THERMAL BEHAVIOUR OF GYPSUM BASED COMPOSITES

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DTA/TG and X-ray investigations were carried out on different building composites in order to examine their relative hydration processes. The presence of lime, hemihydrate gypsum, ferosilicate, and some other wastes as leaner and hydrophobic additive in different proportions into composites provokes hydration reactions, leading to calcium silicate hydrate (CSH), ettringite and an intermediate phase formation with varying chemical composition of calcium, aluminum, silicon and sulfur.

DTA curves indicate several transformations taking place between composites components, related to hydration of some phases. The content of ettringite component corresponds to the properties and it is used as an indicator for the possibility of industrial application. It is found out that gypsum based cementitious binders could be used as building material in the industry. The same time it is confirmed that the selected wastes could be considered as secondary raw materials.

Keywords: binders, composites, DTA/TG, ettringite, gypsum, wastes

Introduction

In many industrially developed countries the generated industrial solid wastes such as fly ash and gypsum are often deposited, creating risk for pollution of environment [1]. However, those wastes contain valuable inorganic components such as oxides of silicon, aluminium, calcium, iron and sulphate and they may be utilized in the concrete, plaster, ceramic or cement industries. To reduce pollution and disposal of those industrial wastes, there is a need to develop new methods and technologies for building materials production. The pozzolanic reactivity of fly ash is well known and on the base of it different compositions are proposed [2]. Recently, a ternary mixture, known as Fal-G, containing fly ash, lime, and gypsum has been used for production of construction materials in a small scale in India [3, 4].

The aim of this paper is to investigate the formation of cementitious binders based on gypsum, lime, fayalite and some other wastes mixtures.

Experimental

Raw materials and methods

Plaster gypsum, lime, fayalite, waste sand and slime were used for composites production. The FGD-gypsum dihydrate from Maritsa-East–2 thermal power station with content of 32.00% CaO, 45.4% SO_3, 0.26% Fe_2O_3, 0.03% MgO, 0.02% water, 20.51% crystal water and 1.8% others was dehydrated at

atmospheric pressure in laboratory scale furnace. Calcium sulphate half-hydrate, with 8.23% total water content was obtained after several hours dewatering at 120°C and identified by IR and differential thermal analysis (TG-DTA) [5]. Some properties and physical-mechanical characteristics have been determined [6]. The waste fayalite from copper smelter converter slag processing in Chelopech Mining EAD with initial moisture content 12.23 mass% is also used. Before use it was dried at 362 K for completely evaporation of water. The dry fayalite content in mass% is as follows: 61.97FeO, 30.85SiO_2, 3.41Al_2O_3, 1.72$CaSO_4$, 0.78Cu, 0.26Zn, 0.41Mg, 0.22Na_2O and 0.38K_2O. Building lime, waste sand as well as waste slime and water were also used for gypsum–lime cementation composites production. Utilization of all components is based on their chemical composition and possibility to be hydrated forming gypsum–lime binders. Different mixtures are worked out in order to determine degree of hydration. The content of gypsum and fayalite were varied from 30 to 60%, lime – from 4 to 12% and waste sand – from 5.5 to 7.5% (by mass%). Slime content has been kept constant at 0.3%. For better plasticity 0.2% Poliox plasticizer is used. Selected quantities are on the base of previously worked out experiments.

The binders designated as 'type A were produced by blending lime, calcined FGD gypsum (β-$CaSO_4 \cdot 0.5H_2O$), fayalite, waste sand, slime and plasticizer in a mass ratios of 4:30:59:6.5:0.3:0.2 for A1, 8:30:55:6.5:0.3:0.2 for A2 and 12:30:52:5.5:0.3:0.2 (by mass%) for A3 subtype gypsum–lime binders. For the other group of mixtures, designated as binder B, the ratios are as follows: for B1 – 4:44:44:7.5:0.3:0.2; for

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B2 – 8:42.5:42.5:6.5:0.3:0.2 and 12:41:41:5.5:0.3:0.2 (by mass%) for B3 subtypes, respectively. The ratios between the composite components in type C binder are: for C1 – 4:58:30:7.5:0.3:0.2; for C2 – 8:55:30:6.5:0.3:0.2 and for C3 – 12:52:30:5.5:0.3:0.2. The mixtures were extruded, using plasticimeter 'Netzsch-450' and the dehydration of obtained samples was studied after 28 days.

