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The Investigation of the Hydratation of Semi-hydrate Phosphogypsum by Thermal Analysis Methods

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By applying the method of thermal analysis it was investigated the kinetics of the hydration process of semi-hydrate phosphogypsum, which is a waste, generated in the production of extractive orthophosphoric acid in JSC Lifosa. The mineralogical composition of phosphogypsum ($CaSO_4 \cdot 0.5\,H_2O$ and $CaSO_4 \cdot 2\,H_2O$) under hydration was calculated. The heat quantity consumed during the dehydration of phosphogypsum was established, and the mechanical and physical properties of semi-hydrate phosphogypsum were analysed also.

Keywords: semi-hydrate phosphogypsum, hydratation, thermal analysis, mineral fertilizers.

INTRODUCTION

Phosphogypsum is a by-product, which is generated, in the technological process of producing orthophosphoric acid. This material ($CaSO_4 \cdot 0.5\,H_2O$, 95 % pure) is distinguished by binding properties, i.e. when mixed with water it undergoes hydration, binds and hardens.

Our previous investigations showed that setting time and compression strength of semi-hydrate phosphogypsum is different. It was established that the properties of materials depend on the composition of apatite used, the technological parameters of phosphoric acid production and the content of admixtures [1 – 3]. But in these studies it wasn't discussed hydratation of semi-hydrate phosphogypsum.

Close investigation of hydratation is necessary because it could help to find methods to control this process. This control is necessary in case of use phosphogypsum for the production of gypsum binding materials.

Hydratation process may be investigated using different methods: X-ray diffraction [4 – 6], electrical conductivity [7 – 9] and thermal analysis. By applying the method of thermal analysis, i.e. thermogravimetry (TG) and differential scanning calorimetry (DSC) it is possible to determinate the mineralogical composition of material [10, 11]. Elbeyli I.Y. *et al.* [12], Mandal P.K., Mandal T.K. [13], Strydom C.H. *et. al.* [14] and Strydom C.A. *et. al.* [15] employed this method for the investigation of final product from phosphogypsum. On the other hand, TG and DSC methods could be useful exploring the process of hydratation. Therefore our aim was to apply this method for analyze of the hydration process of semi-hydrate phosphogypsum.

MATERIALS AND METHODS

In this research two types of semi-hydrate phosphogypsum were used, they were made from apatites from Kirov and Kovdor (Russia) mines. All phosphogypsum were taken in the JSC "Lifosa" directly from a band transporter and dried in 100 ±5 °C temperature.

The chemical composition of materials was performed using PW 2404 X-Ray diffraction spectrometer. The semi-hydrate phosphogypsum for investigation was formed into tablets: 4 g of material and 0.4 g of wax, under the 10 t pressures.

The hydration water, which means ignition loss in phosphogypsum, was calculated after heating the materials in 400 °C temperatures.

The pH measurements were conducted in suspension (W/G = 10) by pH-meter 673 M.

The specific surface area of powder was determined by the method of Blain [16].

The physical and mechanical properties of phosphogypsum were established according to the GOST 23789-79 methods [17]. The only exception was that 2×2×2 cm size samples were formed up. Until complete hydration they were kept in a desiccator above water. At certain moments of time the compression strength and the degree of hydration, i.e. the quantity of hydration water, of the samples were determined. Compressed samples were submersed into absolute alcohol (further process of hydration was stopped) and crushed with a pestle. The obtained mass was filtrated and dried in 50 °C temperatures.

Employing a complex method of differential scanning calorimetry and thermogravimetry and using STA 409PC thermographer (NETSCH – Geratebau GmbH) thermal analysis was performed of the prepared samples. Thermal experiments were carried out between ambient temperature and 400 °C in an air atmosphere at a heating rate of 10 °C/min. Three curves were registered: DSC – differential scanning calorimetry, TG – thermogravimetry, DTG – differential thermogravimetry.

Both the ignition loss and the heat amount consumed during dehydration were calculated by using NETSCH Termokinetic Analysis computer programme of derivatogram processing [18].

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Table 1. The chemical composition of the semi-hydrate phosphogypsum, %

Semi-hydrate phosphogypsum	CaO	MgO	SO_3	P_2O_5	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	F	Other	Ign. loss
Kovdor	40.12	0.03	51.26	1.10	0.41	0.07	–	–	0.01	0.08	0.35	7.25
Kirov	38.19	0.01	49.79	1.40	0.34	0.21	0.10	0.26	0.08	0.08	2.76	6.90

RESULTS AND DISCUSSION

The chemical composition of semi-hydrate phosphogypsums got from apatites taken from different areas is presented in Table 1.

