

# INFLUENCE OF THE TECHNOLOGICAL PARAMETERS ON THE STRUCTURE AND PROPERTIES OF HEMI-HYDRATE PHOSPHOGYPSUM

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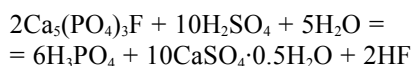
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*Industrial way of the production of ortho-phosphoric acid from apatite of various areas results in the waste product  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  having different structure and properties. To study the effect of the technological parameters on the formation of hemi-hydrate phosphogypsum, laboratory experiments of the decomposition of Kola apatites with sulphuric acid have been carried out and the properties of hemi-hydrate phosphogypsum investigated. The regulation the technological parameters of decomposition makes possible to obtain hemi-hydrate calcium sulphate which is characterized by well pronounced crystal structure and by good binding and physical-mechanical properties without additional processing.*

## INTRODUCTION

When producing one ton of ortho-phosphoric acid during the technological process, up to four tons of by-product: hemi-hydrate  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  or dihydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  phosphogypsum is formed. Currently, JSC "Lifosa" produces ortho-phosphoric acid by decomposing apatites with sulphuric acid according to so-called hemi-hydrate technology:



The main component is hemi-hydrate phosphogypsum  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , that corresponds to gypsum binding material according to the chemical composition, so it can be used to produce this building material and products of gypsum.

Our previous research [1,2] and industrial experience demonstrate that binding characteristics of hemi-hydrate phosphogypsum are not stable. In order to use this material, it is necessary to know the reasons for variation in the properties.

According to some authors [3, 4, 5, 6] technological parameters of the process of decomposing apatites with sulphuric acid and properties of the product obtained largely depend on the chemical composition of the raw material (apatites), temperature of decomposition and concentration of sulphuric acid. The reaction speed is greatest when the initial concentration of sulphuric acid in the liquid phase is about 30 %, but in this case very fine and frequently aggregated crystals are obtained [3].

The data [5] are available that the shape of forming calcium sulphate and size of the crystals depend on temperature, concentration of the acid, conditions of mixing and the degree of over saturation. They also depend on the ratio of  $\text{Ca}^{2+}$  to  $\text{SO}_4^{2-}$  ions in the solution and the concentrations of the Mg, Al, F compounds admixture. If there is  $\text{Ca}^{2+}$  surplus, the crystals form in the shape of tiny, fine needles of 20-80  $\mu\text{m}$ , and when there is  $\text{SO}_4^{2-}$  surplus, on the contrary, gypsum crystals are up to 100  $\mu\text{m}$  wide and a few hundred microns long.

Great influence on crystallization of hemi-hydrate gypsum is exerted by the quantity of  $\text{SO}_3$  in the liquid phase. In case  $\text{SO}_3$  is 10.5 - 17.4 g/l more crystals of tiny needle shape are formed [7].

Natural phosphates (apatites) contain a great quantity of Mg, Al, Fe and other compounds soluble in acids [3, 5], which make slower the reaction with sulphuric acid and have influence on crystallization of hemi-hydrate calcium sulphate. Al and F compounds that make complex  $[\text{AlF}_n]^{(3-n)+}$  ions in the solution have the greatest influence. They can be sorbed on the edges of the corresponding crystals, make conditions for the formation of isometric plated dihydrate gypsum crystals and hemi-hydrate gypsum hexagone edged prism crystals which easily joined into agglomerates [8, 9].

Dehydration of dihydrate and hemi-hydrate calcium sulphate in the solution of phosphoric acid accelerates in the presence of free  $\text{H}_2\text{SO}_4$ , and it becomes slower, if there are  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  ions [5]. The presence of  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  as additives affects calcium sulfate crystallization and leads to the formation of anhydrite, and calcium sulphate hemi-hydrate [10].

The important aspect is the high of crystallinity degree of phosphogypsum, which brings higher efficiency of filtration during the industrial process and improves binding properties of the final product [6].

The authors [11] presented facts about crystallization of phosphogypsum in a continuous phosphoric acid industrial plant (78°C, free sulfate 1.6-2.4 %,  $P_2O_5$  in filter acid 26-28 %, solid content 0-30 % and  $30 \pm 1.5$  %). The results show, that at the early stages of crystallization the primary nucleation was predominant. The secondary nucleation occurred at 5 hr running time (12.5 % solid content). Crystal growth rates were about 18.4  $\mu\text{m/hr}$  at 30 % solid content. In the steady state (16 hr running time and 30 % solid content), the mean diameter of the crystals and the average specific surface area is about 25  $\mu\text{m}$  and 0.69  $\text{m}^2/\text{g}$ , respectively.

