Thermochimica Acta, 74 (1984) 35–44
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY TO THE STUDY OF THE SYSTEM PHOSPHOGYPSUM–LIME–ALUMINIUM HYDROXIDE–WATER

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(Received 9 August 1983)

ABSTRACT

The formation of calcium sulphoaluminate hydrates by hydrothermal reactions among phosphogypsum, lime and aluminium hydroxide has been studied in order to evaluate the possibility of disposal of phosphogypsum by conversion into products useful as building materials.

The investigation has been carried out with the aid of differential scanning calorimetry as the chief experimental technique.

Reaction products in different experimental conditions have been identified and quantitative data have been obtained in order to define optimum conditions with regard to both consumption of phosphogypsum and yield of calcium sulphoaluminate hydrates.

INTRODUCTION

Hydrothermal reactions between gypsum and oxides or hydroxides of calcium and aluminium are worthy of consideration because, owing to the formation of calcium sulphoaluminate hydrates, low-density hardened products can be obtained which are of potential use as building materials [1–8].

Phosphogypsum (PG) is a sludge containing mainly (about 90%) calcium sulphate dihydrate, which is produced in large amounts in the wet process for the manufacture of phosphoric acid. This by-product is mainly disposed of by means of applications in the cement industry [9–12]. Furthermore, the use of PG appears attractive as a substitute for natural gypsum in the hydrothermal processes referred to above.

TABLE 1

Chemical	Composition (wt.%) of phosphogypsum
Loss on ignition	22.9
CaO	34.3
SO_3	40.0
P_2O_5	1.8
SiO_2	1.4

In the light of these considerations it is of importance to define the most appropriate conditions in order to favour the conversion of PG towards useful products.

The aim of this work is, therefore, to study the behaviour of the system PG–C–AH_3–H * under different conditions of temperature and composition, making use of differential scanning calorimetry as the principal experimental technique.

EXPERIMENTAL

The phosphogypsum employed in the experimental runs was supplied by Montedison S.p.A. Its chemical composition is shown in Table 1. Other reagents were analytical grade $Al(OH)_3$(bayerite) and CaO obtained by thermal decomposition of analytical grade $CaCO_3$.

Mixtures of phosphogypsum, lime, aluminium hydroxide and CO_2-free water in different weight ratios were cured under 100% r.h. in a glass reactor. Precautions were taken in order to avoid CO_2 contamination. The compositions of the mixtures examined are reported in Table 2. Compositions M and T are stoichiometric for the formation of calcium monosulphoaluminate hydrate $3\ CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\ H_2O$ and calcium trisulphoaluminate hydrate $3\ CaO \cdot Al_2O_3 \cdot 3\ CaSO_4 \cdot 32\ H_2O$, respectively. T5, T10 and T20 contain, respectively, 5, 10 and 20% phosphogypsum in excess over composition T.

Curing temperature was varied between 25 and 80°C; the water/solid ratio was 0.75. At the end of fixed ageing times, samples were taken and the reaction stopped by drying under vacuum in the presence of P_2O_5. The complete set of ageing times for each experimental condition is listed in Table 3.

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 goniome-

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

TABLE 2

Compositions (wt.%) of the mixtures examined

	PG	CaO	$Al(OH)_3$
M	38.2	32.0	29.8
T	64.9	18.2	16.9
T5	65.8	17.8	16.4
T10	67.1	16.8	16.1
T20	69.0	15.8	15.2

ter, a PW 1965/30 proportional counter and a PW 1390 channel control. Cu*Kα* radiation was used.

Calcium trisulphoaluminate hydrate was prepared for use as standard in quantitative analysis according to the procedure reported by Berman and Newman [13].

RESULTS AND DISCUSSION

Qualitative analysis

The identification of reaction products by thermal analysis has been made on the basis of a great deal of data available in the literature concerning calcium aluminate hydrates and related phases [14–28].

