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HYDRATION OF MIXTURES CONTAINING FLY-ASH, LIME AND PHOSPHOGYPSUM

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ABSTRACT

The behaviour of the system fly-ash–lime–phosphogypsum–water has been studied at 25 and 40°C and in the range of composition up to 30 parts of phosphogypsum per 100 parts of a 60/40 mixture of fly-ash and lime.

When compared to pure gypsum, phosphogypsum appears to be equally or more effective.

Varying the ratio gypsum/fly-ash varies the ratio with which the two major hydration products, calcium silicate and trisulphoaluminate hydrates, are formed. This is important as far as durability and mechanical strength development are concerned.

INTRODUCTION

At the present time one of the most serious environmental problems is the disposal of solid wastes, both of industrial and municipal origin.

Fly-ash is by-produced in large amounts in coal-fired electrical-energy generation plants. It is an artificial pozzolana and is successfully employed in the field of blended cements and concrete where its ability to harden by reacting with lime is exploited [1].

Hardening can also take place when calcium sulphoaluminate hydrates are formed on contact of sulphate-containing materials with a proper source of lime and alumina in the presence of water [2].

Phosphogypsum is one of the calcium sulphate-rich residues, so-called "chemical gypsums", which are produced in large amounts in some industrial processes. Phosphogypsum comes from the wet process for the manufacture of phosphoric acid and has great potential to be used as a substitute for natural gypsum [3–9].

In the light of these considerations, an investigation has been undertaken on the behaviour of the system fly-ash–lime–phosphogypsum–water in view

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of a possible application for the disposal of the above by-products. In the system being considered, fly-ash acts as a source of reactive silica and alumina, and then hardening is expected to take place due to the formation of the major phases, calcium silicate and sulphoaluminate hydrates. In particular the calcium silicate hydrates produced by the lime–pozzolana reaction are responsible for durability and, at later stages, mechanical strength, while calcium sulphoaluminate hydrates give faster hardening. Mechanical strength development can be expected to develop rapidly, depending on the calcium sulphate/fly-ash ratio.

For the sake of comparison the investigation has been extended to the system fly-ash–lime–pure gypsum–water.

The chief experimental technique was differential scanning calorimetry.

EXPERIMENTAL

The phosphogypsum and fly-ash employed in the experimental work were supplied by Montedison S.p.A. and Saarbergwerke A.G., respectively. Their chemical compositions are given in Table 1. Other reagents were analytical grade $CaSO_4 \cdot 2H_2O$ and $Ca(OH)_2$.

Fly-ash was analysed for particle size distribution, by both sieve analysis and Coulter Counter analysis (fraction < 45 μm). The results are reported in Table 2. The other reagents were found to be finer, as none of them left residues on the 45-μm sieve.

Mixtures of phospho- or pure gypsum, fly-ash, hydrated lime and CO_2-free water were cured in polyethylene bags at constant temperatures of 25 and 40°C. The compositions of the mixtures examined are reported in Table 3. The weight ratios of compositions ALG10, ALG20 and ALG30 are such to ensure the same ratios between calcium sulphate and the mixture of fly-ash and hydrated lime as for compositions ALP10, ALP20 and ALP30, respectively. The water/solid ratio was 0.6.

TABLE 1

Fly-ash and phosphogypsum compositions (wt%)

Component	Fly-ash	Phosphogypsum
Loss on ignition	2.5	22.9
CaO	6.2	34.3
SO_3	5.0	40.0
P_2O_5	–	1.8
SiO_2	44.4	1.4
Fe_2O_3	13.8	–
Al_2O_3	25.1	–

TABLE 2

Fly-ash size distribution

Size (μm)	wt%	Size (μm)	wt%
By sieve analysis			
> 250	0.2	63–90	5.6
180–250	0.4	45–63	8.2
125–180	1.3	< 45	81.7
90–125	2.6		
Size (μm)	**vol%**	**Size (μm)**	**vol%**
By Coulter Counter analysis			
> 40.84	4.1	5.11–6.43	8.2
32.42–40.84	6.2	4.05–5.11	6.6
25.73–32.42	5.7	3.22–4.05	4.4
20.42–25.73	9.3	2.55–3.22	2.7
16.21–20.42	8.8	2.03–2.55	1.3
12.87–16.21	10.1	1.61–2.03	0.6
10.21–12.87	11.4	1.28–1.61	0.3
8.10–10.21	10.4	<1.28	0.3
6.43–8.10	9.6		

At the end of fixed ageing times (i.e., 1, 3, 7, 14, 28, 56, 91 and 182 days at 25°C and 1, 3, 7, 14, 28 and 56 days at 40°C) 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 water was determined by ignition at 850°C; unreacted lime was determined by extraction following the Franke method [10].