JSC "Lifosa" decomposes apatites by using sulphuric acid of 93 % concentrations at 87-95°C temperature [12]. To increase the speed of crystallization of hemi-hydrate calcium sulphate and decrease the possibility of forming a new concentration centre, the degree of over saturation of calcium sulphate in the liquid phase is kept between 0.2-0.5.

When summarizing the literature data, it is possible to state that the structure and properties of by-product of decomposition of apatites with sulphuric acid depends on the chemical composition of the raw material (apatite). In addition, temperature of the technological process and the concentration of the sulphuric acid are very important. As the JSC "Lifosa" technological process is coordinated in such a way to obtain phosphoric acid of higher concentration and in greater quantities, no attention is focused on the characteristics of waste. On the other hand, if hemi-hydrate calcium sulphate has regular crystal structure, the filtrating process on the band filter is easier and lower content of  $P_2O_5$  remains in the waste. Therefore it is reasonable to regulate the production of phosphoric acid in accordance with the properties of phosphogypsum as well.

The objective of the work is to study the effect of the technological process on the structure and properties of hemi-hydrate gypsum resulting from decomposition of Kola apatites with sulphuric acid.

## EXPERIMENTAL

The chemical composition of Kola apatite samples (calculated for the dry product) is (%): CaO: 34.5;  $SO_3$ : 2.9; MgO: 2.8;  $R_2O_3$ : 16.8;  $P_2O_5$ : 41; F: 1.7; loss on ignition at 1000°C: 0.27 %. Specific surface area is 100  $\text{m}^2/\text{kg}$ . Figure 1, curve 1, shows corresponding the X-ray diffraction pattern.

Phosphogypsum (hemi-hydrate calcium sulphate) is a production waste of the phosphoric acid  $H_3PO_4$  which forms up when decomposing Kola apatites. The chemi-

cal composition of the phosphogypsum samples (calculated for the dry product) was (%): CaO: 31.0-37.0;  $SO_3$ : 48.0-54.0;  $SiO_2$ : 0.3-0.6;  $R_2O_3$ : 0.5-1.5;  $Na_2O$ : 0.24-0.32;  $K_2O$ : 0.04-0.08; total  $P_2O_5$ : 0.91-2.86; water soluble  $P_2O_{5ws}$ : 0.52-2.65; total  $F_c$ : 0.14-0.48; water soluble  $F_{ws}$ : 0.015-0.33. The moisture in phosphogypsum was 20-25 %, loss on ignition at 400°C was 5.9-8.6 %, density was 750-800  $\text{kg/m}^3$ , specific surface area by Blain was 102  $\text{m}^2/\text{kg}$ . The X-ray diffraction pattern is shown in figure 1, curve 2.

The chemical composition of the medical gypsum samples (calculated for the dry product) was (%): CaO: 36.5;  $SO_3$ : 53.9; MgO: 1.6; others: 2.8; loss on ignition at 400°C was 6.8 %. Specific surface area was 320  $\text{m}^2/\text{kg}$ . The X-ray diffraction pattern is presented by curve 4 in the figure 1.

In addition, we studied the gypsum widely applied in construction having chemical composition (%): CaO: 38.2;  $SO_3$ : 50.1; others: 4.9; loss on ignition at 400°C was 6.8 %. Specific surface area was 500  $\text{m}^2/\text{kg}$ . The X-ray diffraction pattern is shown in figure 1 by the curve 5.

Phosphogypsum (hemi-hydrate calcium sulphate) was formed during the reaction of sulphuric acid with Kola apatite, which has been carried out in the reactor of 3 l content with the constant stirring rate. The product was then filtered on vacuum filter and dried at  $110 \pm 5^\circ\text{C}$ .

