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STUDY OF THERMAL BEHAVIOUR UP TO 1550° OF MATERIALS CONTAINING CALCIUM SULPHATE

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Thermal analysis up to 1550 °C on natural and synthetic materials containing $CaSO_4$ revealed the temperature ranges of dehydration, impurity content decomposition and $CaSO_4$ decomposition. $CaSO_4$ decomposition starts above 1200 °C and proceeds in several steps, depending on the CaO content. $CaSO_4$ forms several eutectic compositions with CaO (at 1340, 1390, 1410 and 1450 °C), each decomposition step being preceded by the formation and fusion of a eutectic composition, the decomposition taking place in the melt.

The thermal decomposition of calcium sulphate in the pure state or in various materials is a disputed subject in the literature; it depends upon the conditions and duration of burning, the particle size of the material subjected to calcination, and especially the amount and nature of impurities in the raw material. For instance, the starting temperature of $CaSO_4$ decomposition is given variedly as 900, 1000, 1030 or 1200° [1–6].

In the present paper, the thermal behaviour of natural and synthetic $CaSO_4$ within the temperature range 20–1550°, and the influence of CaO on the decomposition $CaSO_4 \rightleftharpoons CaO + SO_3$, were studied by thermal analysis.

CaO is the most frequent impurity in the raw material; it results from $CaSO_4$ decomposition, forming with it eutectic compositions of the type $m\text{CaSO}_4 \cdot n\text{CaO}$ [5, 12], and it plays an important part in the setting and hardening processes of some binders based on $CaSO_4$ [3–5].

Systems containing $CaSO_4$ in various forms have mostly been studied by thermal analysis, within different temperature ranges [7–12], under different experimental conditions [13–17] or in industry [18], and by other methods too [19, 20].

Experimental

A Paulik–Paulik–Erdey 2895 derivatograph equipped with a gas titrimeter was used in the determinations.

In order to find experimentally the end of the decomposition, and since the melt obtained up to 1550°, penetrating through the pores of the Al_2O_3 crucible while

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cooling, is welded to the bead of the thermocouple, a multiplate sample holder was used for the sample housing.

The working sensitivities for TG were 200 and 500 mg. The maximum working temperatures were 250° and 1550°, and the heating rates were 2.5 and 7.5° per minute, respectively. To obtain the TGT curve, nitrogen with a flow rate of 25 l/h was used as carrier gas, and NaOH solution at $pH = 9.0$ with 1% hydrogen peroxide as absorbent solution, the analysis being effected up to 1300°. The sample amount was 500 mg and Al_2O_3 was used as reference substance.

The substances and materials studied were as follows:

$CaSO_4$ p.a., plaster for construction (containing preponderantly β-$CaSO_4 \cdot 0.5\ H_2O$), pottery plaster, phosphogypsum, plaster containing preponderantly α-$CaSO_4 \cdot 0.5\ H_2O$, gypsum from various sources and therefore with different structures (the test speciments being referred to in the paper as gypsum, monocrystal gypsum and microcrystalline gypsum), and systems consisting of $CaSO_4$ and CaO of various compositions. For each system a great number od determinations were carried out. A selection of the experimental data obtained is presented.

Results and discussion

The results obtained are illustrated in Figs 1–6 and Table 1.

The effect recorded in the temperature range 20–60° (Figs 1 and 3) is assigned to the loss of water absorbed from the atmosphere from the surface of particles of α-$CaSO_4 \cdot 0.5\ H_2O$ and β-$CaSO_4 \cdot 0.5\ H_2O$ (component of plaster for construction), with maximum rate at 40°. This points to the metastability of the semihydrate as against the hydrate [5, 20] and demonstrates the necessity to keep semihydrate samples in an oven at 60° before chemical analysis.

The loss of crystal water from $CaSO_4$ dihydrate and from the α and β semihydrates, with the formation of anhydrite III, takes place in the temperature range 90–220°.

The dehydration kinetics is strongly influenced by the structure and by impurities in the material, as well as by the conditions under which the process takes place, such as temperature, heating rate, vapour pressure, humidity and particle size [5, 7, 8, 11, 13–20].

Although our determinations were carried out under the same experimental conditions, Figs 1–3 show the influence of the structure on the dehydration range.

The gypsum samples exhibit loss of crystal water in two distinct steps, at 90–140° and 140–170° (Fig. 3).

Monocrystal and microcrystalline gypsum lose crystal water in the range 90–220°, similarly in two steps (Fig. 2), but with different kinetics than for natural gypsum [5].

