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DIFFERENTIAL THERMAL ANALYSIS AND GIPSUM BINDERS

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Abstract

The application of differential thermal analysis as a method for identification of gypsum thermal treatment products is presented in this work. First for distinction α from β form of $CaSO_4 \cdot 0.5H_2O$, and second for recognition of undesirable double salt $Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$ formed during gypsum hydrothermal treatment in sodium salt solutions. Also, the application of differential thermal analysis for study of products of setting and hardening processes of β-anhydrite is presented here.

Keywords: thermal gypsum treatment, gypsum binders, hemihydrate, insoluble anhydrite, differential thermal analysis.

1. Introduction

The dehydration of gypsum ($CaSO_4 \cdot 2H_2O$), natural gypsum (selenite, alabaster) as well as so called waste gypsums (citrogypsum, phosphogypsum, borogypsum, FGD gypsum, etc.), is carried out in order to obtain: α-hemihydrate (α-$CaSO_4 \cdot 0.5H_2O$), or β-hemihydrate (β-$CaSO_4 \cdot 0.5H_2O$) or β–anhydrite (β-$CaSO_4$). When mix with water (in

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presence, or without additives) mentioned products of gypsum dehydration form $CaSO_4 \cdot 2H_2O$ and harden and can be used as binders in building industry, in medicine, in dentistry, etc.

The dehydration of gypsum can be performed under "dry", or "wet" conditions. A dry process is very simple and consists in gypsum heating in electric oven at suitable temperature. Two products: β-hemihydrate at 130-150 °C and β-anhydrite at 600-700 °C can be obtained on this way [1, 2]. A wet process is more complex. It consists in

hydrothermal gypsum treating in liquid medium, either in water at an increased pressure at a temperature between 110 and 160 °C [3] or in aqueous solutions of salts and inorganic acids at the respective boiling temperatures and atmospheric pressure [1, 4, 5]. The product of the hydrothermal process is usually the high-grade product - the α-hemihydrate [1, 4, 6, 7], but also the β-hemihydrate and the γ-anhydrite (γ–$CaSO_4$), depending on the process conditions (temperature, time of hydrothermal treatment, etc.), can be formed [3,8]. Besides, undesirable reactions between liquid media (salts) and calcium sulphate can take place during hydrothermal processes, giving double salts or complexes [9, 10].

The identification of products of gypsum dehydration performs by means of fallowing instrumental methods: X-ray diffraction analysis (XRD), infrared spectroscopy (IR) and differential thermal analysis (DTA).

The aim of this work was to emphasize the importance of DTA application for identification of products of gypsum dehydration. Namely, in this work two cases in which the identification of products of gypsum dehydration can not be realized without DTA are presented. First case is identification of a form of hemihydrate (α or β) and second case is identification of a double salt sodium pentacalcium sulphate trihydrate ($Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$), which can be formed, as undesirable product, during a hydrothermal treatment of gypsum in sodium salt solutions.

Also, the application of DTA for study of products formed during setting and hardening processes of β-anhydrite (mixed with water without additive and with water in presence of additive, e.g. Na_2SO_4) is shown.

2. Experimental

Natural selenite of very high chemical purity (0.33 mass % impurity) was used in the experiment.

In order to obtain hemihydrate of calcium sulphate the dehydration of selenite (size fraction –0.250+0.125 mm) was performed under "dry" conditions in laboratory electric oven at 130 °C during 3 hours (product 1), as well as under "wet" conditions, e.g. in salt solutions (products 2-7). The procedure for "wet" method was: ten grams of selenite (size fraction -0.125+0.25 mm) was boiled (at atmospheric pressure) in 50 cm^3 of aqueous salt solutions - 1 M and 2 M LiCl (products 2 and 3), 1 M and 2 M $NaNO_3$ (products 4 and 5), as well as 1 M and 2 M NaCl (products 6 and 7). The times of boiling were: 300 min for all 1 M solutions and 200 min for all 2 M solutions. The solid products obtained after boiling the selenite for the mentioned time intervals were separated from the solutions by vacuum filtration, rinsed in boiled distilled water to remove any trace of ions, and dried at 105 °C.

All mentioned seven products of selenite dehydration were investigated by means of XRD, IR-analysis and DTA.