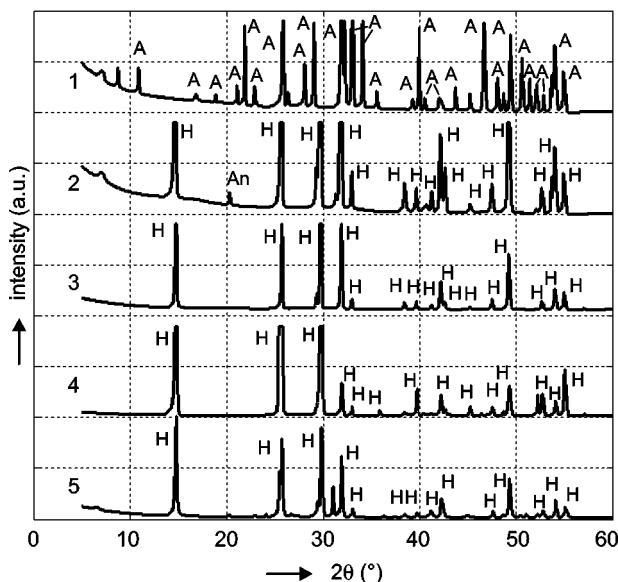


Figure 1. The X-ray diffraction patterns of Kola apatite and hemi-hydrate gypsum: 1 - Kola apatite, 2 - industrial hemi-hydrate gypsum, 3 - hemi-hydrate gypsum produced in the laboratory, 4 - medical gypsum, 5 - building material from gypsum. A - apatite, I - illite, H - hemi-hydrate gypsum, An - anhydrite.

In order to determine the amount of water-soluble admixtures; phosphogypsum was mixed with distilled water at the ratio 1:2. After half-an-hour of mixing the pulp was strained through a thick filter. Some part of water-soluble admixtures grew into the phosphogypsum crystals. They were determined by the procedure, when phosphogypsum washed in the aforementioned manner was mixed with distilled water (the solution should not be saturated with  $\text{CaSO}_4$ , i.e. the  $\text{CaSO}_4$  concentration should not be higher than 2.0 g/l). After the filtration, the admixture amount in the solution was analyzed. The undissolved particles were investigated using the microscope, X-ray diffraction analysis and chemical analysis. The amounts of total  $\text{P}_2\text{O}_5$ , water soluble and free phosphoric acid in phosphogypsum were determined according to GOST 20851 by using the yellow phosphor-vanadium-molybdenum complex. The total amount of other admixtures was analyzed by the complete chemical analysis according to GOST 5382. The  $\text{pH}$  measurements were conducted in suspension ( $\text{W/G} = 10$ ) by  $\text{pH}$ -meter 673 M. The physical-mechanical properties of gypsum binding material were determined according to the standard VS 23789-79. The specific surface was determined with the Blain apparatus.

The microscopic analysis was conducted with electronic microscope LEO 440i OXFORD ISIS; the voltage 20 kV, the current 50-200 pA, operating distance 15-20 mm. The surface of materials was gold-plated.

The X-ray powder diffraction data were collected with DRON-6 with Bragg-Brentano geometry by using Ni-filtered  $\text{Cu K}_\alpha$  radiation and graphite monochromator, operating with voltage 30 kV and emission current 20 mA. The step-scan covered the angular range  $5-60^\circ$  ( $2\theta$ ) in steps of  $2\theta = 0.02^\circ$ .

## RESULTS AND DISCUSSION

We compared the properties of phosphogypsum obtained in the laboratory with the properties of industrial, medical and building gypsum to evaluate the influence of the technological parameters on the structure and properties of the product.

Decomposition of apatites in the laboratory scale was performed under given technological conditions of the production of phosphoric acid in JSC "Lifosa" [12]. Table 1 summarizes the parameters of the procedure.

The physico-mechanical properties of gypsum binding material are presented in table 2.

The ratio of liquid to solid phases ( $\text{L/S}$ ) and the ratio of the quantity of apatite to phosphoric acid ( $\text{A/A}_\text{p}$ ) have been kept constant:  $\text{L/S} = 4.15$  and  $\text{A/A}_\text{p} = 1$ . The duration (4, 6 and 8 h) of isothermal exposure and the quantity of sulphuric acid have been changed that the ratio of apatite to sulphuric acid  $\text{A/A}_\text{s}$  would be 1.03, 1.09 and 1.14. The reaction has been carried out at 80, 90 and  $97^\circ\text{C}$  temperature. In all cases under above conditions pure hemi-hydrate calcium sulphate has been obtained. Their X-ray diffraction patterns are identical. One of them is presented in figure 1, curve 3.

Physical and mechanical properties of phosphogypsum produced in the laboratory become better due to the increase in the synthesis temperature and in the duration of isothermal exposure. The prepared material shows the best physical and mechanical properties at  $97^\circ\text{C}$ , when the duration of isothermal exposure was 8 h and the ratio of apatite to sulphuric acid was  $\text{A/A}_\text{s} = 1.03$ . Its compression strength was 2.25 MPa after 2 h, while for dry samples it was 9.0 MPa and after grinding up till specific surface area  $550 \text{ m}^2/\text{kg}$  the compression strength after 2 h of hydrating was 7.0 MPa and for dry samples it was 27.0 MPa.

