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ИССЛЕДОВАНИЕ ПРОДУКТОВ ВЗАИМОДЕЙСТВИЯ ТЕХНИЧЕСКОГО ГИПСА С КАРБОНАТОМ НАТРИЯ: ХИМИЧЕСКИЙ И ФИЗИКО-ХИМИЧЕСКИЙ АНАЛИЗ

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Фосфорная кислота и фосфорсодержащие удобрения производят примерно 7 млрд. т фосфогипса (ФГ), который занимает сельскохозяйственные территории и ухудшает экологическую обстановку в близлежащих регионах. ФГ может быть использован в качестве мелиоранта или удобрения, термохимически переработан для производства серной кислоты и цемента, применен в строительных материалах и изделиях, а также может быть источником для получения сульфатов аммония, калия, натрия и карбоната кальция. Кроме того, его можно использовать в качестве пигмента, наполнителя для бумаги и резины. Одним из потенциальных методов переработки является щелочная конверсия ФГ в сульфат натрия и карбонат кальция. Процесс зависит от многих факторов, таких как: температура, время контакта, концентрация и расход карбоната натрия. Степень конверсии $CaSO_4$ ($К_{конв.}$) является основным показателем образования осадка карбоната кальция и раствора сульфата натрия. Химический анализ как твердой, так и жидкой фаз показывает, что при концентрации 20% карбоната натрия, 110% расхода карбоната натрия и температуре 80 °С в течение 30 мин достигается максимальный коэффициент конверсии - 97,07%. В данной работе установлено, что оптимальными условиями процесса являются: расход карбоната натрия – 105%, раствор карбоната натрия – 20%, время контакта - 60 мин и температура процесса – 80 °С. Результаты сканирующей электронной микроскопии и рентгеноструктурного анализа показывают морфологию, структуру и состав упаренной жидкой фазы и осадка из твердой фазы.

Ключевые слова: фосфогипс, карбонат натрия, коэффициент конверсии, карбонат кальция, сульфат натрия

PRODUCT INVESTIGATION BASED ON TECHNICAL GYPSUM REACTION WITH SODIUM CARBONATE: CHEMICAL AND PHYSICOCHEMICAL ANALYSES

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Phosphoric acid and phosphorus-containing fertilizers produce approximately 7 bil. t of phosphogypsum (PG), which occupies agricultural territories and worsens ecological conditions in nearby regions. PG can be utilized as an ameliorant or fertilizer, thermochemically treated to produce sulfuric acid and cement, used in building materials and products, and converted to obtain ammonium, potassium, sodium sulfates, and calcium carbonate. It can also be used as a pigment, filler paper, and rubber. One potential method is the alkaline conversion of PG to sodium sulfate and calcium carbonate. The process depends on temperature, contact time, concentration, and sodium carbonate consumption. The conversion coefficient ($C_{conv.}$) of $CaSO_4$ in PG is the main indi-

cator of the calcium carbonate precipitate and sodium sulfate solution formation. Chemical analysis of both solid and liquid phases reveals that the maximum $C_{conv.}$ value is 97.07% at a concentration of 20% sodium carbonate, 110% sodium carbonate consumption, and 80 °C for 30 min. The optimal conditions for the process include sodium carbonate consumption of 105%, 20% sodium carbonate solution, 60 min contact time, and 80 °C process temperature. SEM and XRD analysis reveal the morphology, structure, and composition of the evaporated liquid phase and precipitation from the solid phase.

Keywords: phosphogypsum, sodium carbonate, conversion coefficient, calcium carbonate, sodium sulfate

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INTRODUCTION

According to the U.S. Geological Survey, the global production of phosphate ore will be increased to 70 m. t of P_2O_5 (220 m. t of phosphate by 2050), and this is an annual increase of 2.5% of P_2O_5 [1].

The basis for the production of the phosphorus-containing fertilizers volume is the sulfuric acid decomposition of phosphate raw materials to produce wet process phosphoric acid (WPA). However, such production suffers from the accumulation of waste as phosphogypsum (PG), amounting to 150-180 m. tons per year [2, 3]. This causes a negative impact on the environment, occupying useful land areas.