Dehydration process was studied by MOM Q-1500D derivatograph in temperature range 293–1723 K. Heating rate was 5 K min^{-1} and sample's mass 400±0.4 mg. Zirconium crucibles were with 8 mm inner diameter and 20 mm height. For identification of generated phases after thermal treatment X-ray powder diffraction method is applied, using TUR M 62 apparatus with CoK$_\alpha$ radiation. JCPDS data was used for identification (JCPDS, Powder Diffraction File (PDF), Set 1-89, Joint Committee on Diffraction Standards, Philadelphia PA, 2001).

Results and disscusion

On the base of DTA/TG curves and X-ray diffraction data obtained, entahalpy changes and final solid phase are determined. Figures 1–4 and Tables 1–3 represent TG-DTA curves of binder's types A, B and C, hydrated for 28 days respectively. The first endothermic effect (Figs 1–3) shows that ettringite is the main hydration product. It forms during composites treatment/mixing and extrusion/ and its area increases, when mass ratio gypsum–lime is higher. This is an indication that this thermal effect is due to the dehydration of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$). Any way it should be considered the possibility of overlapping with the endothermic effect of small quantities of calcium silicate hydrate (CSH). Such overlapping explains the slight movement of the endothermic effect of the ettringite from 373 K to higher temperatures at about 395 K. The ettringite is formed by the reaction of tetracalcium aluminate ($3CaO \cdot Al_2O_3$) formed by the reaction of lime, waste sand and fayalite, with gypsum added to the composites in different ratios. The second endothermic peak is observed at about 439 K for A3, B and C types of binders and it represents the releasing of water from dihydrate gypsum. Due to its relative low quantity in binders A1 and A2 the absence of such peak is registered. The third endothermic peak is located at temperatures 690–695 K and it could be attributed to the transformation of soluble to insoluble anhydrate $CaSO_4(III) \rightarrow CaSO_4(II)$ [7]. The exothermic effect, observed for the pure hemihydrate samples about 493 K, for mixtures investigated is about 690 K. It is reasonable to expect the exothermic reaction to occur at higher temperature range, because some of the mixture's components are acting as a re-
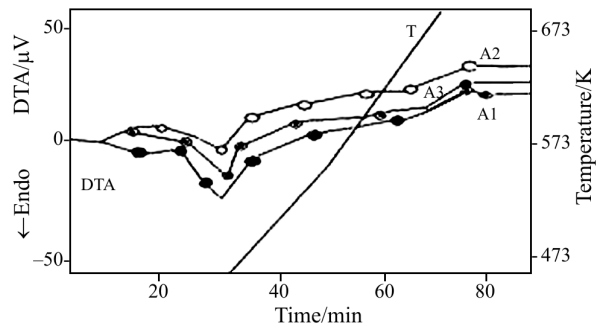

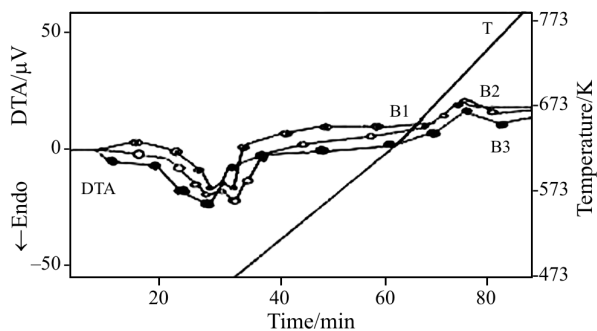**Fig. 1** DTA curves of cementitious binders type A