The XRD powder technique was used. All samples were examined under the same conditions, using a Philips PW 1729 X-ray generator, a Philips PW 1710 diffractometer and the original APD software. The radiation source was an X-ray LLF tube with copper radiation and a graphite monochromator. The radiation was $\lambda CuK_{\alpha 1}$=0.15405 nm. The anode tube load was 40 KV and 35 mA. Slits of 1.0 and 0.1 mm were fixed. Samples were pressed into standard aluminium frames and measured in the 2θ range from 5° to 100°. Each 1/50° (0.02°) was measured for 0.5 s.

IR absorption spectra of the products were recorded with a Perkin Elmer spectrophotometer 782 in the range from 4000 to 400 cm^{-1}, using the KBr pressed disc technique.

A Derivatograph C (MOM, Budapest) was used for DTA of products: 1, 2, 3, 4 and 5. The sample mass was 0.04 g, and the atmosphere was air (in all five analyses). The heating rate was 20 °C·min^{-1}, in the range 20 to 1000 °C for products 1, 4 and 5. For products 2 and 3 the heating rate was 10 °C min^{-1}, in the range 20 to 500 °C. A Netsch STA 409 EP instrument was used for DTA of products 6 and 7.The sample mass was 0.04 g, and atmosphere was air. The samples were heated from 20 to 1000 °C at a heating rate of 20 °C min^{-1}.

In order to obtain insoluble anhydrite, e.g. β-anhydrite, the dehydration of selenite (size fraction –0.125+0.25 mm) was performed in laboratory electric oven at 650 °C during 4 hours (product 8). The chemical composition of this product was examined by IR analysis in the same way as it was mentioned forward. The product 8 was mixed with water without additive and with water in presence of additive (Na_2SO_4) at water/powder ratio of 0.33. On this way prepared two samples, after 28-day setting and hardening, were pulverized and DT analysed. The Chevenard Joimer instrument of type A.D.A.M.E.L. was used to obtain their differential thermal analysis curves. The weight of samples was 70 mg and the heating rate was 3.5 °C/min.

3. Results and discussion

Table 1. and Table 2. show the X-ray analytical results and. the characteristic absorption bands from IR spectra of the obtained products (from 1 to 7), respectively.

Table 1. X-ray diffraction data of the products

Product	The interplanar spacings, d (nm)				
1 (prepared by dry method)	0.5915	0.3444	0.2986	0.2795	0.1841
2 (obtained in 1 M LiCl)	0.5980	0.3459	0.2998	0.2806	0.1846
3 (obtained in 2 M LiCl)	0.5978	0.3459	0.2996	0.2807	0.1847
4 (obtained in 1 M $NaNO_3$)	0.5979	0.3462	0.2997	0.2804	0.1846
5 (obtained in 2 M $NaNO_3$)	0.5959	0.3455	0.2994	0.2799	0.1845
6 (obtained in 1 M NaCl)	0.5952	0.3442	0.2988	0.2794	0.1838
7 (obtained in 2 M NaCl)	0.5990	0.3463	0.3001	0.2803	0.1850

Table 2. IR data of the products

Product	Wavenumbers of absorption bands (cm^{-1})						
1 (prepared by dry method)	3615	3560	1620	1150-1090	1010	660	600
2 (obtained in 1 M LiCl)	3615	3560	1620	1150-1085	1010	660	600
3 (obtained in 2 M LiCl)	3600	3555	1615	1155-1085	1005	650	600
4 (obtained in 1 M $NaNO_3$)	3610	3550	1620	1150-1090	1005	655	600
5 (obtained in 2 M $NaNO_3$)	3610	3555	1625	1155-1095	1010	660	600
6 (obtained in 1 M NaCl)	3610	3550	1625	1150-1095	1010	660	600
7 (obtained in 2 M NaCl)	3600	3550	1620	1150-1095	1005	655	600

The X-ray results (Table 1.) were interpreted by using JCPDS (ASTM) card 33-310 and they confirmed that all products (from 1 to 7) were $CaSO_4 \cdot 0.5H_2O$.

According to literature data [11, 12, 13, 14] the IR spectra of all products (Table 2.) contain the absorption bands which are characteristic of $CaSO_4 \cdot 0.5H_2O$ and it was congruous with X-ray results. On the basis of the presented results in Table 1. and Table 2. it was concluded that all products of selenite dehydration (from 1 to 7) were hemihydrate of calcium sulphate. However, on the basis of these results it could not be possible to differentiate α and β forms of $CaSO_4 \cdot 0.5H_2O$, because their IR spectra and X-ray diffraction patterns are identical [11, 14, 15, 16].