The composition of semi-hydrate phosphogypsum made from Kovdor apatite, if compared with semi-hydrate phosphogypsum from Kirov apatite, bears larger quantity of CaO and MgO but less amounts of Al_2O_3, P_2O_5 and other admixtures. Consequently, Kovdor apatite is cleaner in respect of calcium sulphate and apart from that, it is less contaminated. These facts have major impact on the hydration of the samples formed as well as related physical and mechanical properties during period of hardening (Table 2).

Hydration and hardening are one of the main factors predetermining the quality of gypsum binding material. Therefore, it is very important to analyse and explain regularities and reasons of these processes.

Kovdor phosphogypsum bound and hardened quickly than Kirov phosphogypsum. After 2 hours from the beginning of mixing its compressive strength equals 2.0 MPa. In the meantime Kirov phosphogypsum didn't start binding and hardening after 2 hours and acquired its initial, even though small compressive strength (0.75 MPa) only after 14 days (Table 2).

These properties depend on the rate of hydration process of semi-hydrate phosphogypsum, which can be evaluated by ignition loss of the material. This method is employed only to determine total ignition loss, i.e. the hydration water belonging to semi-hydrate calcium sulphate $CaSO_4 \cdot 0.5\,H_2O$ and dihydrate calcium sulphate $CaSO_4 \cdot 2\,H_2O$.

At the same time, using differential scanning calorimeter, temperature and exchange of heat as well as the rate of the change of sample mass were established under identical conditions. The DSC, TG and DTG derivatograms were obtained. Analysing these curves it is possible to evaluate changes taking place in a sample.

When applying the method of derivatographic analysis for hydration researches of phosphogypsum, it is possible to calculate the quantities of $CaSO_4 \cdot 0.5\,H_2O$ and $CaSO_4 \cdot 2\,H_2O$ during the period of hardening.

It is known that at the time of dehydration of dihydrate gypsum, at 120 – 170 ºC temperature, 1.5 H_2O molecules are splitted off (1 reaction), and at 170 – 210 °C temperature the remaining 0.5 molecules of H_2O are splitted off (2 reaction). These processes are reflected by two endothermic effects in DSC curve, loss of mass in TG curve, and the rate of exchange of mass in DTG curve [10 – 15].

$$CaSO_4 \cdot 2\,H_2O \rightarrow CaSO_4 \cdot 0.5\,H_2O + 1.5\,H_2O \quad (1)$$

$$CaSO_4 \cdot 0.5\,H_2O \rightarrow CaSO_4 + 0.5\,H_2O \quad (2)$$

The derivatogram of semi-hydrate phosphogypsum from Kirov apatite (DSC curve, Fig. 2a) contains just one endothermic effect, which has maximum at 192.7 ºC temperature. This indicates that the phosphogypsum contains only semi-hydrate calcium sulphate (ignition loss – 6.9 %). In the meantime, calorimetric DSC curve of semi-hydrate phosphogypsum from Kovdor apatite shows two endothermic effects: at 139.7 and 190.7 ºC temperatures (Fig. 1a). Therefore, we can draw a conclusion that Kovdor semi-hydrate phosphogypsum is hydrated and consists of semi-hydrate and dihydrate calcium sulphate (ignition loss – 7.25 %).

At the time H_2O molecules are split off under indicated temperatures, a sharp decrease of mass occurs, which is reflected in TG curve. At the time of heating hydrated phosphogypsum the 1.5 H_2O and 0.5 H_2O molecule splitting reactions' peaks of endothermic effects are covered each other (around 170 ºC), therefore, according to thermogravimetric curve TG it's quite problematic to determine which part of recorded mass change belongs to one and which to the other reaction. Additional information is given by the curve of differential thermogravimetric analysis DTG. Basing on DTG curve, it is possible to qualitatively and quantitatively evaluate TG curve.

