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DTA STUDY OF THE HYDRATION OF SYSTEMS OF INTEREST IN THE FIELD OF BUILDING MATERIALS MANUFACTURE

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The hydration processes of mixtures containing calcined gypsum, blastfurnace slag or fly ash, portland cement and/or hydrated lime, able to generate calcium trisulphoaluminate and silicate hydrates, have been studied by means of differential thermal analysis. Samples were aged at 55°,70° and 85°C for 16, 24 and 48 hours, followed by a further curing at room temperature and humidity up to 28 days.

In the case of the systems containing slag, the optimum pre-curing temperature is 55°C and increasing the pre-curing time from 16 to 48 hours leaves the hydration degree almost unchanged.

In the case of the systems containing fly ash the optimum pre-curing temperature is 85°C. Increasing the pre-curing time from 16 to 24 hours enhances the hydration degree. The further increase to 48 hours reduces the selectivity towards calcium trisulphoaluminate hydrate.

In all the systems investigated the post-curing at room temperature and humidity has no significant effect on the hydration degree.

Finally, the influence of the nature of raw materials depends not only on the characteristics of each component, but also on those of the others.

Keywords: building materials, DTA, hydration

Introduction

Hydrating mixtures containing gypsum and oxides or hydroxides of calcium and aluminium are worthy of consideration because they generate calcium trisulphoaluminate hydrate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), a compound characterized by good binding properties and low density [1, 2]. Systems of this type are suitable for the manufacture of performed building elements inasmuch as

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Table 1 Major chemical constituents of the raw materials /wt%

Materials	CaO	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	Na2O	K_2O	CO_2	SO_3	P_2O_5	F	H_2O
Natural Gypsum	32.60	3.33	0.35	0.03	0.22	0.06	0.01	0.12	0.00	43.40	0.01	0.00	20.70
Phosphogypsum 1	32.60	0.05	0.23	n.d.	0.02	0.22	0.16	0.08	n.d.	44.90	0.47	0.70	20.50
Phosphogypsum 2	33.80	0.01	n.d.	n.d.	n.d.	0.33	n.d.	n.d.	0.10	46.30	0.58	1.06	17.77
Blast-furnace slag 1	41.13	33.17	14.15	0.48	1.57	7.00	0.03	0.38	n.d.	2.58	0.00	n.d.	0.20
Blast-furnace slag 2	39.40	34.80	18.10	0.69	0.21	2.15	0.30	0.53	n.d.	0.78	0.04	n.d.	0.20
Fly ash 1	4.80	56.80	25.50	2.20	4.20	1.50	3.00	0.19	n.d.	0.40	0.00	n.d.	0.40
Fly ash 2	3.40	59.30	23.30	1.10	4.52	1.12	0.50	1.83	n.d.	0.37	0.16	n.d.	0.30
Portland cement	63.80	22.22	4.52	0.31	3.60	1.72	0.18	0.42	n.d.	2.43	0.05	n.d.	0.93
Hydrated lime	72.80	n.d.	n.d.	n.d.	n.d.	0.71	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24.39

satisfactory mechanical strengths are obtained only when curing is carried out at temperatures higher than room temperature. However the use of calcined gypsum as a source of sulphate may advantageously contribute to strength at very early ages because of its rapid setting [3, 4].

Industrial by-products, like fly ash and blast-furnace slag, may be employed as sources of alumina in the mixtures to be hydrated. The reactive silica contained in these by-products can produce also calcium silicate hydrates which add mechanical strength and durability to the hydrated systems at later ages [5]. When necessary, the required CaO content of the generating mixtures can be given by portland cement and/or hydrated lime.

Furthermore, phosphogypsum, another important by-product, may be employed instead of natural gypsum. Such a replacement is particularly interesting inasmuch as it can enhance the rate of hydration [6, 7] and generate higher mechanical strength in the cured mixtures [8].

In this work DTA has been used for studying the hydration processes of mixtures containing calcined gypsum, fly ash and blast-furnace slag, portland cement and/or hydrated lime. The influence of curing time and temperature, as well as that of the nature of the raw materials on the hydration process has been examined and discussed.

Experimental

The chemical composition of the materials used is indicated in Table 1. Table 2 shows the composition of the mixtures investigated.

Table 2 Composition of the systems investigated / wt%

System	Calcined gipsum	Slag	Fly ash	Portland cement	Hydrated lime
A	28.5	–	43.0	–	28.5
B	18.5	61.5	–	20.0	–
C	26.0	–	43.3	17.4	13.3
D	20.0	69.0	–	10.0	1.0
E	28.3	–	47.2	10.0	14.5

The calcined natural gypsum was prepared by hydration in a laboratory oven at 140°–145°C for 16 hours, followed by conditioning for 24 hours at 67% R.H. and 21°C.