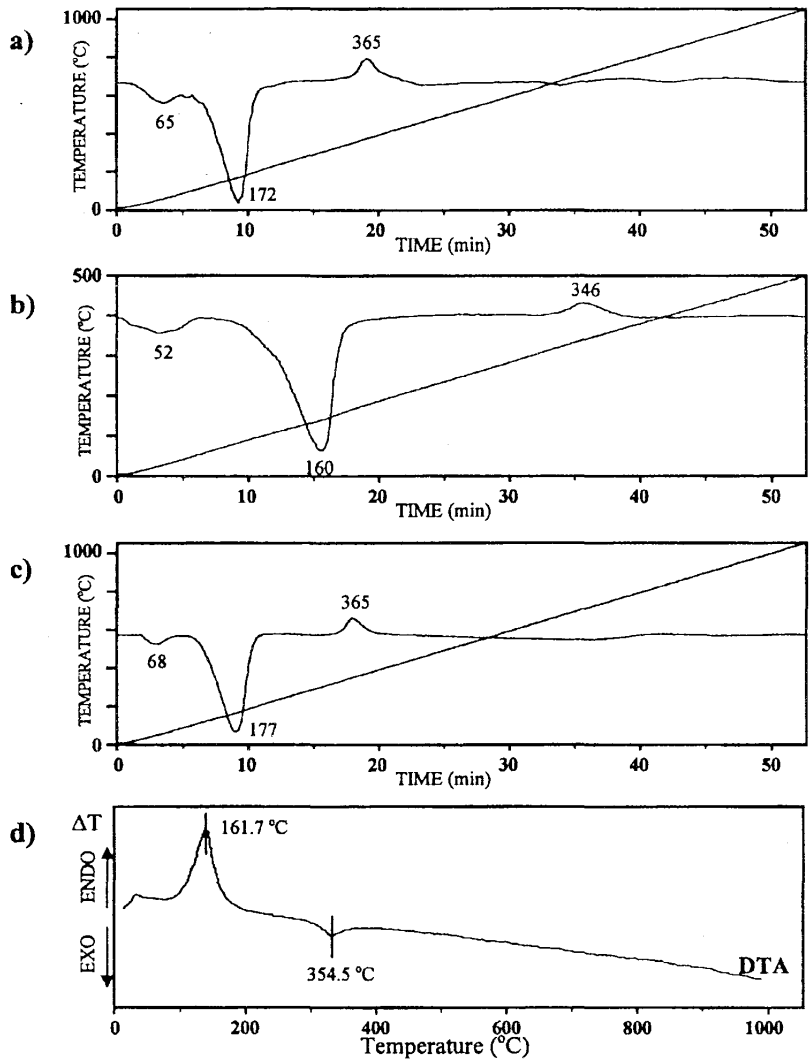

Fig. 1. DTA curves of: a) product 1 (prepared by dry method); b) product 2 (prepared in 1 M LiCl; c) product 4 (prepared in 1 M $NaNO_3$); d) product 6 (prepared in 1 M NaCl).

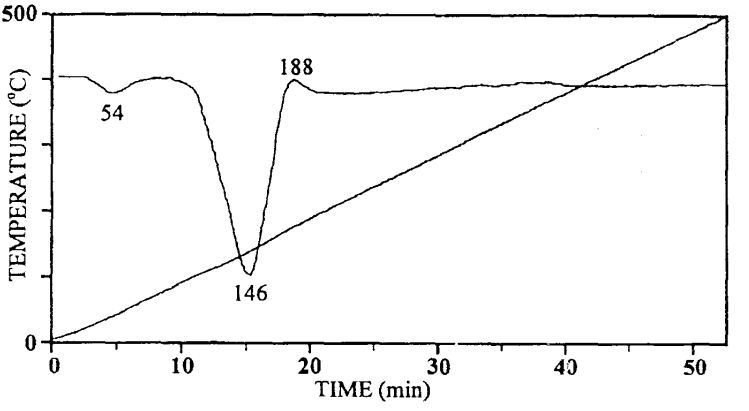

Fig. 2. DTA curve of product 3 (prepared in 2 M LiCl).