At the time when dehydration reactions are taking place, DTG curve shows a point (in Fig. 1 – 2 marked by A) whereat is registered the end of the first reaction and the beginning of the second reaction [19]. According to our results, the greater phosphogypsum is hydrated (quantity of $CaSO_4 \cdot 2H_2O$ is bigger), the more the mentioned point A shifts to the side of higher temperatures. Therefore, one can state that it is impossible to precisely fix the end of the first reaction and the beginning of the second reaction of hydrated phosphogypsum. In a certain temperature interval and for a certain time both reactions are taking place. The greater phosphogypsum is hydrated the wider is temperature interval and for a longer time the first reaction takes place since more heat (of higher temperature) is required for the dehydration of phosphogypsum. In all derivatograms it is evident that dehydration of semi-hydrate phosphogypsum is started when dehydration of dihydrate phosphogypsum isn't finished in full, so in DSC curve endothermic effects are covered each other.

In TG curve it is marked point A', which corresponds to the point A in DTG curve, and calculated the change of mass, i.e. the quantity of hydration water and the quantities of $CaSO_4 \cdot 0.5\,H_2O$ and $CaSO_4 \cdot 2\,H_2O$. For instance, after 20 minutes total ignition loss of Kovdor phosphogypsum is 14.04 % (Fig. 1c). It means that the phosphogypsum consists of the mixture of dihydrate and semi-hydrate calcium sulphate. When analysing TG curve, one can notice that in the temperature interval of 130 – 170 ºC 1.5 H_2O molecules split off (1 reaction). By using