The phosphogypsums were calcined in a kettle to the 'second boil' as in industry and conditioned as above.

Specimens of the investigated mixtures were paste hydrated using a water/solid ratio equal to 0.5, sealed in plastic envelopes and submitted to a pre-curing treatment at 55°, 70° and 85°C for 16, 24 and 48 hours.

This treatment was followed by a post-curing at room temperature and humidity up to 28 days. At and pre- or post-curing time the specimens were ground in acetone to stop the reaction, dried with ether and stored in a desiccator. The dried specimens were analysed by differential thermal analysis using a Netzsch STA 409 and a Stanton STA 780 apparatus.

The identification of unconverted reactants and neo-formed hydration products has been made on the basis of literature data [9, 10]. In particular, calcium silicate hydrate, calcium trisulpho- aluminate hydrate, gypsum, calcium monosulphoaluminate hydrate, tricalcium aluminate hydrate and calcium hydroxide are detected by means of endotherms at 80±5°C, 115±15°C, 160±20°C, 200°, 300° and 470±10°C, respectively.

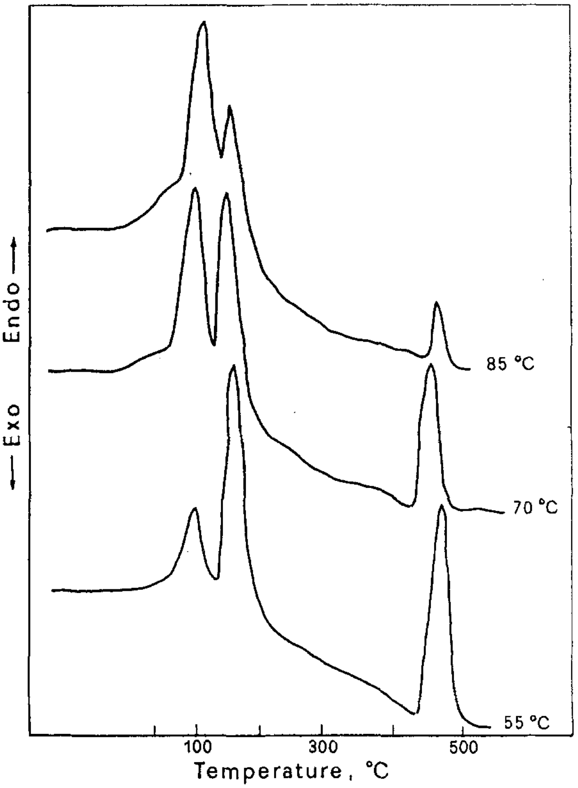

Fig. 1 DTA curves of samples of composition A containing calcined natural gypsum, fly ash, and hydrated lime, aged 16 hours at 55°, 70° and 85°C

Results and discussion

Influence of pre-curing temperature

Figure 1 shows the DTA curves relative to the samples of composition A pre-cured 16 hours at 55°, 70° and 85°C.

It is clearly seen that the intensities of the peaks relative to $CaSO_4 \cdot 2H_2O$ and $Ca(OH)_2$ decrease as the pre-curing temperature increases while that of the neo-formed calcium trisulphoaluminate hydrate peak increases. Starting from 70°C calcium silicate hydrate is also detected.

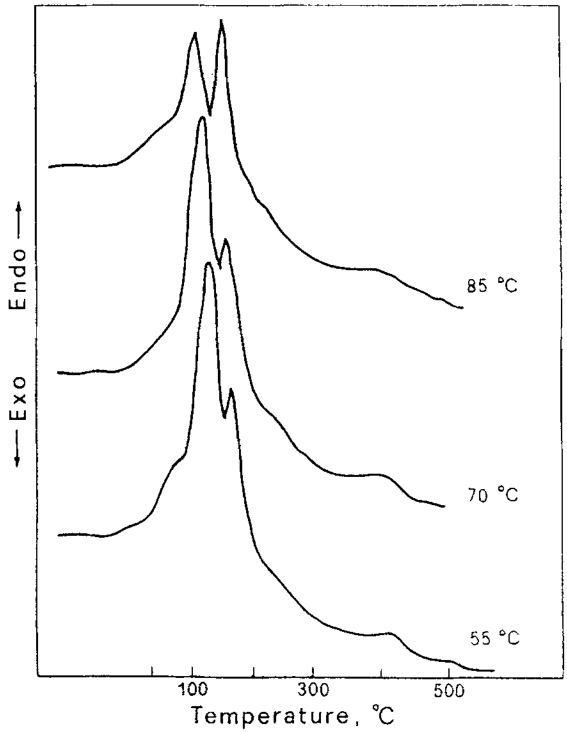

Fig. 2 DTA curves of samples of composition B containing calcined natural gypsum, slag 1, portland cement, aged 16 hours at 55°, 70° and 85°C

Figure 2 shows the DTA curves relative to the samples of composition B pre-cured 16 hours at 55°, 70° and 85°C.