DTA curves of the products: 1 (hemihydrate prepared by dry method), 2 (hemihydrate obtained in 1 M LiCl), 4 (hemihydrate obtained in 1 M $NaNO_3$) and 6 (hemihydrate obtained in 1 M NaCl) are presented in Figure 1., whereas the DTA curve of product 3 (hemihydrate obtained in 2 M LiCl) is presented in Figure 2. As indicated by the presented data, the differential curves of all four products in Fig. 1. exhibit a large endothermal peak (at 172, 160, 177 and 161.7 °C, Fig. 1.a, 1.b, 1.c and 1.d, respectively), which correspond to transformation of hemihydrate ($CaSO_4 \cdot 0.5H_2O$) into soluble anhydrite ($CaSO_4$), and a small exothermal peak (at 365, 346, 365 and 354.5 °C in Fig. 1.a, 1.b, 1.c and 1.d, respectively), which is due to the conversion of soluble anhydrite (γ-$CaSO_4$) to insoluble anhydrite (β-$CaSO_4$). Very small endothermal peaks in DTA curves on Fig. 1.a, 1.b and 1.c at 65, 52 and 68 °C, respectively confirm small amount of absorbed water in the products 1, 2 and 4. The DTA curve in Fig. 2. has a large endothermal peak at 146 °C (transformation of hemihydrate to soluble anhydrite) and a small, sharp exothermal peak at 188 °C (conversion of soluble to insoluble anhydrite). There is, also, a small endothermal peak at 54 °C (Fig. 2.) which is due to absorbed water. The DTA curve in Figure 2. (for hemihydrate prepared in 2 M LiCl), in contrast to all DTA curves in Figure 1. (for hemihydrate obtained in 1 M solutions of LiCl, $NaNO_3$ and NaCl, or prepared by dry method), has the exothermal peak directly following the endothermal peak.

It means that the rate of transition of soluble anhydrite to insoluble anhydrite is greater for hemihydrate obtained in 2 M LiCl solution, than for hemihydrate obtained in 1 M solutions of LiCl, $NaNO_3$ and NaCl, or hemihydrate prepared by dry method. According to literature data [1, 15, 16, 17, 18, 19, 20] four DTA curves in Fig. 1. are differential thermograms of β-$CaSO_4 \cdot 0.5H_2O$ and the DTA curve in Fig. 2. is differential thermogram of α-$CaSO_4 \cdot 0.5H_2O$. Namely, according to mentioned literature data the difference between two forms of hemihydrate is in the perfection of their crystallities what is manifested in their differential thermal analysis exotherms; a small exotherm directly follows a large endotherm in DTA curve of α-form and it is located at lower temperature than an exotherm in DTA curve of β-form. This is very evidently comparing Fig. 1. and Fig. 2. presented in this work.

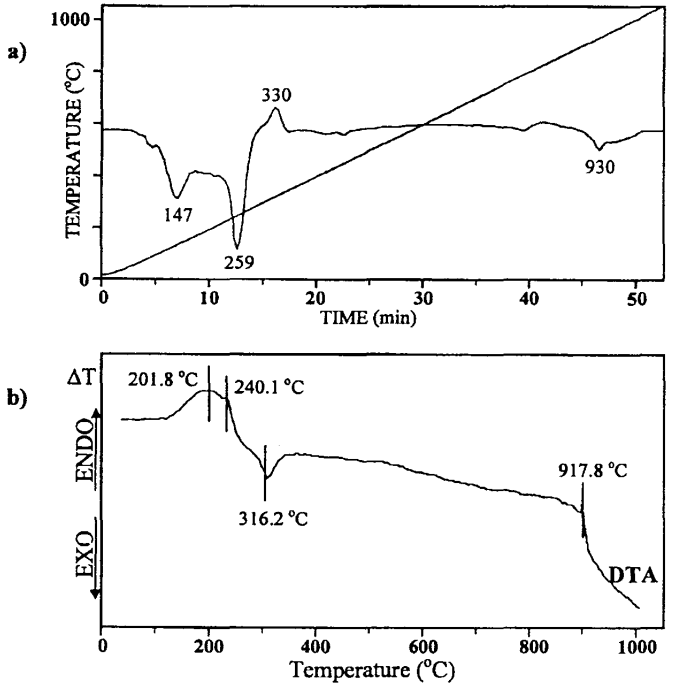

Fig. 3. DTA curve of: a) product 5 (prepared in 2 M $NaNO_3$); b) product 7 (prepared in 2 M NaCl).