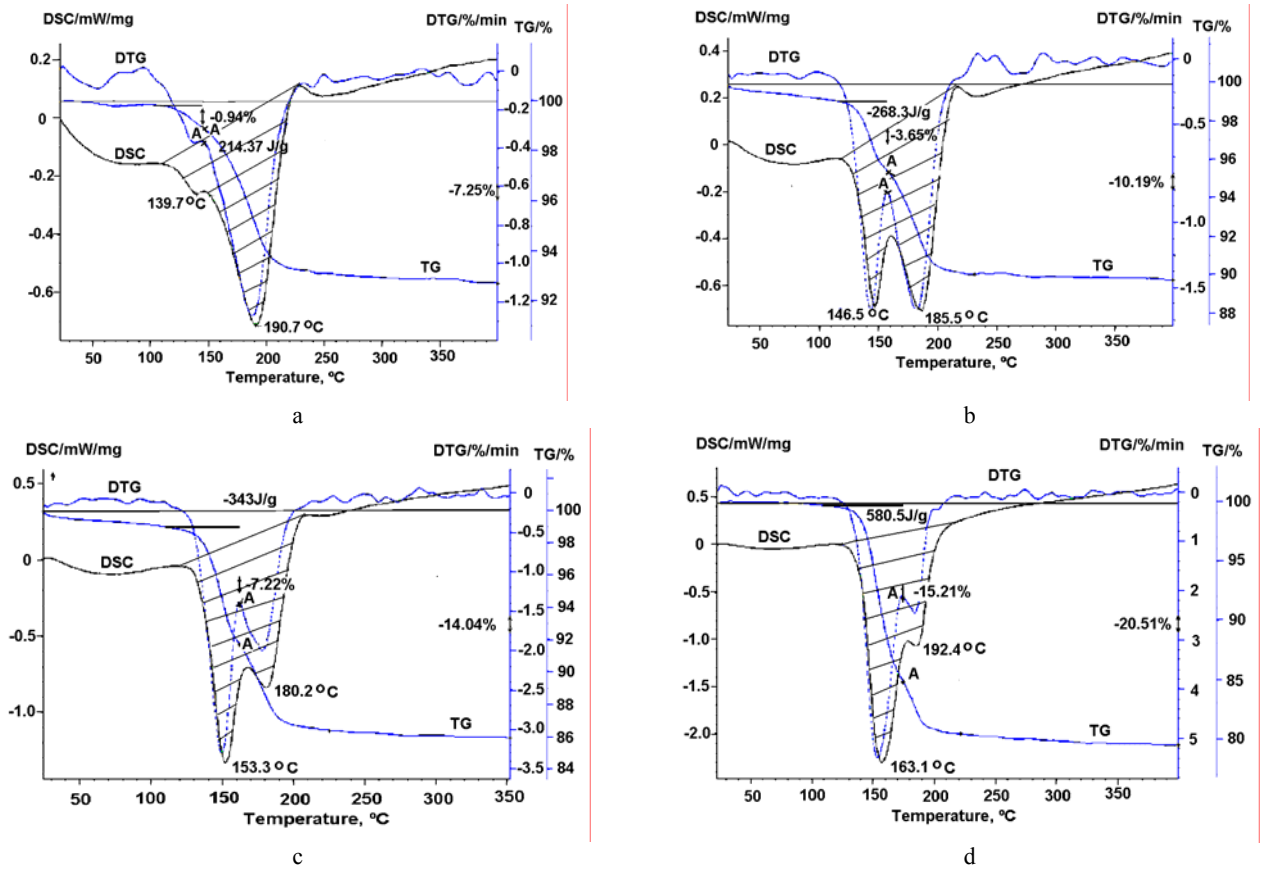

Fig. 1. TG-DTG-DSC curves of the Kovdor phosphogypsum. a – initial material, b – after 5 minutes of hydratation, c – after 20 minutes of hydratation, d – after 120 minutes of hydratation

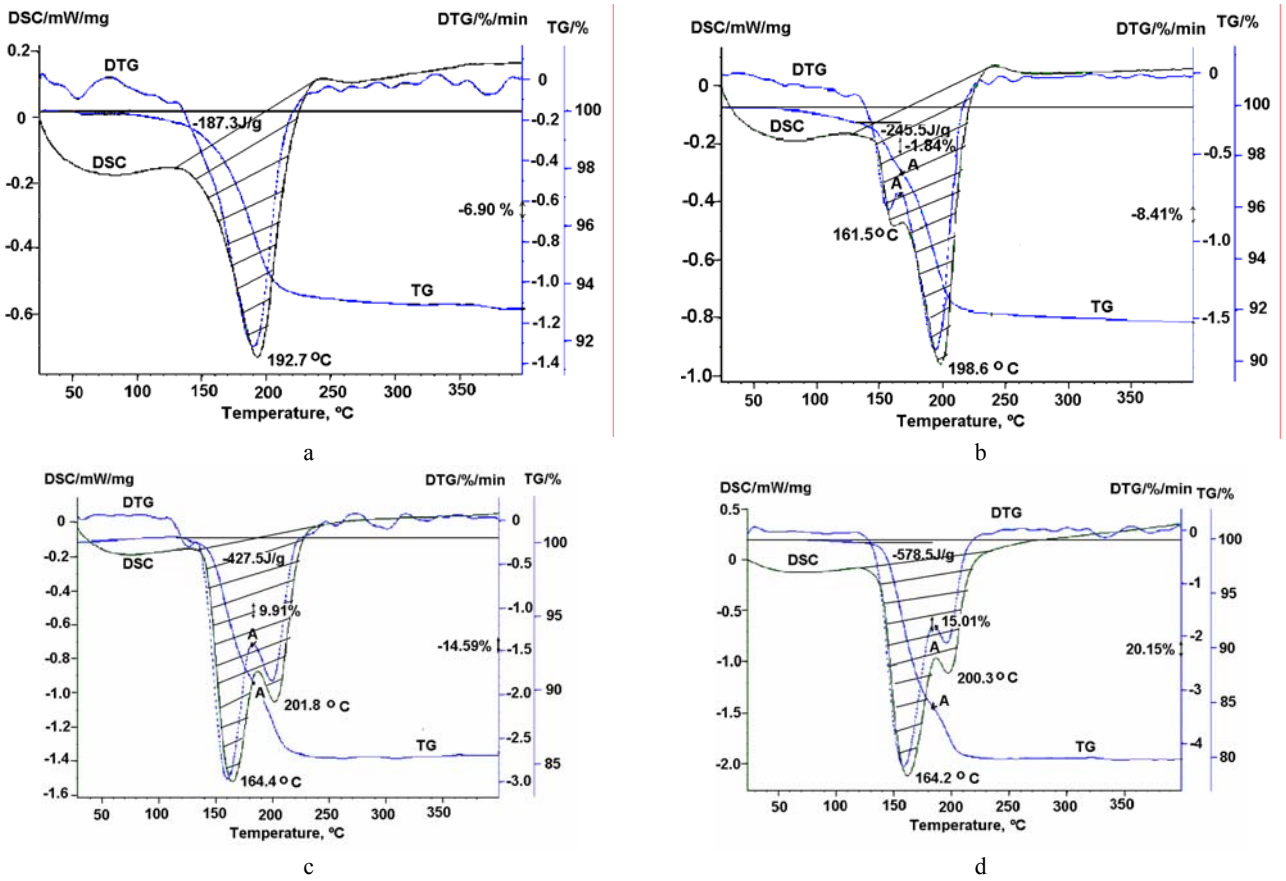

Fig. 2. TG-DTG-DSC curves of the Kirov phosphogypsum. a – initial material, b – after 3 days of hydratation, c – after 14 days of hydratation, d – after 105 days of hydratation