In this case the yield of the hydratation products is, at 55°C, much higher than that observed in the previous system at the same temperature. It is also seen that the hydration degree decreases as the pre-curing temperature increases.

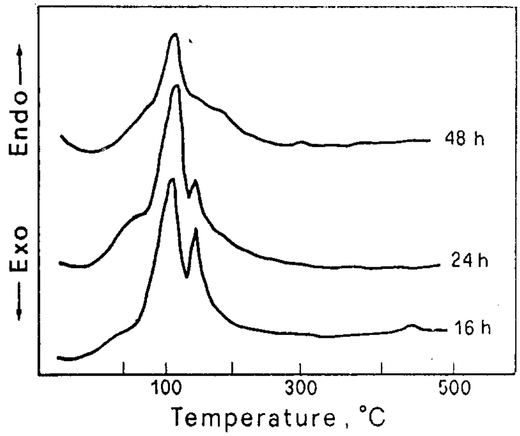

Fig. 3 DTA curves of samples of composition C containing calcined phosphogypsum 1, fly ash 1, portland cement and hydrated lime, aged 16, 24 and 48 hours at 55°C

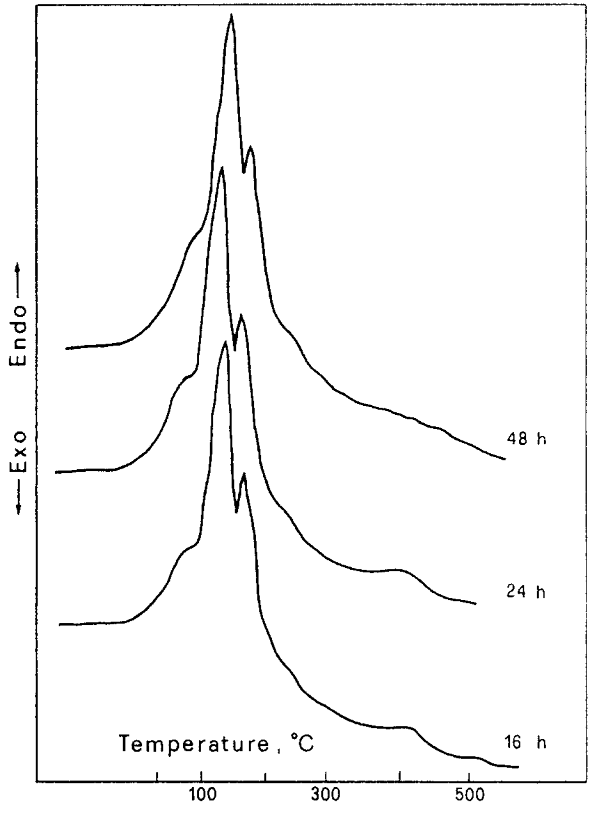

Fig. 4 DTA curves of samples of composition B containing calcined natural gypsum, slag 1 and portland cement, aged 16, 24 and 48 hours at 55°C

From a qualitative point of view, the behaviour of system A is common to the other systems containing fly ash and that of the system B is common to the other systems containing slag. Hence, the former systems are kinetically favoured by an increase in temperature, while the latter ones are negatively affected by thermodynamic equilibrium factors as the temperature increases.

Influence of pre-curing time

Figure 3 shows the DTA curves relative to the samples of composition C pre-cured 16, 24 and 48 hours at 85°C.

Increasing the pre-curing time from 16 to 24 hours enhances the hydration degree. The further increase to 48 hours causes a decrease of the intensity of the calcium trisulphoaluminate hydrate peak due to decomposition into calcium monosulphoaluminate hydrate ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$) and tricalcium aluminate hydrate ($3CaO{\cdot}Al_2O_3{\cdot}6H_2O$).

Figure 4 shows the DTA curves relative to the samples of composition B pre-cured 16, 24 and 48 hours at 55°C. It is clearly seen that no significant differences in the conversion into the main products are observed as the pre-curing time increases from 16 up to 48 hours.