The production of WPA is carried out by three known methods: dihydrate ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot 0.5H_2O$) and anhydride ($CaSO_4$) and which are the main sources of PG formation. Among the above, the most common is the dihydrate method as it is relatively simple and reliable in operation:

$$Ca_5(PO_4)_3F(s) + 5H_2SO_4(aq) + 2H_2O(l) \rightarrow$$
$$\rightarrow 3H_3PO_4(aq) + 5CaSO_4{\cdot}2H_2O(s) + HF(g) \qquad (I)$$

In the production of 1 ton of P_2O_5 in the form of WPA, on average, 4-6 tons of PG are formed. To date, the producers of WPA and phosphate fertilizers have accumulated about 7 bil. t of PG (USA, Russia, China, Brazil, *etc.*) [4, 5].

For instance, during sulfuric acid processing at JSC "Ammofos-Maxam" (Uzbekistan) 1 ton of washed calcined concentrate (WCC-26), composition (wt.%): 25.77 P_2O_5; 52.70 CaO; CaO:P_2O_5 = 2.05; 1.20 MgO; 0.63 Fe_2O_3; 1.15 Al_2O_3; 2.67 SO_3; 3.60 CO_2; 6.88 n.d. 2.378 t of wet PG is formed (1.594 kg of the solid phase and 782 kg of the liquid phase), or upon receipt of 1 t of P_2O_5 (with a yield of 92% in WPA), 10012 kg of wet PG (6708 kg of the solid phase and 3304 kg of the liquid phase) [6].

PG can affect on the environment with irreparable damage as negative as other technogenic hard wastes [7]. Because its nanoparticles <0.1 μm in size are of great ecological importance for life on our planet and the quality of the atmosphere. According to some sources, PG is a source of water, air, and soil pollution, which can injure human health and the ecosystem [8].

PG in its composition has more than 85% $CaSO_4$, strong acidity (pH < 3), and high moisture content, today only 15% of the world volume of FG is processed as building materials, agricultural fertilizers, ameliorants to stabilize acidic and alkaline soils, as well as setting regulator in the production of Portland cement [9-12].

In addition, PG is recommended for paving, the production of sulfuric acid, building gypsum, as well as raw materials for the extraction of rare earth elements (REE) and a medium for CO_2 binding and drainage improvement [13-14]. Despite positive feedback from developers and researchers, the problem of PG utilization is still challenging.

The most promising is the alkaline method of PG processing [15-22]. Generally, gypsum $CaSO_4$ is affected by salt solution such as $Na_2SO_4 – CaCl_2$-CO_2-H_2O, studied at 25 °C [23]. Therefore, study [25] on solubility of $CaSO_4$ become a reason for its interaction in alkaline solution. (Physicochemical Modeling of Precipitating and Dissolving of Gypsum in Chloride Solutions).

The most promising is the alkaline method of PG processing [15-22]. The essence of the conversion method for the processing of PG underlies equations (2-4): methods for converting gypsum with an ammonium carbonate solution [15], potassium carbonate [16] or sodium carbonate [14, 17-22], which contribute to the conversion of gypsum into more valuable products, such as ammonium and potassium sulfate, used in agriculture as fertilizers, as well as sodium sulfate, widely used in detergents, glass, *etc*. As regards to a by-product, calcium carbonate, will serve as a raw material for a highly consumed building material.

$$CaSO_4(s) + (NH_4)_2CO_3(aq) \rightarrow CaCO_3(s) + +(NH_4)_2SO_4(aq) \quad \text{(II)}$$

$$CaSO_4(s) + K_2CO_3(aq) \rightarrow \rightarrow CaCO_3(s) + K_2SO_4(aq) \quad \text{(III)}$$

$$CaSO_4(s) + Na_2CO_3(aq) \rightarrow \rightarrow CaCO_3(s) + Na_2SO_4(aq) \quad \text{(IV)}$$

At mentioned above, for economic reasons, the most suitable method is soda processing [17-22]. In these works, the process of calcium sulfate conversion is widely covered under the following parameters: sodium carbonate concentration – 240-260 g/dm^3, S : L = = 1 : 3, temperature 40-90 ^{o}C, the conversion coefficient of 96-98% [17]; sodium carbonate concentration constitutes 0.1 to 1 mol/l, molar ratio – $CaSO_4/CaCO_3$ = = 1.72, temperature – 25 ^{o}C, agitating time – 30 min, while the conversion coefficient is 96-98% [19]; the concentration of sodium carbonate is 30 %, L : S = 2 : 1, the temperature is 60 ^{o}C, the time is 10 min, and the conversion coefficient is 95.2 % [20].