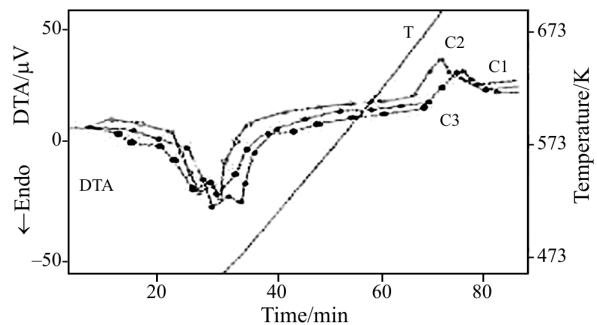**Fig. 2** DTA curves of cementitious binders type B

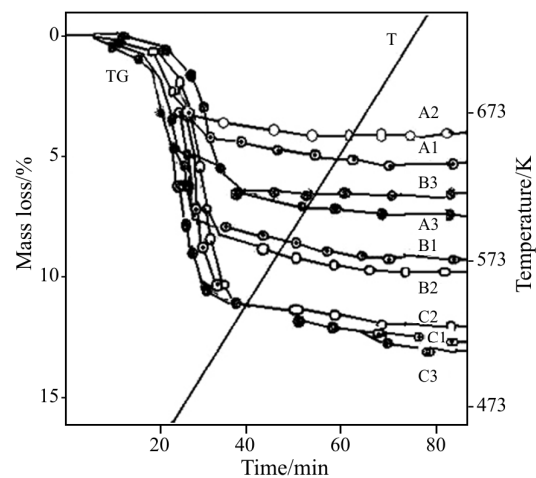**Fig. 3** DTA curves of cementitious binders type C

Fig. 4 TG curves of cementitious binders types A, B and C

Table 1 Temperature ranges and observed mass losses for type A binders at different stages of decomposition

Binder type	Stage	Stage's mass	Temperature/K		Thermal effect/g/g·10^{-2}	Compound
			start	end		
A1	I	2.99	390	473	–	ettringite
	II	0	693	735	0.37	$CaSO_4(II)$
			Total mass loss – 4.98%			
A2	I	2.49	395	466		ettringite
	II	0	698	724	0.05	$CaSO_4(II)$
			Total mass loss – 4.00%			
A3	I	0.75	298	403	–	water
	II	3.25	403	441		ettringite
	III	2.25	441	493		gypsum
	IV	0	695	734	0.45	$CaSO_4(II)$
			Total mass loss – 7.00%			

Table 2 Temperature ranges and observed mass losses for type B binders at different stages of decomposition

Binder type	Stage	Stage's mass	Temperature/K		Thermal effect/g/g·10^{-2}	Compound
			start	end		
B1	I	4.76	398	441		ettringite
	II	1.75	441	488		gypsum
	III	0	690	751	0.75	$CaSO_4(II)$
			Total mass loss – 8.77%			
B2	I	0.75	298	398	–	water
	II	5.74	398	443		ettringite
	III	1.75	441	488		gypsum
	IV	0	690	748	1	$CaSO_4(II)$
			Total mass loss – 9.23%			
B3	I	0.49	298	383	–	water
	II	3.99	383	425		ettringite
	III	1.49	425	468		gypsum
	IV	0	678	740	1.25	$CaSO_4(II)$
			Total mass loss – 6.23%			

Table 3 Temperature ranges and observed mass losses for type C binders at different stages of decomposition

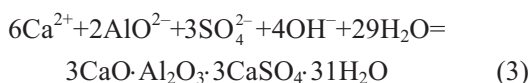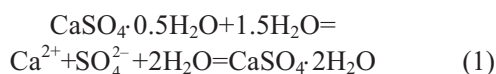| Binder type	Stage	Stage's mass	Temperature/K		Thermal effect/g/g·10^{-2}	Compound
			start	end		
C1	I	1	338	411	–	water
	II	7.27	411	453		ettringite
	III	2.25	453	490		gypsum
	IV	0	691	748	1.25	$CaSO_4(II)$
			Total mass loss – 12.00%			
C2	I	1.25	321	394	–	water
	II	6.5	394	422		ettringite
	III	3	422	491		gypsum
	IV	0.25	676	765	2.25	$CaSO_4(II)$
			Total mass loss –11.75%			
C3	I	0.99	323	380	–	water
	II	6.98	380	442		ettringite
	III	2.49	442	488		gypsum
	IV	0.25	691	725	0.45	$CaSO_4(II)$
			Total mass loss – 12.22%			

tarder. The registered thermal effects corespond to the results achieved by [1, 8] in similar composites.