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 PW1730/10 generator, a PW1050/70 goniometer, a PW1965/30 proportional counter and a PW1390 channel control. Cu $K\alpha$ radiation was used.

TABLE 3

Compositions examined (wt. ratios)

Mixture	Fly-ash	$Ca(OH)_2$	Phosphogypsum	Pure gypsum
AL	60	40	–	–
ALP10	60	40	10	–
ALP20	60	40	20	–
ALP30	60	40	30	–
ALG10	60	40	–	8.6
ALG20	60	40	–	17.2
ALG30	60	40	–	25.8

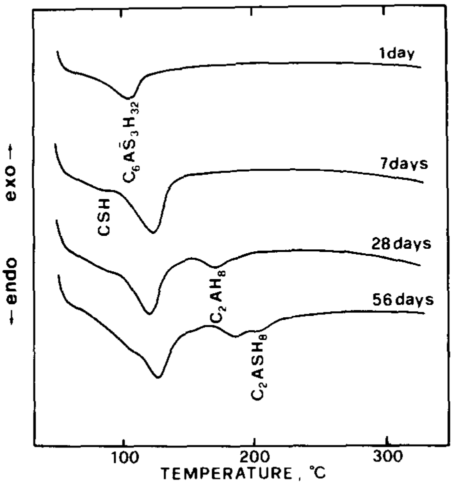

Fig. 1. Thermograms of samples of composition AL at 25°C and different ageing times.

RESULTS AND DISCUSSION

Qualitative analysis

The identification of unconverted gypsum and neo-formed hydration products has been made on the basis of literature data [11–13].

Figure 1 shows the thermograms of some samples of composition AL cured at 25°C. The endothermic effect observed at 1 day ageing is related to calcium trisulphoaluminate hydrate, $C_6A\bar{S}_3H_{32}$ * whose formation is due to the presence of sulphates in the fly-ash. More endotherms are observed as the ageing time increases, owing to the formation of other hydration products. At 7 days calcium silicate hydrate, CSH, appears and at 28 days a new endotherm reveals the presence of dicalcium aluminate hydrate, C_2AH_8. Besides these phases, gehlenite hydrate, C_2ASH_8, is detected after 56 days, and, starting from that time, no difference in the qualitative composition of the samples is observed up to 182 days.

The examination of the thermograms relative to the samples cured at 40°C from 1 to 56 days does not show significant differences as far as the two major phases ($C_6A\bar{S}_3H_{32}$ and CSH) are concerned; the only difference is that one of the two minor phases, C_2ASH_8, does not appear.

As regards the systems containing phospho- or pure gypsum, both at 25 and 40°C, the following considerations can be made: (a) adding calcium sulphate considerably increases the amount of $C_6A\bar{S}_3H_{32}$ produced; (b)

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* Common cement chemistry nomenclature is used: C = CaO; S = SiO_2; A = Al_2O_3; $\bar{S}$ = SO_3; H = H_2O.

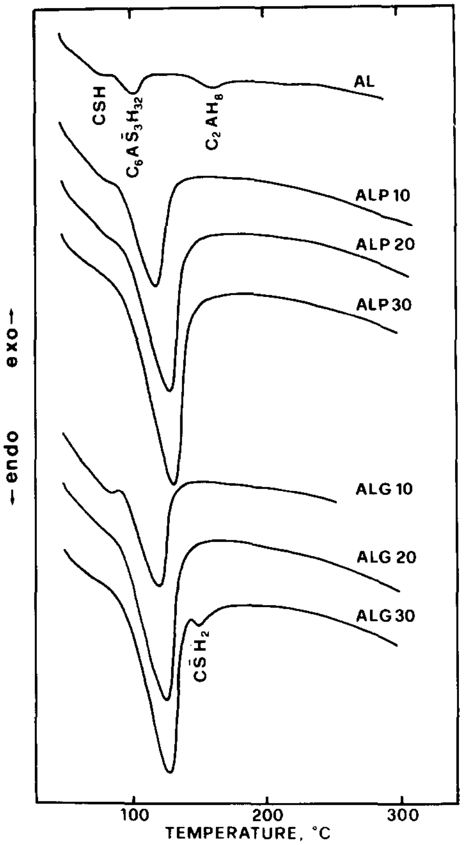

Fig. 2. Thermograms of samples aged 56 days at 40°C.

CSH also forms, even if its detectability is made more difficult by the closeness of the much larger effect related to $C_6A\bar{S}_3H_{32}$; (c) the minor hydration products, observed for composition AL, do not form. This is seen in Fig. 2, where the thermograms of the samples aged 56 days at 40°C are shown for all the compositions tested.