The following considerations are pertinent to hydrated samples of composition M. At 25°C there is no evidence of neo-formed products until 4 days; at longer times only one more endothermic effect besides those of the reagents appears, related to the presence of calcium trisulphoaluminate hydrate $C_6A\bar{S}_3H_{32}$; as shown in Fig. 1a, the signals of the reagents are still present up to the longest ageing time (32 days). At higher temperatures an increase of reaction rate is observed and other neo-formed phases are detected. At 40°C $C_6A\bar{S}_3H_{32}$, which appears as early as after 2 days, is the only reaction product until 4 days; at 7 days (Fig. 1b) a new endotherm reveals the presence of calcium monosulphoaluminate hydrate $C_4A\bar{S}H_{12}$ and PG is almost completely converted. At longer times the intensities of the signals related to PG, AH_3, $C_6A\bar{S}_3H_{32}$ and $C_4A\bar{S}H_{12}$ do not change appre-

TABLE 3

Summary of ageing times (days) for each experimental condition

	25°C	40°C	60°C	80°C
M–T	1, 2, 4, 8, 14, 22, 32	1, 2, 4, 7, 11, 17, 25	1, 2, 3, 6, 9, 13, 17	1, 2, 3, 5, 8, 12, 16
T5–T10–T20		1, 2, 4, 7, 12, 19, 28	1, 2, 4, 7, 11, 15, 21	

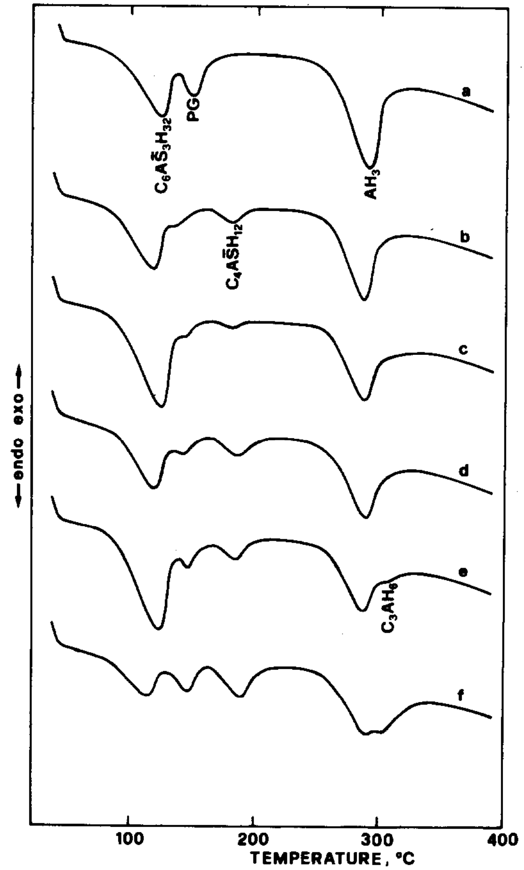

Fig. 1. Thermograms of samples of composition M at different temperatures and ageing times. (a) 25°C, 32 days; (b) 40°C, 7 days; (c) 60°C, 1 day; (d) 60°C, 17 days; (e) 80°C, 3 days; (f) 80°C, 16 days.

ciably. Figure 1c shows that at 60°C both the sulphoaluminates appear as early as after 1 day together with PG in a small amount; Fig. 1d, referred to 17 days, indicates that, as the ageing time is increased, the concentration of PG remains almost constant, while those of $C_6A\bar{S}_3H_{32}$ and $C_4A\bar{S}H_{12}$ decrease and increase respectively. At 80°C both the sulphoaluminates are detected after 1 day, but the ratio $C_4A\bar{S}H_{12}/C_6A\bar{S}_3H_{32}$ is higher than that observed at 60°C. Figure 1e shows the presence of the cubic tricalcium aluminate hydrate C_3AH_6 after 3 days. Figure 1f, referred to 16 days, indicates that, as at 60°C, the ratio $C_4A\bar{S}H_{12}/C_6A\bar{S}_3H_{32}$ increases with the ageing time; furthermore, the amount of unconverted PG is greater than that observed at 40 and 60°C.

As far as composition T is concerned, the results of the qualitative analysis are as follows. At 25°C $C_6A\bar{S}_3H_{32}$ is the only reaction product detected and its amount is appreciable after 14 days; the thermogram of Fig.