In contrast to [17, 19, 20], in [18, 22] the processing of PG was carried out as follows. The conversion of gypsum was studied using 5, 10, and 15% PG suspensions at a molar ratio of Na_2CO_3 to $CaSO_4$ in gypsum (0.8, 1.4), times of 60 and 120 min, and stirrer speeds of 100, 300, and 500 rpm. The optimal condition for PG conversion turned out to be: concentration of PG suspension – 5 %, molar ratio $Na_2CO_3/CaSO_4$ = 2, stirrer rotation speed – 500 rpm and mixing time – 105 min. In [22], 1 kg of PG was preliminarily treated with 3 liters of 5 % citric or sulfuric acids at 60 °C for 30 min at a stirrer speed of 150 rpm. Then acidified gypsum in the second process was additionally treated with sea water in the amount of 1.5 L of water per 1 kg of PG for 30–45 min in order to get rid of heavy metal impurities. Purified PG after drying (at 65 °C for 24 h) was treated in a sodium carbonate solution at room temperature for 1.5 h. As a result, sodium sulfate was obtained with a purity of 94.9% [22].

Should be noted that sodium sulfate is of both fundamental and applied chemistry sciences, in which can describe polymorphism and polycrystalline skills [16].

Analyzing the results of the above works, we can conclude that PG from WCC-26 can be processed into sodium sulfate and chalk using a sodium carbonate solution.

The purpose of this study is to investigate various technological parameters for the process of PG conversion with soda (consumption norm and concentration of sodium carbonate, contact time, process temperature).

EXPERIMENTAL

PG was taken from JSC “Ammofos-Maxam” Fertilizer Company in Uzbekistan. The samples were preliminarily washed with distilled water and then dried. Afterward, dry PG was crushed to a particle size of 0.20 mm. Chemical composition of PG contents (wt.%): 33.28 CaO; 47.60 SO_3; 0.7 P_2O_5; 0.14 Al_2O_3; 0.05 Fe_2O_3; 0.41 F. To carry out the PG conversion process, we used sodium carbonate produced at UE Kungrad Soda Plant. The concentration of the Na_2CO_3 solution was ranged 10, 15, 20, and 30% and consumption of towards the gypsum in PG was taken as 100, 105 and 110% of the stoichiometry for the formation of sodium sulfate and calcium carbonate (equation 4). The contact time varied from 15 to 120 min. The temperature was studied in the range from 20 to 90 °C.

Generally, to understand the yield product from the reaction some indicators are accepted, for instance, conversion degree or like one.

To determine the degree of gypsum conversion, the following formulas were proposed in [17-20]:

$$\alpha = (SO_4^{2-}\,(L)/\,(SO_4^{2-}\,(S) \times 100\% \quad \text{(V)}$$

where, α – conversion degree, %; SO_4^{2-} (L) – content of sulfate ions in the solution, g; SO_4^{2-} (S) – content of sulfate ions in the solid phase (precipitate), g.

However, we accept conversion coefficient ($C_{conv.}$) to calculate in terms of complexity elimination during the process as:

$$C_{conv.} = 1 - \frac{m_1 \cdot W_1 - m_2 \cdot W_2}{m_1 \cdot W_1}\,\% \quad \text{(VI)}$$

where, m_1 and W_1 are the weight and mass fraction of SO_3 in the sample of PG, g.; m_2 and W_2 are the weight and mass fraction of SO_3 in the sample of washed and precipitation of PG after conversion, g.

Experiments on the determination of $C_{conv.}$ were carried out as follows: after completion of the conversion process, the reaction mass was filtered on a Buchner funnel under a residual pressure of 100-150 mm Hg, using one layer of filter paper.

Then the solid phase was washed with hot distilled water (80 °C) at a ratio of PG to H_2O = 1:4. The thus obtained wet washed precipitate was subjected to drying at 95 °C, and then, together with the liquid phase, the content of Na_2O, CaO, SO_3, and CO_2 was analyzed according to known methods [25]. Na_2O was determined by flame photometry on a Sherwood model 360 instrument (Germany), and CaO was determined by complexometric titration.

Morphological studies of the samples surface of sodium sulfate and calcium carbonate crystals obtained from the liquid and solid phases were carried out using a SEM-EVO MA 10 scanning electron microscope (Carl Zeiss, Germany) with an Aztec Energy Advanced X-Act-Oxford Instruments X-ray spectrometer.

This device is designed for microscopic analysis of structure and defects, including the determination of the local elemental composition using energy dispersive spectroscopy. Crystal images were taken at various scales ranging from 100 μm, 20 μm, and 10 μm using Smart SEM software. The pictures were taken triple and one of them was chosen.