The above results indicate that the effect of pre-curing time cannot be considered separately from that of temperature, due to the thermal instability of calcium trisulphoaluminate hydrate.

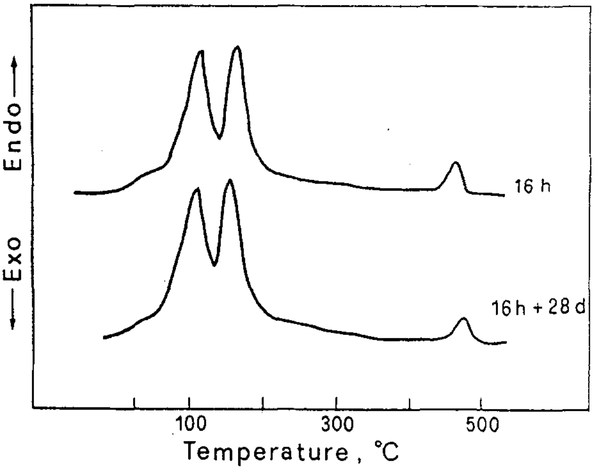

Fig. 5 Effect of a 28-day post-curing at room temperature and humidity on the sample of composition C containing calcined natural gypsum, fly ash 1, portland cement and hydrated lime, pre-cured 16 hours at 70°C

Influence of post-curing time

Figure 5 shows the effect of a 28 days post-curing at 25°C, 50% R.H. on the sample of composition C pre-cured 16 hours at 70°C. It is clearly seen that conversion is only slightly enhanced. This behaviour is common to all the systems investigated.

Influence of the nature of raw materials

Figure 6 shows the DTA curves relative to some samples of composition D pre-cured 24 hours at 55°C. The various samples have been prepared using three different sources of sulphate and two different slags.

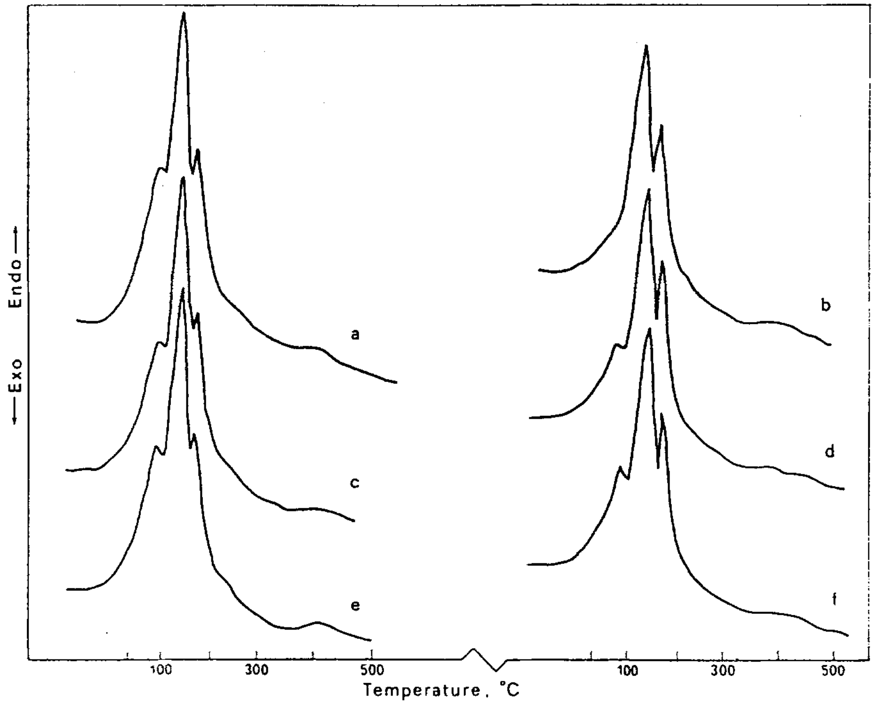

Fig. 6 DTA curves of samples of composition D aged 24 hours at 55°C
(a)-calcined natural gypsum, slag 1, portland cement and hydrated lime;
(b)-calcined natural gypsum, slag 2, portland cement and hydrated lime;
(c)-calcined phosphogypsum 1, slag 1, portland cement and hydrated lime;
(d)-calcined phosphogypsum 1, slag 2, portland cement and hydrated lime;
(e)-calcined phosphogypsum 2, slag 1, portland cement and hydrated lime;
(f)-calcined phosphogypsum 2, slag 2, portland cement and hydrated lime

Comparing thermoanalytical curves (a) and (b) clearly shows that, in the presence of natural gypsum, slag 1 is more reactive than slag 2, with regard to the formation of both the main hydration products.