Table 1. The effect of reaction parameters on the properties of hemi-hydrate gypsum.

No	Reaction parameters			Liquid phase		Solid phase			
	Ratio $\text{A/A}_\text{s}$	Temperature ( $^\circ\text{C}$ )	Time (h)	$\text{P}_2\text{O}_5$ (%)	$\text{SO}_4^{2-}$ (g/l)	$S$ ( $\text{m}^2/\text{kg}$ )	$\text{pH}$	$\text{P}_2\text{O}_5$ (%)	
								Total	Water soluble
1.	1.03	80	4	15.79	138.3	350	3.70	2.50	0.37
2.	1.14	80	4	20.13	148.8	350	3.45	2.90	0.40
3.	1.03	90	4	17.80	150.2	350	3.70	2.75	0.37
4.	1.09	90	4	33.68	238.5	350	3.28	2.50	0.58
5.	1.03	90	6	19.30	148.3	350	3.15	2.30	0.48
6.	1.03	80	8	16.35	158.7	350	3.64	2.35	0.39
7.	1.03	97	8	27.17	56.69	350	5.05	0.40	0.04
8*.	1.03	91	6	35.00	25.00	102	2.74	1.50	0.96
9*.	1.03	91	6	35.00	25.00	102	3.30	0.98	0.35

\* - industrial hemi-hydrate gypsum, A - apatite,  $\text{A}_\text{s}$  - sulphuric acid.

Table 2. The physical and mechanical properties of hemi-hydrate gypsum.

No	Ratio W/G	Setting time		Ignition loss (%)		Compression strength (MPa)	
		Initial (min)	Final (min)	Till the beginning of hydration	After 2 hour of hydration	After 2 hour of hydration	Dry samples
1.	0.80	9	12	6.40	19.00	2.50	4.50
2.	0.89	22	33	5.95	18.78	3.00	8.30
3.	0.84	10	12	6.09	19.30	3.00	5.00
4.	0.90	14	18	6.52	18.60	0.60	2.60
5.	0.88	22	24	5.77	19.28	2.00	7.50
6.	0.80	11	14	6.09	19.45	3.00	5.20
7.	0.78	3	5	5.16	18.90	2.25	9.00
8.*	0.75	-	-	5.91	5.91	-	-
9.*	0.72	342	420	8.64	9.81	-	1.60
10.**	0.38	12	14	6.80	19.24	9.54	28.50

\* - industrial hemi-hydrate gypsum, \*\* - medical gypsum, W - water.

Table 3. The effect of grinding on the properties of hemi-hydrate gypsum.

No	Specific surface (m <sup>2</sup> /kg)	Setting time		Ratio W/G	Ignition loss (%)		Compression strength (MPa)	
		Initial (min)	Final (min)		Till the beginning of hydration	After 2 hour of hydration	After 2 hour of hydration	Dry samples
1.	660	6	10	0.51	6.40	19.01	7.75	14.00
	350	9	12	0.80		19.00	2.50	4.50
2.	550	14	18	0.52	5.95	18.90	5.50	12.00
	350	22	33	0.89		18.78	3.00	8.30
7.	550	2	4	0.49	5.16	18.95	7.00	27.00
	350	3	5	0.78		18.90	2.25	9.00
8.*	332	-	-	0.44	5.91	5.91	-	-
	102	-	-	0.75		5.91	-	-
9.*	340	335	410	0.44	8.64	9.96	-	6.50
	102	342	420	0.72		9.81	-	1.63
10.**	500	4	7	0.48	6.88	17.10	7.00	14.90

\* - industrial hemi-hydrate gypsum, \*\* - binding material from gypsum.

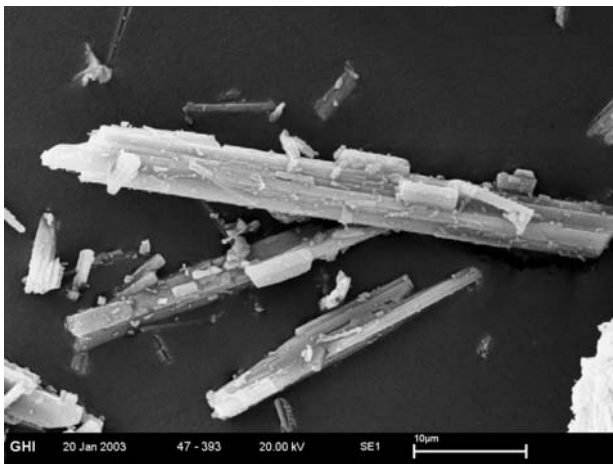


Figure 2. SEM micrograph of hemi-hydrate calcium sulphate obtained in the laboratory:  $P_2O_{5c} = 0.4\%$ ,  $P_2O_{5w.s.} = 0.04\%$ , loss on ignition = 5.16 %.