Table 2. The physical and mechanical properties of semi-hydrate phosphogypsum

Semi-hydrate phospho-gypsum	S, m^2/kg	Ign. loss, %	pH	W/G	Setting time, min		Ignition loss after minutes (min), h our (h) and days (d), % / Compressive strength after minutes (min), h our (h) and days (d), MPa							
					Initial	Final	5 min	20 min	2 h	1 d	3 d	14 d	105 d	dry sample
Kovdor	150	7.25	4.0	0.80	5	10	10.19 / –	14.04 / 0.75	20.31 / 2.0	20.51 / 2.3	20.51 / 2.3	20.51 / 2.3	20.51 / 2.3	20.51 / 7.0
Kirov	150	6.90	3.1	0.75	50	75	6.9 / –	6.9 / –	6.9 / –	8.26 / –	8.41 / –	14.59 / 0.75	20.15 / 1.0	20.15 / 1.5

computer data processing programme [18], it was calculated that these split off H_2O molecules account for 7.22 % of the total weight. In order to calculate mineralogical composition of phosphogypsum at a given moment, it is necessary to know total hydration of the substance (the transition of semi-hydrate calcium sulphate to 100 % dihydrate calcium sulphate) (Fig. 1d), which makes up 15.21 % of the weight of analysed phosphogypsum. Therefore, after 20 minutes of hydration, Kovdor phosphogypsum contains 47.47 % of dihydrate calcium sulphate, while the remaining part (52.53 %) consists of semi-hydrate calcium sulphate.

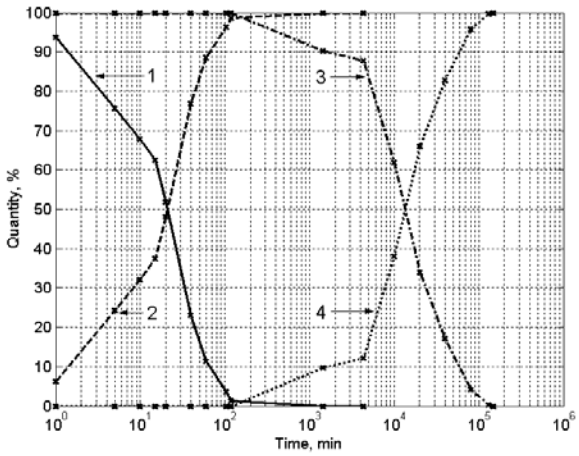

Fig. 3. The kinetics of change in mineralogical composition of semi-hydrate phosphogypsum on the time of hydration: 1 – Kovdor $CaSO_4 \cdot 0.5\,H_2O$, 2 – Kovdor $CaSO_4 \cdot 2\,H_2O$, 3 – Kirov $CaSO_4 \cdot 0.5\,H_2O$, 4 – Kirov $CaSO_4 \cdot 2\,H_2O$

Other curves of Kirov and Kovdor phosphogypsum were evaluated in an analogous way and the quantity of semi-hydrate and dihydrate calcium sulphate under certain moments in time was calculated. According to the results, kinetic curves of changes in mineralogical composition of Kirov and Kovdor phosphogypsums during the time of their hydration are presented in Fig. 3.

In practice it is very important to know the mineralogical composition after determining the quantity of hydration water. Therefore, basing on the data of derivatographic analysis it was formed the curves (Fig. 4), depicting the dependence of mineralogical composition of phosphogypsum on the quantity of hydration water.

As it was having already mentioned, when heating phosphogypsum between ambient temperature and 400 °C temperature, it undergoes dehydration and bound water splits off from it. This process absorbs heat (endothermal process). The larger amount of water is removed the larger quantity of heat is consumed. As we can see from DSC curves (Fig. 1, 2), the areas of endothermic effects are different. When applying a special thermogram processing computer programme [18] we have calculated the heat amount consumed during the dehydration of phosphogypsum (Fig. 5).