The plasters containing preponderantly β-$CaSO_4 \cdot 0.5\ H_2O$ undergo dehydration in the range 90–140°, and those with α-$CaSO_4 \cdot 0.5\ H_2O$ in the range 90–180° (Fig. 1).

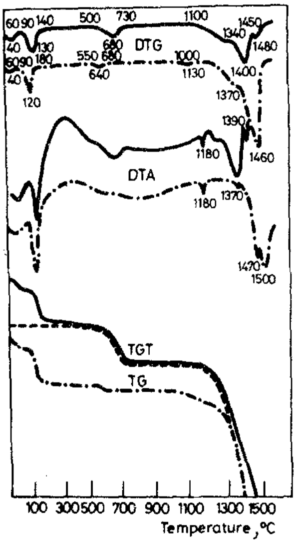

Fig. 1 TG, DTG and DTA curves of plaster of constrcution and plaster rich in α-$CaSO_4 \cdot 0.5\ H_2O$; TGT curve of plaster of construction. ——— plaster, —·—·— α-$CaSO_4 \cdot 0.5\ H_2O$

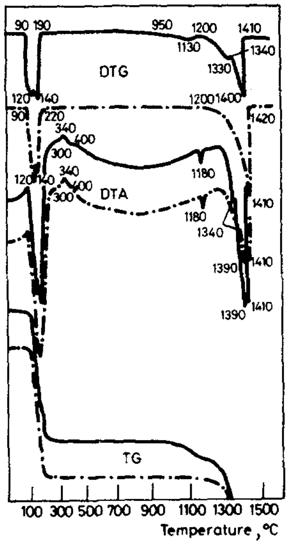

Fig. 2 TG, DTG and DTA curves of two crystalline samples of natural gypsum. ——— monocrystal gypsum, —·—·— monocrystalline gypsum

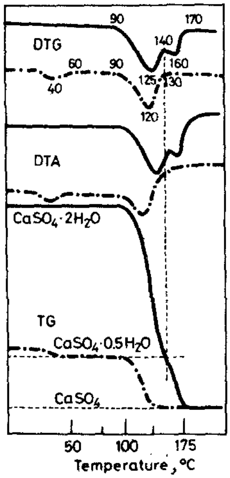

Fig. 3 Dehydration of gypsum and plaster for construction (heating rate 2.5 deg/min). ——— gypsum, —·—·— plaster

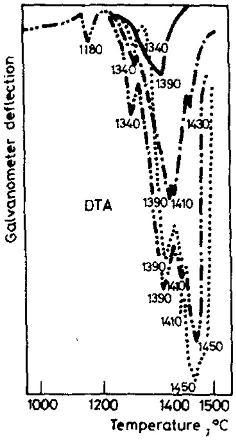

Fig. 4 Differential thermal analysis curves for $CaSO_4$ and mixtures of $CaSO_4$ and CaO in various mass ratios. $W_{CaSO_4} : W_{CaO}$; ——— 10 : 0, —·—·— 10 : 0.25, —··—··— 10 : 0.50, ... 10 : 2.00

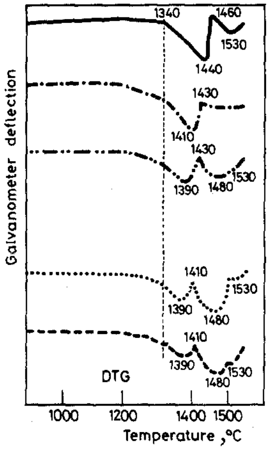

Fig. 5 DTG curves for $CaSO_4$ and mixtures of $CaSO_4$ and CaO in various mass ratios. $w_{CaSO_4}:w_{CaO}$: ——— 10 : 0, —.—.— 10 : 0.25, —..—..— 10 : 0.50, ... 10 : 2.00, – – – – – 10 : 4.00

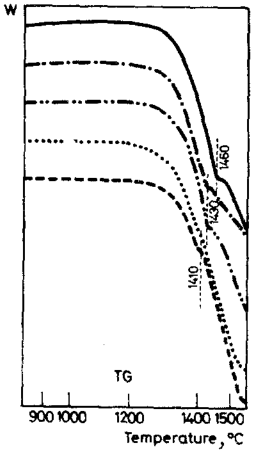

Fig. 6 TG curves for $CaSO_4$ and mixtures of $CaSO_4$ and CaO in various mass ratios. $w_{CaSO_4}:w_{CaO}$: ——— 10 : 0, —.—.— 10 : 0.25, —..—..— 10 : 0.50, ... 10 : 2.00, – – – – – 10 : 4.00

Table 1 $CaSO_4$ amount in various decomposition steps for synthetic mixtures of $CaSO_4$ p.a. and CaO p.a.