The characteristics of PG and its conversion products were determined by X-ray diffraction (XRD) analysis. XRD patterns were taken on a LabX XRD-6100 X-ray diffractometer (Shimadzu, Japan) with Cu-anode radiation, scanning step 4°/min. (ω/2θ-coupling), the intensity measurement time at the scanning points was 0.5 s, the tube voltage was 40 kV, the current strength was 30 mA, and the scanning angle was varied from 4 to 80°. Diffraction maxima were identified using the International Center for Diffraction Data, 2013. Phases were identified using Profex and Match! Phase Analysis Report for 2019 and 2021 versions.

RESULTS AND DISCUSSION

The concentration of sodium carbonate was varied in the range from 5 to 30% with the establishment of the solid and liquid phases composition. At the same time, the conversion coefficient, C_{conv}, of gypsum, is established depending on the concentration of the soda solution. The experiments were carried out under constant conditions: sodium carbonate consumption norm – 105%, contact time – 30 min. and temperature – 80 °C. The results are shown in table 1.

Table 1

The composition of the solid and liquid phases of PG conversion products depends on the concentration of sodium carbonate (Na_2CO_3 norm – 105%, contact time – 30 min, temperature – 80 °C)

***Таблица 1.* Состав твердой и жидкой фаз продуктов конверсии PG зависит от концентрации карбоната натрия (норма Na_2CO_3 – 105%, время контакта – 30 мин, температура – 80°C)**

Concentration of Na_2CO_3, %	Content, %					Concentration of Na_2SO_4, %
	W_{moist}	CaO	SO_3	Na_2O	CO_2	
Solid phase						
5	43.68	42.3	12.2	10.6	36.5	-
10	38.64	44.9	11.1	9.08	37.7	-
15	29.41	45.7	8.93	7.08	38.7	-
20	23.95	48.6	4.58	3.73	40.9	-
25	21.19	48.8	4.16	3.24	42.0	-
30	19.35	50.7	3.54	2.67	42.5	-
Liquid phase						
5	94.20	0.63	3.25	2.88	0.16	7.12
10	86.10	0.75	6.51	5.31	0.33	12.10
15	83.47	0.78	10.7	8.77	0.41	17.08
20	75.64	0.80	16.0	13.0	0.59	20.32
25	67.41	0.86	21.6	17.5	0.71	25.08
30	62.87	0.93	24.8	19.6	0.82	30.46

It can be seen from the table that with an increase in the concentration of sodium carbonate, the content of CaO and CO_2 in the solid phase increases from 42.32 to 50.73% and from 36.56 to 42.57%, respectively. On the other hand, the content of SO_3, Na_2O and humidity decrease from 12.23 to 3.54%, from 10.68 to 2.67% and 43.68 to 19.35%, respectively. The higher the concentration of sodium carbonate, the lower the water content in the sediment. In the liquid phase, a different picture is observed. The content of SO_3 and Na_2O, on the contrary, increases from 3.25 to 24.81% and from 2.88 to 19.62%, respectively. At the same time, the contents of CaO and CO_2 in the liquid phase decrease from 0.632 to 0.930% and from 0.168 to 0.828%, respectively. The formation of SO_3 and Na_2O in the liquid phase indicates the appearance of sodium sulfate in the range from 7.12 to 30.46%, respectively, for a Na_2CO_3 solution concentration in a range from 5 to 30%.

An increase in the concentration of sodium carbonate from 5 to 30% leads to an increase in the conversion coefficient of calcium sulfate in PG from 82.14 to 95.44% (Fig. 1). The optimal concentration of sodium carbonate can be considered 20%, at which of gypsum conversion coefficient is achieved 94%.

The effect of the sodium carbonate composition norm on the solid and liquid phases, as well as the of gypsum conversion coefficient at a constant sodium carbonate concentration of 20%, contact time of 30 min and a temperature of 80 °C was studied (Table 2 and Fig. 2). From Table 2 it follows that with an increase in the sodium carbonate norm from 100 to 110% of the stoichiometry, the content of CaO and CO_2 in the solid phase gradually increases from 47.61 to 50.60 and from 40.21 to 42.70%, respectively.