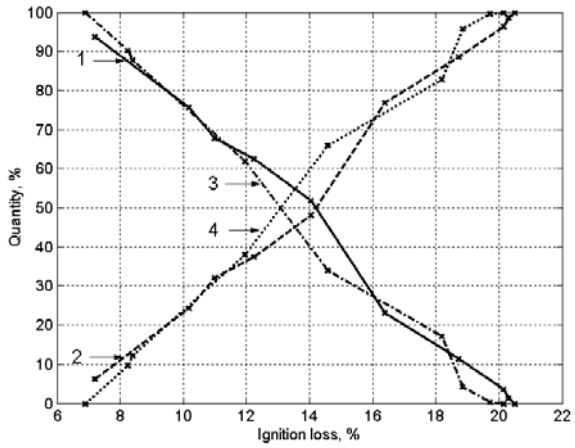

Fig. 4. The dependence of mineralogical composition of phosphogypsum on the quantity of hydration water: 1 – Kovdor $CaSO_4 \cdot 0.5\,H_2O$, 2 – Kovdor $CaSO_4 \cdot 2\,H_2O$, 3 – Kirov $CaSO_4 \cdot 0.5\,H_2O$, 4 – Kirov $CaSO_4 \cdot 2\,H_2O$

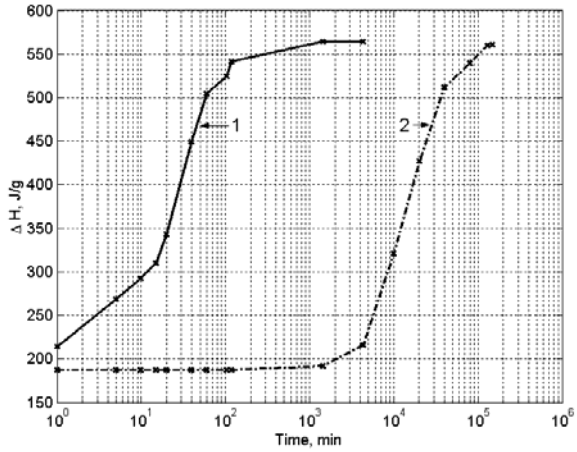

Fig. 5. The dependence of heat amount consumed during dehydration of phosphogypsum on the time of its hydration 1 – Kovdor phosphogypsum, 2 – Kirov phosphogypsum

Initial dehydration of phosphogypsum is consumed different amounts of heat: 187.3 J/g for Kirov and 214.37 J/g for Kovdor. Complete hydration of Kovdor phosphogypsum's ignition loss makes up 20.15 % and Kirov – 20.51 %. Heat of dehydration respectively is 580.5 J/g and 578.5 J/g. According to (3) it was determinated hydratation heat of phosphogypsum: Kovdor – 366.13 J/g and Kirov – 391.2 J/g.

$$H = H^{semihydr.} - H^{dihydr.}, \quad (3)$$

where: $H^{semihydr}$ is the amount of heat consumed for dehydration of semi-hydrate phosphogypsum, J/g; H^{dihydr} is the amount of heat consumed for dehydration of dihydrate phosphogypsum, J/g.

When analysing the hydration process of phosphogypsum, it was noticed a correlation between the amounts of heat consumed during dehydration of hydrated phosphogypsums (Fig. 5) and the change in mineralogical composition of phosphogypsum (Fig. 3).

CONCLUSIONS

1. By applying the method of derivatographic analysis, it was determined the change in mineralogical composition of phosphogypsum ($CaSO_4 \cdot 0.5\,H_2O$ and $CaSO_4 \cdot 2\,H_2O$) at the time of its hydration. The dependencies of mineralogical composition of phospshogypsums on the duration of hydration and the quantity of hydration water were composed.

2. With reference to results of derivatographic analysis of hydrated phosphogypsum it can be stated that dehydration of semi-hydrate phosphogypsum starts when dehydration of dihydrate phosphogypsum isn't finished in full, so in DSC curve endothermic effects are take place simultaneously.

3. By applying the method of derivatographic analysis we have calculated the quantity of heat necessary for the dehydration of hydrated phosphogypsum. It was determined that the higher is the quantity of dihydrate phosphogypsum, the larger quantity of heat is consumed for its dehydration.

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