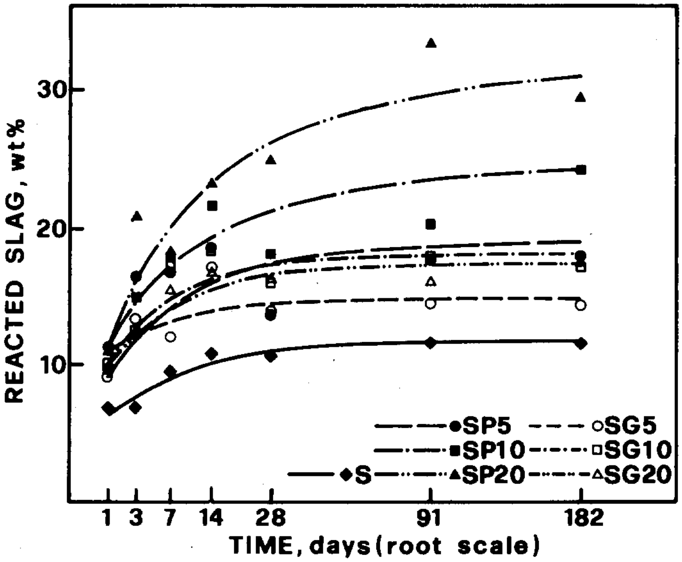

Fig. 9. Effect of composition on the overall rate of conversion of slag.

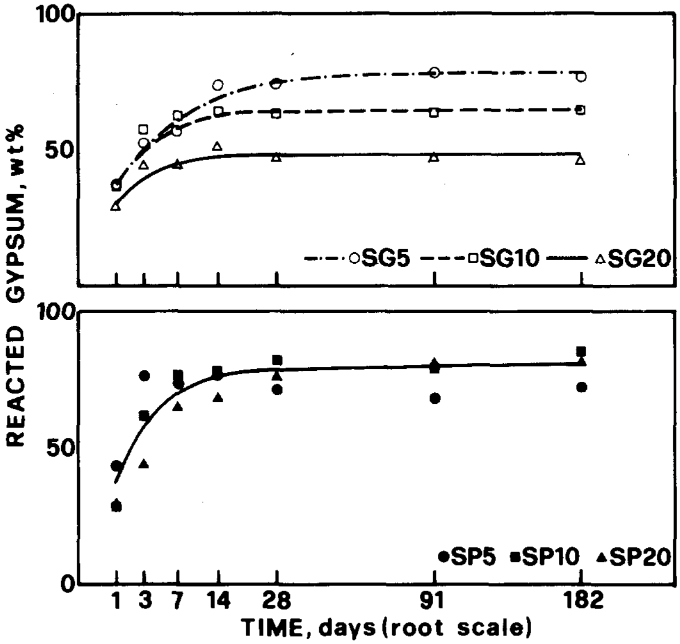

Fig. 10. Conversion of $CaSO_4 \cdot 2\,H_2O$ vs. time in mixtures containing phospho- and pure gypsum.

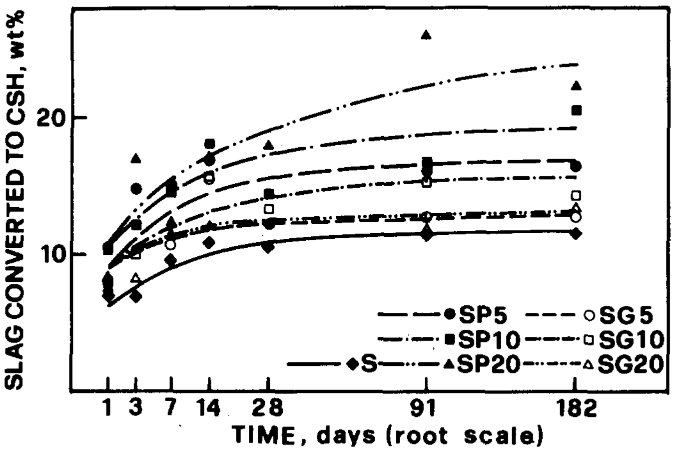

Fig. 11. Effect of composition on the rate of conversion of slag to CSH.

CONCLUSIONS

It has been found that phosphogypsum can be advantageously employed as an activator of blast-furnace slag hydration. When compared to pure gypsum, the overall hydration kinetics is enhanced, and both calcium silicate hydrate and calcium trisulphoaluminate hydrate are formed faster. Therefore, the binding action, linked to the formation of the above hydration products, can be expected to develop more rapidly.

Phosphogypsum impurities are also responsible for the observed difference in the hydration mechanism that, as the initial calcium sulphate/slag ratio increases, the fractional conversion of pure gypsum decreases, while that of phosphogypsum remains constant. This feature is particularly attractive in view of possible applications for disposing of an industrial by-product such as phosphogypsum.

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