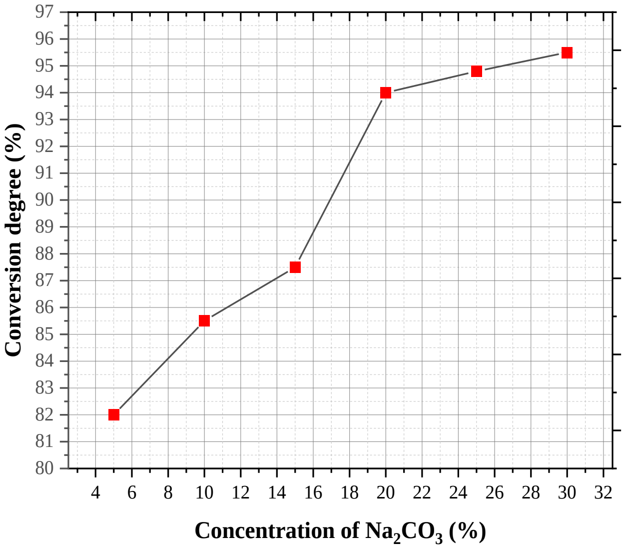


Fig. 1. Calcium sulfate conversion coefficient versus sodium carbonate concentration

Рис. 1. Зависимость коэффициента конверсии сульфата кальция от концентрации карбоната натрия

Table 2

The composition of the solid and liquid phases of phosphogypsum conversion products depending on the sodium carbonate rate (Na_2CO_3 concentration – 20%, contact time – 30 min, temperature – 80 °C)

Таблица 2. **Состав твердой и жидкой фаз продуктов переработки фосфогипса в зависимости от содержания карбоната натрия (концентрация Na_2CO_3 – 20%, время контакта – 30 мин, температура – 80 °C)**

Norm of Na_2CO_3, %	Content, %					Concentration of Na_2SO_4, %
	W_{moist}	CaO	SO_3	Na_2O	CO_2	
Solid phase						
100	27.03	47.6	5.70	4.26	40.2	-
105	23.95	48.6	4.58	3.73	40.9	-
110	22.86	50.6	2.15	1.84	42.7	-
Liquid phase						
100	77.45	0.65	14.4	11.2	0.52	19.83
105	75.64	0.70	16.0	13.0	0.59	20.32
110	73.35	0.24	17.5	14.8	0.22	20.89

The similar phenomena are observed with respect to the liquid phase, where the content of SO_3 and Na_2O increases from 14.45 to 17.54 and from 11.28 to 14.84%, respectively. Wherein, the moisture content in the solid and liquid phases varies from 27.03 to 22.86 and from 77.45 to 73.35%, respectively.

An increase in the gypsum conversion coefficient from 92.65 to 97.07% (Fig. 2) slightly affects the concentration of the sodium sulfate production solution, only from 19.83 to 20.89% (Table 2). An increase in the norm of sodium carbonate, although it allows the maximum conversion of gypsum into sodium sulfate, but at the same time there is sodium carbonate in the composition of the solution. In this regard, the optimal norm of sodium carbonate can be considered 105%, where the conversion coefficient of gypsum exceeds 97%.

The influence of contact time on the composition of the liquid and solid phases, as well as on the conversion coefficient of gypsum and the concentration of the production solution of sodium sulfate was studied in the range from 15 to 120 min, while the process temperature is 80 °C, and the norm and concentration of sodium carbonate are 105% and 20%, respectively. The results are presented in Table 3 and in Fig. 3. From the obtained results, it can be seen that with an increase in the contact time from 15 to 120 min in the solid phase of the conversion products, the content of CaO, SO_3, Na_2O and CO_2 varies within 47.81-50.86; 3.09-6.11; 2.10-3.92 and 39.95-42.35 %, respectively.

Whereas the moisture content before drying is in the range of 22.72-25.14%. In the liquid phase, the content of CaO, SO_3, Na_2O and CO_2 varies within 0.394-0.930; 14.86-17.20; 12.49-13.74 and 0.336-0.613%. From the data, it can be assumed that calcium carbonate is formed in the solid phase, and sodium sulfate is formed in the liquid phase. With the studied contact time in the liquid phase, the content of sodium sulfate is 18.17-20.63%, and water 73.09-76.27%.

In a case, the main indicator, the gypsum conversion coefficient, varies from 92.60 to 96.81% (Fig. 3). The optimal time can be noted as 60 min, at which the conversion coefficient reaches 96.71%.