The examination of curves (a), (c) and (e) indicates that the reactivity of the samples containing slag 1 is not affected by replacing natural gypsum with phosphogypsum. On the other hand, the samples containing the less reactive slag 2 are favourably influenced by each type of phosphogypsum.

Figure 7 shows the DTA curves relative to some samples of composition E pre-cured 24 hours at 85°C.

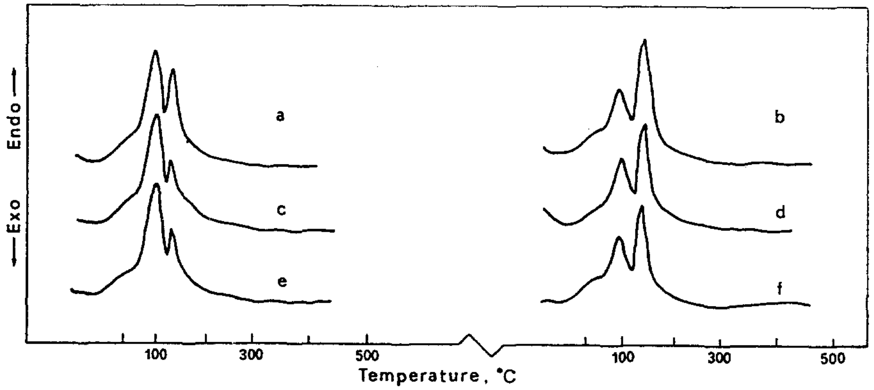

Fig. 7 DTA curves of samples of composition E aged 24 hours at 85°C
(a)-calcined natural gypsum, fly ash 1, portland cement and hydrated lime;
(b)-calcined natural gypsum, fly ash 2, portland cement and hydrated lime;
(c)-calcined phosphogypsum 1, fly ash 1, portland cement and hydrated lime;
(d)-calcined phosphogypsum 1, fly ash 2, portland cement and hydrated lime;
(e)-calcined phosphogypsum 2, fly ash 1, portland cement and hydrated lime;
(f)-calcined phosphogypsum 2, fly ash 2, portland cement and hydrated lime

The various samples have been prepared using the same three sources of sulphate as before and two different fly ashes. The comparison between DTA curves (a) and (b) indicates that, in the presence of natural gypsum, fly ash 1 is more reactive than fly ash 2, especially as far as the formation of calcium trisulphoaluminate hydrate is concerned.

The examination of curves (a), (c) and (e) shows that, in the samples containing the more reactive fly ash, substitution of natural gypsum with each type of phosphogypsum, further enhances the reactivity. On the other hand, such a substitution has little effect, if any, on the samples containing the less reactive fly ash.

The results shown in Figs 6 and 7 allow to draw the conclusion that the influence of the nature of raw materials is quite complex. The role played by each component depends not only on its intrinsic characteristics, but also on those of the other components of any individual mixture.

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Zusammenfassung — Mittels DTA wurden die Hydratationsprozesse von Gemischen aus Gips, Hochofenschlacke oder Flugasche, Portlandzement und/oder Löschkalk untersucht, die zur Bildung von Calciumtrisulfoaluminat und Silikathydraten fähig sind. Die Proben wurden bei 55°, 70° und 85°C für 16, 24 und 48 Stunden lang, im Anschluß daran durch Aushärten bei Raumtemperatur und normaler Luftfeuchte 28 Tage lang gealtert.

Bei der Verwendung von Schlacke beträgt die optimale Vorhärtungstemperatur 55°C und die Erhöhung der Vorhärtungsperiode von 16 auf 48 Stunden ließ den Hydratationsgrad unverändert.

Bei der Verwendung von Flugasche beträgt die optimale Vorhärtungstemperatur 85°C. Die Erhöhung der Vorhärtungsperiode von 16 auf 14 Stunden steigert auch den Hydratationsgrad. Eine weitere Steigerung auf 48 Stunden setzt die Selektivität gegenüber Calciumtrisulfoaluminat-Hydrat herab.

In keinem der untersuchten Systeme hatte das Nachhärten bei Raumtemperatur und normaler Luftfeuchte einen signifikanten Einfluß auf den Hydratationsgrad.

Letztendlich hängt der Einfluß der Ausgangsmaterialien nicht nur von den Eigenschaften jeder einzelnen Komponente, sondern auch von denen der anderen Komponenten ab.