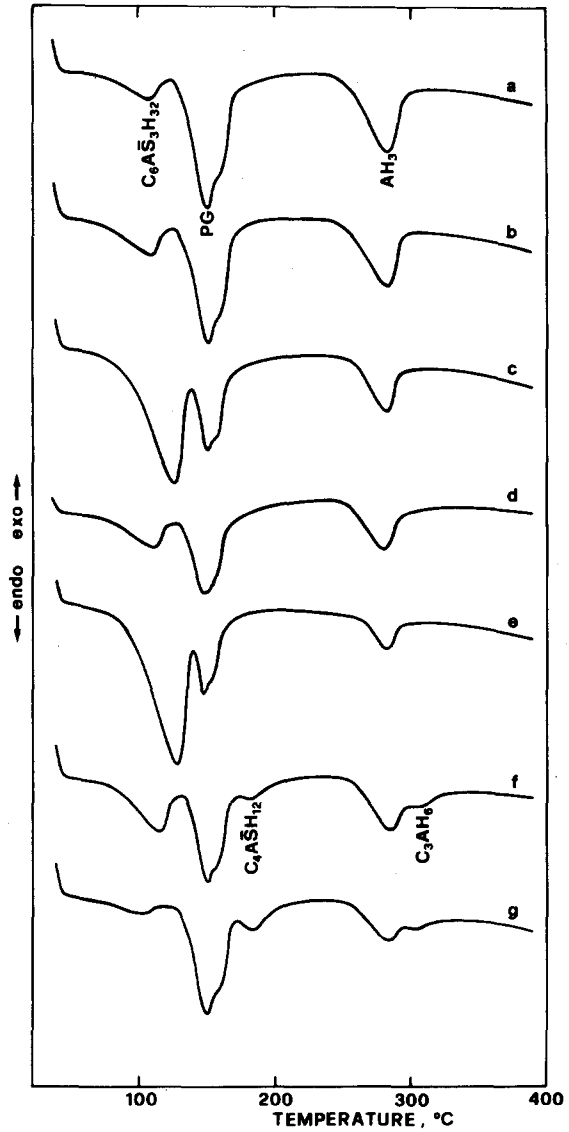

Fig. 2. Thermograms of samples of composition T at different temperatures and ageing times. (a) 25°C, 32 days; (b) 40°C, 4 days; (c) 40°C, 25 days; (d) 60°C, 2 days; (e) 60°C, 17 days; (f) 80°C, 5 days; (g) 80°C, 16 days.

2a, relative to 32 days, shows that the reaction does not proceed to a relevant extent within the ageing period examined. At 40°C the kinetics of formation of $C_6A\bar{S}_3H_{32}$ is much faster: in fact it is detected after 4 days (Fig. 2b) and its concentration considerably increases with the ageing time, as shown in Fig. 2c, referred to 25 days. At 60°C $C_6A\bar{S}_3H_{32}$ is still the only reaction product and its rate of formation is further increased, as shown in Figs. 2d and 2e, referred to 2 and 17 days, respectively. At 80°C both $C_6A\bar{S}_3H_{32}$ and

C_3AH_6 appear after 1 day; then $C_4A\bar{S}H_{12}$ is also detected after 5 days. The amount of unconverted PG is appreciably greater than that relative to 40 and 60°C; furthermore, the ratio $C_4A\bar{S}H_{12}/C_6A\bar{S}_3H_{32}$ increases with the ageing time. Figures 2f and 2g are referred to 5 and 16 days, respectively.

The experimental results described above allow the following reaction set to account for the behaviour of the reaction system under the conditions tested

$$3\,CaO + 2\,Al(OH)_3 + 3\,CaSO_4 \cdot 2\,H_2O \overset{H_2O}{\rightleftharpoons} 3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 32\,H_2O \qquad (1)$$

$$3\,CaO + 2\,Al(OH)_3 + CaSO_4 \cdot 2\,H_2O \overset{H_2O}{\rightleftharpoons} 3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\,H_2O \qquad (2)$$

$$3\,CaO + 2\,Al(OH)_3 \overset{H_2O}{\rightleftharpoons} 3\,CaO \cdot Al_2O_3 \cdot 6\,H_2O \qquad (3)$$

From a kinetic point of view, reaction (1) is the most favoured, and it is the only one to take place at 25°C for both compositions M and T, within the range of ageing time examined. At higher temperatures reaction (2) also takes place, but the temperature at which $C_4A\bar{S}H_{12}$ formation is observed depends on the composition of the reacting system: 40°C for composition M and 80°C for composition T. This is due to an unfavourable effect of increasing PG concentration on the kinetics of calcium sulphoaluminate hydrates synthesis; that is, the apparent order of reactions (1) and (2) with regard to gypsum seems to be lower than that for the other reagents. This conclusion is supported by the following observations: the times at which $C_6A\bar{S}_3H_{32}$ appears for compositions M and T, respectively are 4 and 14 days at 25°C, and 2 and 4 days at 40°C, while at 80°C $C_4A\bar{S}H_{12}$ appears after 1 day for composition M and 5 days for composition T.

The ratio $C_4A\bar{S}H_{12}/C_6A\bar{S}_3H_{32}$ increases as both ageing time and temperature increase because, depending on the more favourable kinetics, reaction (1) approaches equilibrium more rapidly and the further consumption of reagents caused by reaction (2) reduces the equilibrium concentration of $C_6A\bar{S}_3H_{32}$. Both phenomena are favoured by an increase in temperature.

