

# Dehydration of gypsum in the water suspension

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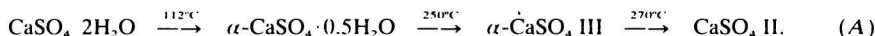
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It was confirmed that dehydration of gypsum in water suspension in an autoclave proceeds through hemihydrate to insoluble anhydrite, giving metastable soluble anhydrite as an intermediate.

Подтвердилось, что дегидрированием гипса во водной суспензии в автоклаве проходит через полигидрат на нерастворимый ангидрит с образованием метастабильного растворимого ангидрита.

Unlike the dehydration of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) on air there are different opinions about the chemism of dehydration in water suspension in an autoclave under hydrothermal conditions. In papers [1—4] it was found by means of the DTA method that the dehydration of gypsum proceeds in the same way as the dehydration on air



The DTA curves *a* and *b* (Fig. 1) show the course of the dehydration. The endothermic peaks at 112 and 250°C correspond to the formation of  $\alpha$  calcium sulfate hemihydrate ( $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) and of the soluble  $\alpha$  anhydrite ( $\alpha\text{-CaSO}_4 \text{ III}$ ). The exothermic peak at 270°C is due to polymorphic change and to the formation of an insoluble anhydrite ( $\text{CaSO}_4 \text{ II}$ ).

This chemism is confirmed also by [5] where at 213°C only  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  was found. Also in [6] on the DTA curve up to 200°C only one endothermic peak at 115°C was found belonging to the formation of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ .

Different type of the chemism of the gypsum dehydration under the same conditions using the DTA method is presented in [7]. According to the curve *c* in Fig. 1 the first endothermic peak at 131°C belongs to the formation of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  since the small exothermic peak at 172°C belongs to the formation of  $\text{CaSO}_4 \text{ II}$  according to the following reaction

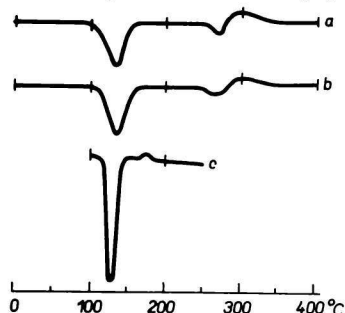
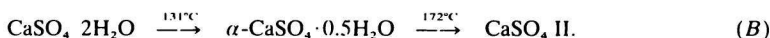


Fig. 1. DTA curves: *a*) natural gypsum; *b*) precipitated gypsum [2]; *c*) natural gypsum [7].

The authors do not admit the existence of  $\alpha$ -CaSO<sub>4</sub> III, not even as a metastable phase.

The results of the phase analysis of products of long-lasting dehydration of gypsum in water suspension in an autoclave at 150—210°C seem to confirm the proposed chemism. The resulting product was always CaSO<sub>4</sub> II [8—19].

### Experimental

The dehydration process of gypsum in water suspension under hydrothermal conditions was followed by the DTA method. Stone Model 200 DTA system and SH-15 BR 2-SS high pressure sample holder with type P platinel II differential thermocouple at 21 MPa pressure of N<sub>2</sub> to 400°C was used. About

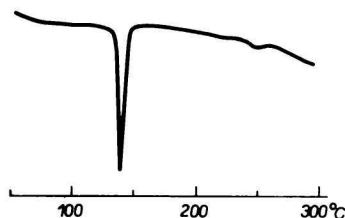


Fig. 2. DTA curve of precipitated gypsum.

35 mg of pure synthetic gypsum and 15 mg of water are placed in a 50  $\mu$ l cup SH-1-13 A which could be fitted with a lid to limit escape of water vapour. A pinhole was made in the lid so as to bring about an equilibrium of the water vapour pressure in the vessel. Sintered Al<sub>2</sub>O<sub>3</sub> was used as a reference. The increase in temperature was 5°C/min. The DTA curve is shown in Fig. 2.

### Discussion

It is evident from the DTA curve in Fig. 2 that the hydration of gypsum in water suspension under hydrothermal conditions proceeds according to the reaction (A) in accordance with papers [1—4]. The endothermic peaks at 130 and 235°C indicate the formation of  $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O and  $\alpha$ -CaSO<sub>4</sub> III, respectively. Next to those a small exothermic peak belonging to the formation of CaSO<sub>4</sub> II is observable. Natural gypsum revealed a very similar DTA curve.

The chemism of the dehydration according to (B) as proposed in paper [7], was not confirmed. This chemism, though thermodynamically possible, is less probable from the crystallochemical point of view. Upon releasing the water of crystallization from the structure of  $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O there is a great probability of formation of  $\alpha$ -CaSO<sub>4</sub> III which has a lattice identical with that of the hemihydrate.

At a slow dehydration of gypsum in an autoclave CaSO<sub>4</sub> II can be formed according to the reaction (A) also at temperatures under 235—250°C because above 25°C there is no thermodynamical equilibrium for the polymorphic change of  $\alpha$ -CaSO<sub>4</sub> III into CaSO<sub>4</sub> II [20].

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