DTA curves of products 5 and 7 (obtained in 2 M solutions of $NaNO_3$ and NaCl, respectively) are shown in Figure 3.. In spite of the endothermic peaks (at 147 and 201.8 °C, Fig. 3.a and 3.b) and the exothermic peaks (at 330 and 316.2 °C, Fig. 3.a and 3.b), which indicated the presence of hemihydrate, there were two endothermic peaks: at 259 and 930 °C in DTA curves of product obtained in 2 M $NaNO_3$ solution (Fig. 3.a) and 240.1 and 917.8 °C in DTA curve of product obtained in 2 M NaCl solution (Fig. 3.b). These peaks confirmed the presence of the double salt $Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$ [21, 22, 23] in the mentioned products. The first endothermic peaks were due to dehydration of $Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$ and its decomposition into soluble anhydrite ($CaSO_4$) and glauberite ($Na_2SO_4 \cdot CaSO_4$) [21,22,23], and the second to melting of products of glauberite decomposition [22]. The presence of a double salt $Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$ in products of selenite dehydration in 2 M solutions of $NaNO_3$ and NaCl couldn't be recognize by X-ray, or IR spectrometric analyses (see Table 1. and Table 2.), which was in connection with the fact that the X-ray diffraction pattern and IR absorption spectrum for the double salt are identical with those for the calcium sulphate hemihydrate (sodium ions replaced calcium isomorphously within the hemihydrate lattice) [21].

IR analysis of product 8 confirmed the β-anhydrite formation (absorption bands at: 1155-1130, 670, 610 and 595 cm^{-1}) according to literature data [11, 13].

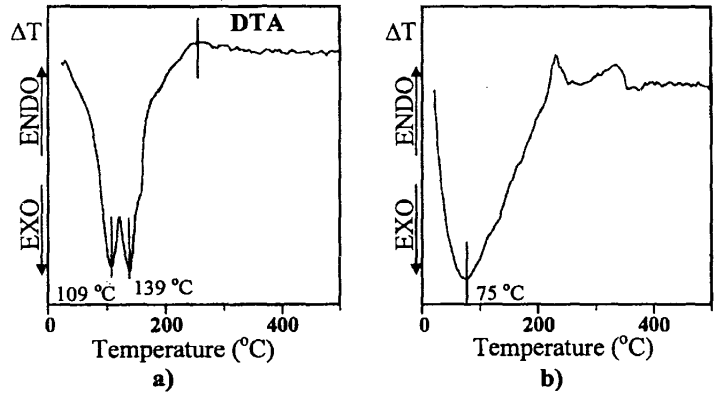

Fig. 4. DTA curves of samples prepared by mixing β-anhydrite: a) with water in presence of Na_2SO_4; b) with water without additive.

The DTA curves of samples prepared by mixing β-anhydrite (obtained in this work) with water in the presence of Na_2SO_4 and with water without additive, after 28-day setting and hardening, are presented in Figure 4.. The DTA curve of the sample prepared with water in presence of additive (Fig. 4.a) posses two endothermic peaks (at 109 and 139 °C) and one exothermic peak (at 250 °C), which is characteristic of $CaSO_4 \cdot 2H_2O$ [22]. These peaks are due to following transformations: 1. $CaSO_4 \cdot 2H_2O$ into β-$CaSO_4 \cdot 0.5H_2O$,

2. β-$CaSO_4 \cdot 0.5H_2O$ into γ-$CaSO_4$ and 3. γ-$CaSO_4$ to β-$CaSO_4$. The DT analysis of the sample prepared with water without additive (Fig. 4.b) indicated the nonformation of $CaSO_4 \cdot 2H_2O$ and showed that the β-anhydrite did not bind with the water without additive. The identification of formation or nonformation of $CaSO_4 \cdot 2H_2O$ by means of DTA is very important because it indicate good or bad mechanical properties of hardened samples.

4. Conclusion

The DTA is a very important and necessary method for identification of gypsum dehydration products (gypsum binders). Also, it can be applied for study of setting and hardening processes of gypsum binders.

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