Calculation data, expressed like peak area/initial mass sample (g/g, i.e. dimensionless parameter), re-garding thermal effects in each stage of dehydration are presented in Tables 2–3. As it can be seen regis-tered thermal effects correspond to initial mass ratio of the components used. Different mass losses, due to

the content of ettringite, calcium silicate hydrate, dihydrate gypsum and the inversion of soluble to insoluble anhydrite, are registered on the TG curves during the thermal treatment of the A, B and C types composites. Data is summarized in Tables 1–3 and Fig. 4. Mass balance calculations indicate the potential presence of unreacted water at the end of the hydration in amounts of 0.75% for A3 subtype, 0.75 and 0.49% for B2 and B3 subtypes respectively; for C1, C2 and C3 it is 1, 1.25 and 0.99% by mass. The losses from ettringite are approximately about 2.9, 4.8 and 6.9 mass% for A, B and C type composites respectively and it is in a good agreement to the initial ratio used. The absence of gypsum phase in A type binders could be explained with the low initial ratio of the components related to the ettringite formation. For composites B and C gypsum content is about 1.66 and 2.58 mass%.

Kerui *et al*. and Marinkovich *et al*. [9, 10] proposed the reactions which may take place in water solution in investigated samples with close composition. On the base of their conclusions and taking into account used ratios in our studies we consider that the following reactions are representing the formation of A, B and C types binders:

$$CaSO_4 \cdot 0.5H_2O + 1.5H_2O =$$
$$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \cdot 2H_2O \qquad (1)$$

$$CaO + H_2O = Ca^{2+} + 2OH^- = Ca(OH)_2 \qquad (2)$$

$$6Ca^{2+} + 2AlO_2^- + 3SO_4^{2-} + 4OH^- + 29H_2O =$$
$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O \qquad (3)$$

The TG curves of gypsum–lime–fayalite composite samples (Tables 1–3 and Fig. 4) confirmed that the mass losses fitted quite well with the above shown mechanism of thermal decomposition of hydrated products and initial components ratio. They are in a good agreement with the thermal effects, registered from the DTA curves (Figs 1–3) too.

Finally the solid phases in the hydrated products have been identified by the X-ray powder diffraction study. Identified solid phases in all dehydrated samples at temperature 1273 K are as follows: $CaSO_4$ (d, Å=3.49$_x$, 2.84, 2.20); $CaSiO_5$ (d, Å=3.03$_x$, 2.99, 2.49); SiO_2 (d, Å=3.34$_x$, 4.25, 1.81); Al_2O_3 (d, Å=2.55$_x$, 2.08, 1.60); $CaSiO_3$ – cubic (d, Å=2.52$_x$, 1.78, 2.06). Additionally in the dehydrated samples B and C existence of monoclinic $CaSiO_3$ (d, Å=2.97$_x$, 3.30, 3.51) and $Ca_2Al_2SiO_7$ (d, Å=2.84$_x$, 1.75, 3.06) is confirmed. Studied mixtures improve their mechanical strength during thermal treatment as the other authors [11–13] stated too.

Conclusions

On base of the investigation made and data obtained for the thermal behaviour of gypsum–lime–fayalite composites the following conclusions could be made:

- The thermal behavior of the new composite products obtained follows the integrated values of the main raw components, but it is more complicate because of the new solid phases formation and dehydratation processes (CSH, ettringite and gypsum phases).
- A, B and C types of composite binders have endo- and exothermal effects proportionally to the gypsum/lime mass ratio.
- Mass losses and endothermic effects determined, correspond well with the changes of the ratio between raw materials used.
- The binders type C is more likely to be used for processing products such as building blocks, tiles, boards, etc. due to the highest ettringite levels formed during hydration processes. Such a processing gives a possibility to utilize some of the wastes and avoid deposition.

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