Other than giving information about the nature of the neo-formed phases, thermal analysis also allows the hydration kinetics to be followed by monitoring the decrease in amplitude of the calcium sulphate endotherm. Table 4 shows the ageing times at which calcium sulphate dihydrate is no

TABLE 4

Times of complete gypsum consumption (days)

Temp. (°C)	ALP10	ALP20	ALP30	ALG10	ALG20	ALG30
25	28	56	91	28	56	182
40	14	28	56	14	28	> 56

longer detected by thermal analysis for all the systems with added gypsum. It is clearly seen that the kinetics of calcium sulphate consumption are favourably influenced by temperature but not by the nature of gypsum added, except for the highest level of addition. In this case phosphogypsum proves to be more reactive than pure gypsum (see Table 4 and Fig. 2).

Quantitative analysis

Figures 3 and 4 show the amount of non-evaporable water, chemically combined in the hydration products, as a function of ageing time for temperatures of 25 and 40°C, respectively. The data have been calculated taking into account the percentage of water contained in each cured sample and that of the corresponding raw mixture, and are compared with the initial sample weight.

At 25°C the favourable influence of added gypsum, both phospho- and pure, becomes evident after 14 days; furthermore, compositions ALP20 and ALG20 give the highest hydration degrees at longer ageing times. Figure 4 shows that at 40°C the hydration kinetics are accelerated so that at 56 days similar hydration degrees are reached to those which require 182 days at the lower temperature. The favourable influence of added gypsum, both phospho- and pure, is also observed at 40°C, but starting from the shorter ageing time of 7 days. The extent of this effect decreases as the amount of added gypsum increases.

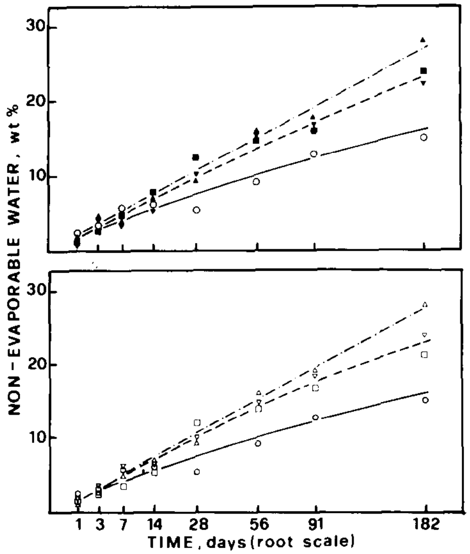

Fig. 3. Effect of composition on the amount of water chemically combined at 25°C. (○——○) AL, (□- - -□) ALP10, (△-·-·-△) ALP20, (▽- - -▽) ALP30, (■- - -■) ALG10, (▲-·-·-▲) ALG20, (▼- - -▼) ALG30.

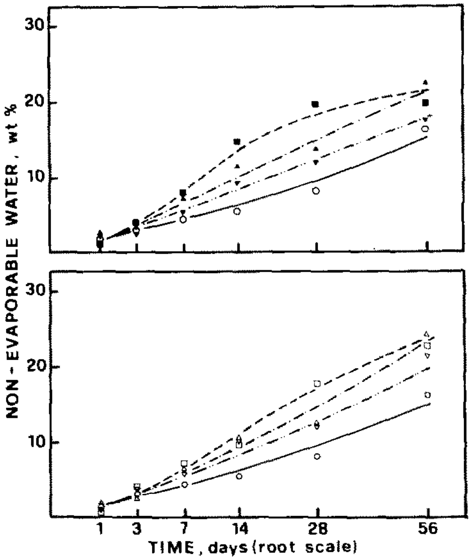

Fig. 4. Effect of composition on the amount of water chemically combined at 40°C. (○——○) AL, (□– – –□) ALP10, (△–·–·–△) ALP20, (▽–· ·–▽) ALP30, (■– – –■) ALG10, (▲–·–·–▲) ALG20, (▼–· ·–▼) ALG30.