Unconverted PG is observed in lower amounts at 40 and 60°C because at lower temperatures its consumption is hindered by kinetic factors, while at higher temperatures it is limited by the equilibrium thermodynamic factors related to reactions (1) and (2).

Reaction (3) takes place only at 80°C for both systems.

The systems of composition T5, T10 and T20 examined at 40 and 60°C show a behaviour similar to that of composition T. Furthermore, the unfavourable effect of an increase of PG concentration on the kinetics of the formation of sulphoaluminate hydrates, as shown by the thermograms of Fig. 3, referred to 40°C and 4 days for the compositions M, T, T5, T10 and T20, is confirmed.

Quantitative analysis

It is well known that, of the two sulphoaluminates, $C_6A\bar{S}_3H_{32}$ gives a prevalent contribution to the development of mechanical strength, owing to its needle-like microstructure [29,30]. For this reason it is worth determining the optimum conditions in order to realize the highest conversion of PG into $C_6A\bar{S}_3H_{32}$.

The comparison among the results of the qualitative analysis indicates that composition T and the temperatures of 40 and 60°C represent the best conditions in the light of the above consideration. In order to evaluate the extent to which $C_6A\bar{S}_3H_{32}$ is produced, a quantitative analysis technique has been developed which makes use of the thermal analysis results.

The peak areas relative to dehydration of unconverted PG and AH_3, as well as neo-formed $C_6A\bar{S}_3H_{32}$, are proportional to the enthalpy changes and then to the concentrations of each phase. The evaluation of PG, AH_3 and $C_6A\bar{S}_3H_{32}$ concentrations can be obtained by means of calibration curves linking the amount of each phase with the corresponding peak area.

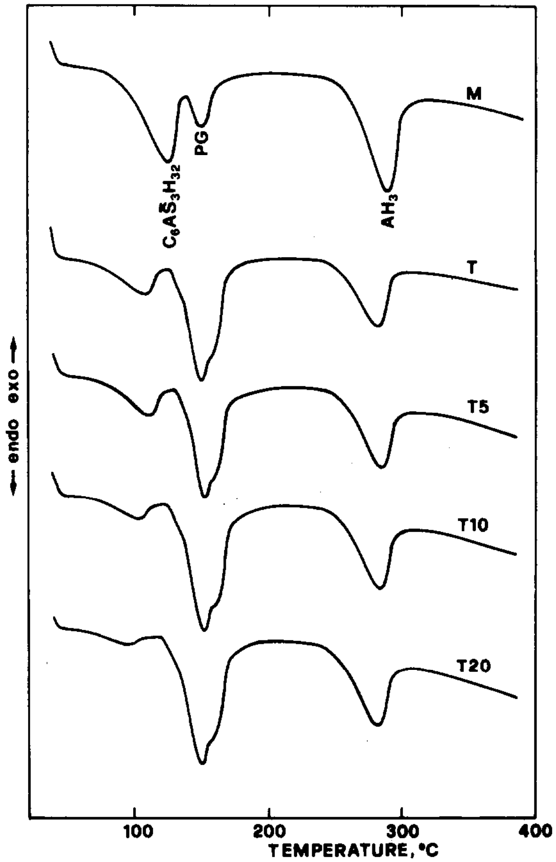

Fig. 3. Thermograms of samples aged 4 days at 40°C.

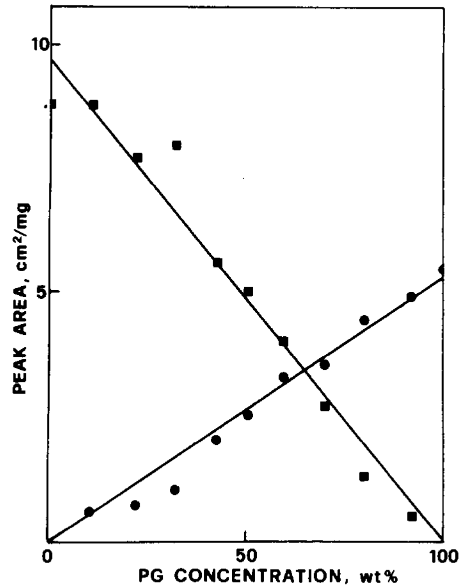

Fig. 4. Calibration plot for PG and $C_6A\bar{S}_3H_{32}$. ●, PG; ■, $C_6A\bar{S}_3H_{32}$.