No.	$m_{CaSO_4}:m_{CaO}$	Temperature range °C	$CaSO_4$, % Decomposed	 Undecomposed
		1200–1340	8.5	
1	10 : 0*	1340–1460	5.8	9
		1460–1550	24.5	
		1200–1340	10	
2	10 : 0.25	1340–1430	44	22
		1430–1550	24	
		1200–1340	10	
3	10 : 0.5	1340–1430	44	12
		1430–1550	34	
		1200–1340	11	
4	10 : 2*	1340–1410	29	0
		1410–1550	60	
		1200–1340	11	
5	10 : 4	1340–1410	22	0
		1410–1550		

* The results represent the average made of three determinations.

In the temperature range 300–400°, the polymorphic transformation of anhydrite III to anhydrite II, seen in the DTA curve (Fig. 2), occurs with maximum rate at 340° for well-crystallized gypsums. This polymorphic transformation is less clearly outlined for the other synthetic gypsums and plasters, phosphogypsum and $CaSO_4$ p.a., the transformation occurs gradually up to 1000°, depending on the impurity content and especially on the pH of the material [9].

In the temperature range 500–730° (Fig. 1), carbonate decomposition takes place, especially that of calcium and magnesium carbonates [10] existing as impurities in the mineral, this effect being recorded for all samples of natural rocks.

To obtain additional information, two more determinations were performed. Simultaneously with the TG, DTG and DTA curves, the TGT curves (Fig. 1) were also recorded of CO_2 and SO_3 obtained during the decomposition; the effect at 500–730° was present in the $CaSO_4$–CaO system as well, the presence of $CaCO_3$ being explained by the fact that CaO added in the presence of water and CO_2 from the oven atmosphere is hydrated and then carbonated.

In some samples, a small weight loss at 950–1200° (Figs 1, 2), assigned to the decomposition of $MgSO_4$ impurity in the natural minerals [10], occurs with maximum rate at 1130°.

The endothermic effect of the polymorphic transformation of anhydrite II to anhydrite I [6] appeared in the DTA curve for all samples at 1180° (Figs 1, 2 and 4).

Above 1200°, the thermal decomposition effect of $CaSO_4$ is recorded (Figs 1, 2 and 4–6); this is produced in 2–4 steps, depending on the CaO content of the system. The second decomposition step for the $CaSO_4$ p.a. sample, which started at 1340°, is assigned to the decomposition of $CaSO_4$ from the eutectic composition (consisting of 18% CaO and 82% $CaSO_4$) formed at 1340° [6] from the CaO resulting in the first decomposition step and part of the remaining $CaSO_4$.

To establish these steps more exactly, thermal curves of mixtures of $CaSO_4$ p.a. and CaO p.a. of different compositions, expressed by mass ratios, were recorded.

The experimental data are illustrated in Figs 4–6 and Table 1. Increase of the CaO added intensified the DTA effect at 1340° (Fig, 4), indicating the formation of a larger amount of eutectic. A new decomposition step was also recorded in the DTG curve (Fig. 5), assigned to new decomposition of $CaSO_4$ from the melt of another eutectic. The effects recorded at 1390, 1410 and 1450° are ascribed to the formation of new eutectic compositions (Fig. 4).

DTA curves (Fig. 4) could be recorded only up to 1500°, because the melt which was formed led to a great difference between the thermal characteristics of the sample as compared to those of the reference substance. Identification of these eutectic compositions is difficult, for the DTA curve is the resultant of all the endothermic processes occurring within this temperature range.

With the increase of CaO in the system, the decomposition is finalized at 1530°, the weights of the last two eutectic compositions increasing at the expense of the first one (Figs 4 and 6, Table 1), this supporting the assumption that the decomposition occurs in the melt of the eutectic.

In gypsum with well-shaped crystals (Fig. 2), only the first 3 eutectics appear as the decomposition is completed up to 1420°.

The impurities in the natural minerals produce slight shifts in the melting temperatures of the eutectics formed (Fig. 1).

Applications

The determinations revealed that $CaSO_4$ starts to decompose at 1200°. Thus, CaO (an activator in the hardening of floor plaster obtained up to 1000° [1–5]) results from the decomposition of $CaCO_3$ impurities in the raw material and not from the decomposition of $CaSO_4$ [1–4].