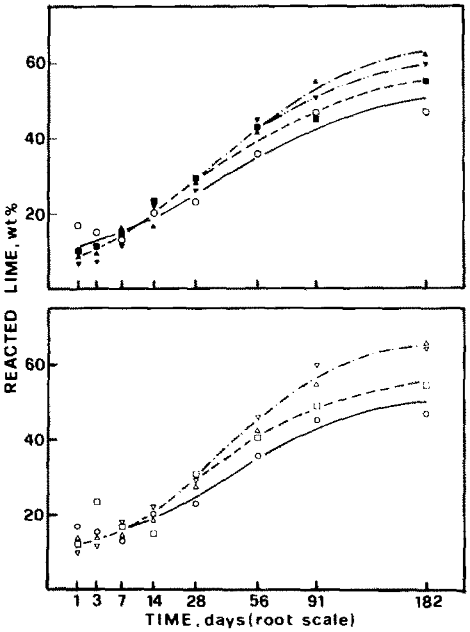

Fig. 5. Conversion of $Ca(OH)_2$ vs. time in the mixture examined at 25°C. (○——○) AL, (□– – –□) ALP10, (△–·–·–△) ALP20, (▽–·–·–▽) ALP30, (■– – –■) ALG10, (▲–·–·–▲) ALG20, (▼–· ·–▼) ALG30.

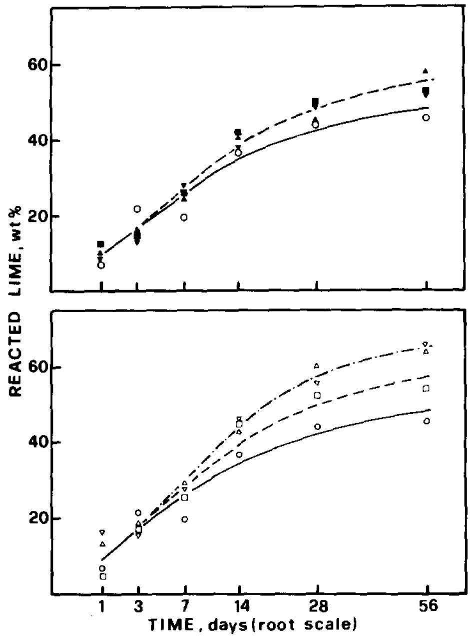

Fig. 6. Conversion of $Ca(OH)_2$ vs. time in the mixtures examined at 40°C. (○———○) AL, (□– – –□) ALP10, (△–·–·–△) ALP20, (▽–·–·–▽) ALP30, (■– – –■) ALG10, (▲– – –▲) ALG20, (▼– – –▼) ALG30.

Figures 5 and 6 show the amount of reacted lime as a function of ageing time at 25 and 40°C, respectively. As for the chemically combined water, the following considerations can be made: (a) adding phospho- or pure gypsum increases the amount of reacted lime; (b) due to a higher hydration rate, the lime fractional conversions at 40°C and 56 days are roughly the same as those reached at 25°C after as many as 182 days.

At 25°C lime conversion increases with increasing the initial sulphate concentration, and no major difference is observed between phospho- and pure gypsum. On the other hand, at 40°C lime conversion does not seem to be influenced by the amount of pure gypsum added, while it reaches higher values on adding increasing amounts of phosphogypsum.

TABLE 5

Lime converted to CSH at the longest ageing times (wt%)

Temp. (°C)	ALP10	ALP20	ALP30	ALG10	ALG20	ALG30
25	45.5	47.5	37.5	45.0	45.0	35.0
40	47.5	47.0	37.0	45.0	37.5	31.0 [a]

[a] This value has been calculated estimating the amount of unconverted gypsum observed in the above conditions as 15% of the initial quantity by the aid of a thermal analysis calibration made in a previous work [8].

Thermal analysis has shown that in the presence of added gypsum, only $C_6A\bar{S}_3H_{32}$ and CSH form. At the times at which gypsum is completely converted (Table 4), by means of simple stoichiometric calculations, it is possible to divide the total amount of reacted lime into the two parts which are chemically combined in $C_6A\bar{S}_3H_{32}$ and CSH. Table 5 shows, for any of the compositions with added gypsum, the amount of lime converted to CSH at the longest ageing times, i.e., 182 days at 25°C and 56 days at 40°C. It is seen that, temperature and type of gypsum being the same, the amount of lime converted to CSH decreases as the amount of added gypsum increases. However, the extent to which this happens is greater in the case of pure gypsum.

CONCLUSIONS

Experimental results have indicated that phosphogypsum can be employed in mixtures containing fly-ash, lime and water to give products which are of potential use as building materials. This is due to the fact that under the conditions tested, calcium trisulphoaluminate hydrate and calcium silicate hydrate form, which are responsible for the development of mechanical strength at early and late ages, respectively.

Phosphogypsum has also shown to be equally or more efficient than pure gypsum. Particularly, both at 25 and 40°C, in the case of the highest addition of gypsum, not only is phosphogypsum more reactive than pure gypsum, but also a larger amount of calcium silicate hydrate is formed. This last feature is also attractive as far as durability is concerned.

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