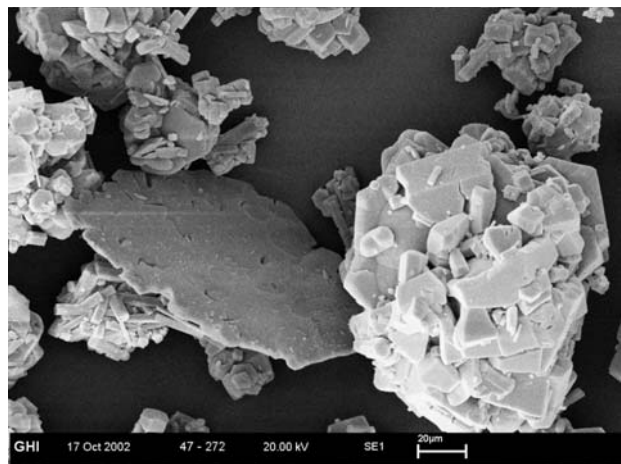


Figure 3. SEM micrograph of industrial hemi-hydrate calcium sulphate:  $P_2O_{5c} = 1.5\%$ ,  $P_2O_{5w.s.} = 0.96\%$ , loss on ignition = 5.91 %.

In addition, the material produced in the laboratory exhibited improved binding and hardening characteristics in comparison with industrial hemi-hydrate. Industrial phosphogypsum ( $P_2O_5 \text{ w.s.} = 0.35 \%$ ) of the same contamination level does not bind and harden after 2 h (loss on ignition = 9.81 %), while the compression strength of gypsum produced in the laboratory gains 3.0 MPa after 2 h (loss on ignition is 18.78 %).

Microscopic investigations of the products have shown that crystalline structure of the material produced in the laboratory is significantly different than crystalline structure of industrial and medical gypsum. It is made of regular oriented crystals of needle shape of 10-50  $\mu\text{m}$  long and 1.5-3.5  $\mu\text{m}$  wide (figure 2) while industrial hemi-hydrate calcium sulphate has irregular oriented crystalline structure (figure 3). The crystalline structure of the material produced in the laboratory has good ability to filtration and acidic admixtures soluble in water can be released easily. When the material is washed with water at 80 - 90°C, the remaining content of  $P_2O_5 \text{ w.s.}$  is only 0.04 %. Figure 4 presents distinctly crystalline structure of medical gypsum.

In order to explain the characteristics gained we performed detailed investigations of solubility and hydration of hemi-hydrate calcium sulphate.

The results of investigation of hemi-hydrate calcium sulphate of different crystalline structure, solubility and hydration, when the specific surface area of materials is the same ( $S = 500 \text{ m}^2/\text{kg}$ ) are described in figures 5 and 6. The solubility of the material produced in the laboratory is greater in comparison with industrial material and it is almost the same as the solubility of building and medical gypsum. When dissolving  $\text{CaSO}_4$  produced in the laboratory its quantity in the solution after 3 min was 7.49 g/l, in medical gypsum it was 7.89 g/l and in the case of industrial gypsum only 3.83 g/l. The hemi-hydrate calcium sulphate produced in the laboratory completely hydrates in 60 min (loss on



Figure 4. SEM micrograph of medical gypsum: loss on ignition = 6.88 %.

ignition is 19.20 %, figure 6 curve 2) and it is almost the same as medical gypsum (loss on ignition is 19.80 %, figure 6, curve 3). The properties of industrial phosphogypsum hydrated only 13.82 % during 2 hours. So it is possible to maintain that the material, which is better crystallized characterize its faster solution and hemi-hydrate hydration.

When summarizing the results of the presented investigation, it is possible to conclude that the controlling of the parameters of decomposing apatites with sulphuric acid makes possible to change the structure and properties of hemi-hydrate gypsum. The crystalline structure of hemi-hydrate is important factor determining its solubility, hydration and compression strength.