Conclusions

Thermal analysis provided information on the dehydration of minerals containing $CaSO_4$ and on the temperature ranges in which transformations occur. The decomposition of $CaSO_4$ starts above 1200°, proceeds in several steps, depending on the impurity content, and is completed at about 1550°.

References

1 C. D. Nenițescu, General Chemistry, Ed. Didactică și Pedagogică, Bucharest 1979, p. 711, 909.

2 R. Ripan and I. Ceteanu, Chemistry of Metals, Ed. Didactică și Pedagogică, Bucharest, 1967, p. 223, 225.

3 Al. Steopoe, Materials of Construction, Ed. Tehnică, Bucharest, 1964, p. 109.

4 I. Ivanov, Materials for Construction, Installations and Equipment, Ed. Revista Construcții, Galați, 1975, p. 213.

5 I. Teoreanu, Technology of Binders and Concrete, Ed. Didactică și Pedagogică, Bucharest, 1967, p. 15–51.

6 Arai Jasuo, Jasul Tomatsu and Sugino Tetsuo, Nippan Kagaku, 5 (1975) 808-13 (Japan); C. A. 83,84048 W (1976).

7 A. A. Kondrashenkov and E. Bobkov, Izv. Akad. Nauk SSSR Neorg. Mater., 164 (1980) 707-9 (in Russian).

8 A. Ward and D. Tood, Ger. Offen, 3.000.314 (1980).

9 I. Teoreanu and S. Balașiu, Materials of Construction, 112 (1981) 69–74 (in Roumanian).

10 D. Todor, Thermal Analysis of Minerals, Ed. tehnică, Bucharest, 1972.

11 M. Murat and C. Comel, C. R. Hoad Sci. Ser. D, 270 (15) (1970) 1849-52 (in French).

12 S. Zima and T. Shishelova, Deposited Doc., Viniti 1978, p. 1020-78, 109-15 (in Russian).

13 I. Tanaka and M. Uchida, Funsai, 25 (1980) 28–33 (Japan), C. A. 95.66779 d (1982).

14 Japanese patent, 80.37.432 (1980).

15 T. Baba and S. Funabashi, Japanese patent, 80.37.434 (1980).

16 K. Nagata, Kogai Shigen Kenkyusho Iho, 8 (4) (1979) 39–51. (Japan), C. A. 91.197845 n (1980).

17 W. Hadrich and E. Kaisersberger, J. Thermal Anal., 1 (1980) 511-16.

18 B. Guilhot and J. P. Caspar, Zem-Kalk-Gips, Ed. B. 34 (3) (1981) 159-63 (in Germanian).

19 E. Karmazsin and M. Murat, Cim., Betons, Platres, Chaux, 715 (1978) 367–72 (in French), C. A. 92.27491 x (1980).

20 G. S. Teimurov and N. M. Mustafaev, Izv. Akad. Nauk SSSR, Neorg. Mater., 15 (8) (1979) 1489-91 (in Russian).

Zusammenfassung — Die thermische Analyse bis 1550 °C von $CaSO_4$ enthaltenden natürlichen und synthetischen Materialien hat gezeigt, daß Temperaturbereiche zu unterscheiden sind, in denen die Dehydratisierung und die Zersetzung von Verunreinigungen und $CaSO_4$ verlaufen. Die Zersetzung von $CaSO_4$ setzt oberhalb 1200 °C ein und verläuft, abhängig vom CaO-Gehalt der Probe, in mehreren Schritten. Es wurde festgestellt, daß Calciumsulfat mit CaO mehrere eutektische Gemische (bei 1340, 1390, 1410 und 1450 °C) bildet. Jedem Zersetzungsschritt geht die Bildung und das Schmelzen eines eutektischen Gemischs voraus. Die Zersetzung selbst geht in der Schmelze vor sich.

Резюме — Проведенный до температуры 1550 °C, термический анализ, природных и синтетических материалов, содержащих сульфат кальция, позволил определить температурные интервалы процессов дегидратации, содержания примесей и разложения сульфата кальция. Разложение последнего начитается выше 1200 °C и протекает в несколько стадий, в зависимости от содержания окиси кальция в образце. Установлено, что сульфат кальция и окись кальция образуют при температурах 1340, 1390, 1410 и 1450 °C несколько эвтектических смесей. Каждой стадии разложения предшествует образование и плавление эвтектики, а само разложение протекает в расплаве.