As in a large number of thermograms, partial overlapping of PG and $C_6A\bar{S}_3H_{32}$ peaks occurred, the calibration for these two components has been performed by means of binary mixtures of known composition. The contribution related to each component was found with the aid of a series of thermograms of pure $C_6A\bar{S}_3H_{32}$ in variable amounts. Figure 4 shows that calibration straight lines were obtained whose slopes are 5.3 and 9.7 cm^2 mg^{-1} for PG and $C_6A\bar{S}_3H_{32}$, respectively. An independent calibration has been obtained for AH_3 with the slope of the resulting straight line equal to 12.8 cm^2 mg^{-1}.

Figures 5 and 6 show the results of the quantitative analysis for the system

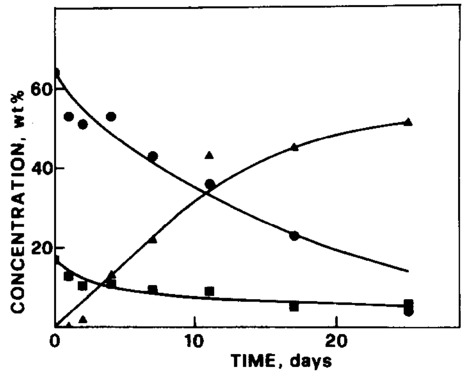

Fig. 5. PG, AH_3 and $C_6A\bar{S}_3H_{32}$ concentrations vs. time for samples of composition T aged at 40°C. ●, PG; ■, AH_3; ▲, $C_6A\bar{S}_3H_{32}$.

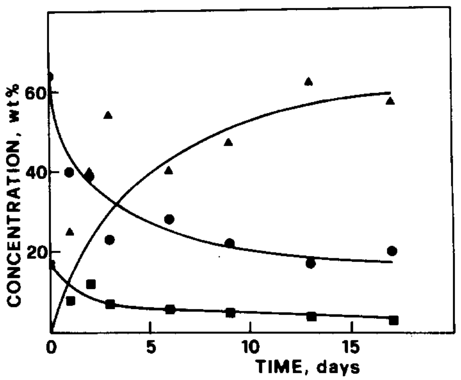

Fig. 6. PG, AH_3 and $C_6A\bar{S}_3H_{32}$ concentrations vs. time for samples of composition T aged at 60°C. ●, PG; ■, AH_3; ▲, $C_6A\bar{S}_3H_{32}$.

of composition T at 40 and 60°C, respectively. It is clear that the higher the temperature, the higher the conversion at the same ageing time: in particular, at 40°C after 25 days $C_6A\bar{S}_3H_{32}$ concentration is about 50%, while at 60°C after 13 days it reaches 60%.

The results of the quantitative analysis extended to composition T at 25°C and to compositions T5, T10 and T20 at 40 and 60°C, are as follows. At 25°C the concentration of $C_6A\bar{S}_3H_{32}$ reaches about 10%. For the compositions with PG in excess the maximum concentration is lower than that for composition T and does not depend significantly on the amount of PG in excess; values at 40 and 60°C are about 40 and 45%, respectively.

The results of Figs. 5 and 6 are also shown in the triangular diagram of Fig. 7 on a CaO-free basis, together with the reaction path relative to the system of initial composition T reacting according to reaction (1). It is seen that, especially at higher conversions, the experimental points are in good agreement with the reaction path, and this gives a valid support to the proposed kinetic scheme.

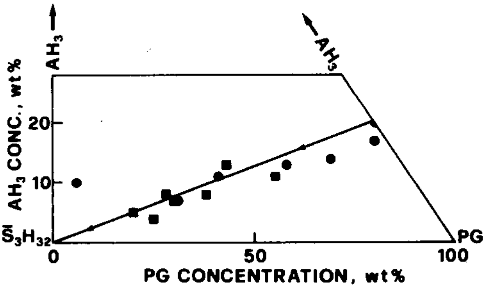

Fig. 7. Reaction path for the system of composition T at 40°C (●) and 60°C (■).

CONCLUSIONS

The results of the qualitative analysis allowed the definition of the chemical reactions taking place in the system phosphogypsum–lime–aluminium hydroxide–water in the temperature range 25–80°C and for different composition ratios.

It has been proved that disposal of phosphogypsum can be directed towards the conversion into products useful as building materials due to their physical properties.

Optimum conditions, in terms of consumption of phosphogypsum and other reagents, as well as yield of sulphoaluminate hydrates, have been identified by means of quantitative analysis: a temperature of 60°C and a composition stoichiometric for $C_6A\bar{S}_3H_{32}$ formation.

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