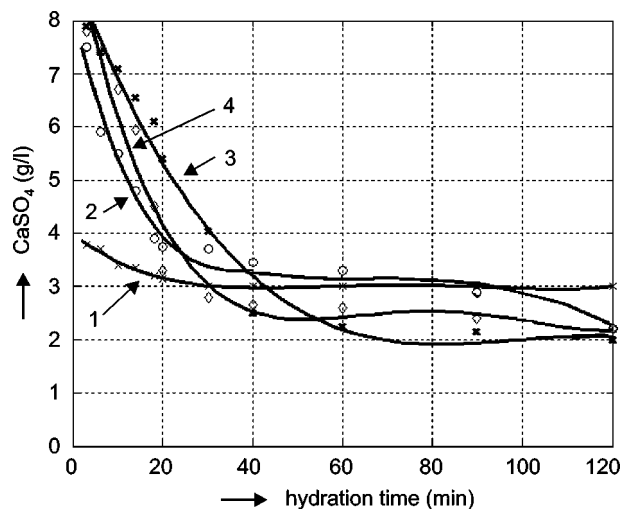


Figure 5. The investigations of solubility of hemi-hydrate gypsum: 1 - Industrial hemi-hydrate gypsum, 2 - hemi-hydrate gypsum produced in the laboratory, 3 - medical gypsum, 4 - building material from gypsum.

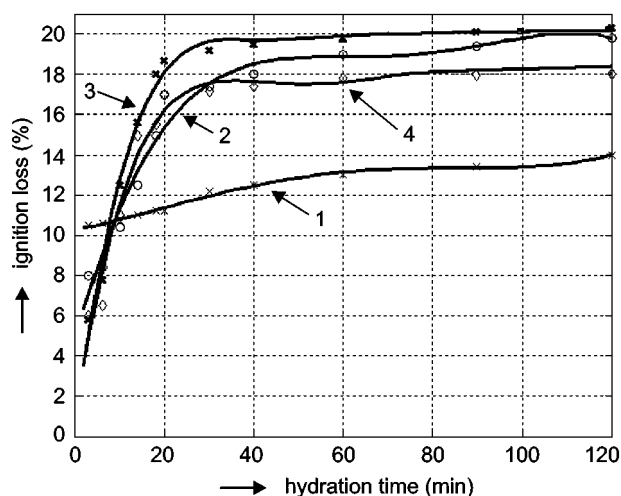


Figure 6. The investigation of hydration of hemi-hydrate gypsum: 1 - Industrial hemi-hydrate gypsum, 2 - hemi-hydrate gypsum produced in the laboratory, 3 - medical gypsum, 4 - building material from gypsum..

## CONCLUSIONS

1. By controlling parameters of the technological process of decomposing apatites by sulphuric acid it is possible to get hemi-hydrate calcium sulphate having appropriate physical and mechanical properties. The optimal conditions for the studied process are 8 hours decomposition at 97°C and the ratio apatite to sulphuric acid 1.03. The hemi-hydrate phosphogypsum produced in these conditions has compression strength 2.25 MPa after 2 h of hydration (9.0 MPa for dry samples). After grinding the compression strength increases up to 7.0 MPa, and for dry samples it becomes 27.0 MPa.
2. Microscopic investigation has shown that by controlling the technological parameters makes possible to increase significantly the degree of crystallinity of the material and to obtain hemi-hydrate phosphogypsum having regularly oriented needle shaped crystals of 10-50 µm long and 1.5-3.5 µm wide.
3. The investigation of solubility and hydration kinetics has proved that prepared hemihydrate calcium sulphate exhibits high value of solubility, fast hydration and good physical and mechanical properties as a consequence of properly crystalline structure of hemi-hydrate calcium sulphate.

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## VLIV TECHNOLOGICKÝCH PARAMETRŮ NA STRUKTURU A VLASTNOSTI HEMIHYDRÁTOVÉ SÁDRY

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Průmyslová produkce kyseliny ortho-fosforečné rozkladem apatitů z různých oblastí přináší odpadní produkt  $\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O}$  s odlišnou strukturou a vlastnostmi. Vliv technologických parametrů na tvorbu hemihydrátové sádry byl sledován při laboratorních experimentech rozkladu kola apatitů kyselinou sírovou. Regulace technologických parametrů tohoto rozkladu umožňuje získat hemihydrát síranu vápenatého s dobře vyvinutou krystalovou strukturou a dobrými pojivými fyzikálně mechanickými vlastnostmi bez následného zpracování.