Temperature is the main factor in the PG conversion process. The effect of temperature at 105% norm and 20% sodium carbonate concentration and time of 30 min was studied (Table 4 and Fig. 4). It is shown that with an increase in temperature from 20 to 90 °C in the solid phase, the content of CaO and CO_2 increases from 48.92 to 51.14 and from 40.19 to 42.57%, and SO_3 and Na_2O decrease from 5.73 to 3.37 and from 4.52 to 2.20%. The wet solid phase before drying has a moisture content of 22.07-23.27%. In respect of the liquid phase, there is a decrease in the content of CaO and CO_2 from 0.714 to 0.403 and from 0.688 to 0.324%; therefore, an increase in the content of SO_3 and Na_2O from 13.96 to 17.64 and from 11.40 to 14.19%.

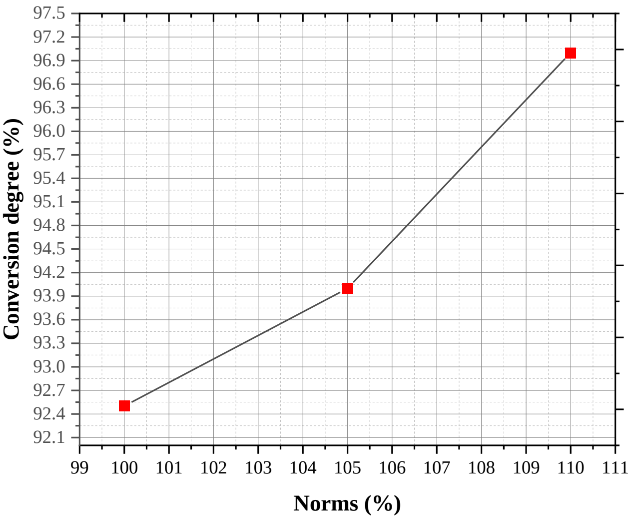


Fig. 2. Calcium sulfate conversion coefficient versus sodium carbonate norm

Рис. 2. Соотношение коэффициента конверсии сульфата кальция и нормы карбоната натрия

Table 3

The composition of the solid and liquid phases of the phosphogypsum conversion products depends on the contact time (Na_2CO_3 norm – 105%, Na_2CO_3 concentration – 20%, temperature – 80 °C)

***Таблица 3.* Состав твердой и жидкой фаз продуктов превращения фосфогипса зависит от времени контакта (норма Na_2CO_3 - 105%, концентрация Na_2CO_3 – 20%, температура – 80 °C)**

Contact time, min	Content, %					Concentration of Na_2SO_4, %
	W_{moist}	CaO	SO_3	Na_2O	CO_2	
Solid phase						
15	25.14	47.8	6.11	3.92	39.9	-
30	23.95	48.6	5.8	3.73	40.9	-
45	23.58	49.5	4.97	3.41	41.4	-
60	23.11	50.6	3.21	2.15	42.2	-
75	22.93	50.7	3.20	2.18	42.2	-
90	22.84	50.8	3.15	2.21	42.2	-
105	22.73	50.8	3.13	2.18	42.3	-
120	22.72	50.8	3.09	2.10	42.3	-
Liquid phase						
15	76.27	0.93	14.8	12.4	0.61	18.17
30	75.64	0.80	15.5	13.0	0.59	18.51
45	74.83	0.63	16.4	13.5	0.44	19.65
60	73.25	0.42	17.3	13.9	0.35	20.13
75	73.26	0.41	17.3	13.9	0.35	20.22
90	73.21	0.40	17.3	13.8	0.35	20.39
105	73.14	0.40	17.2	13.7	0.34	20.56
120	73.09	0.39	17.2	13.7	0.33	20.63

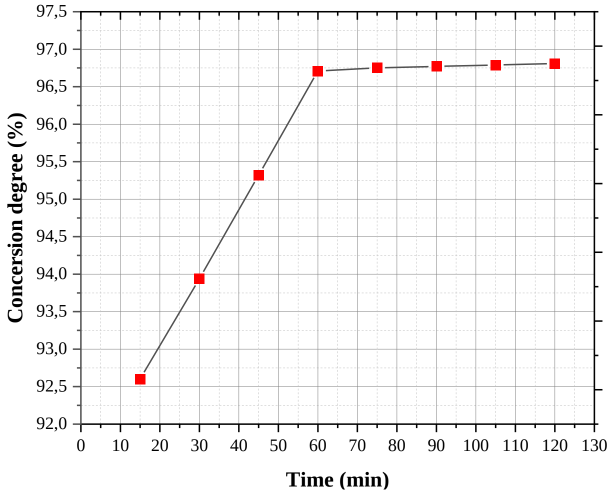


Fig. 3. Dependence of the conversion degree on time
Рис. 3. Зависимость степени преобразования от времени

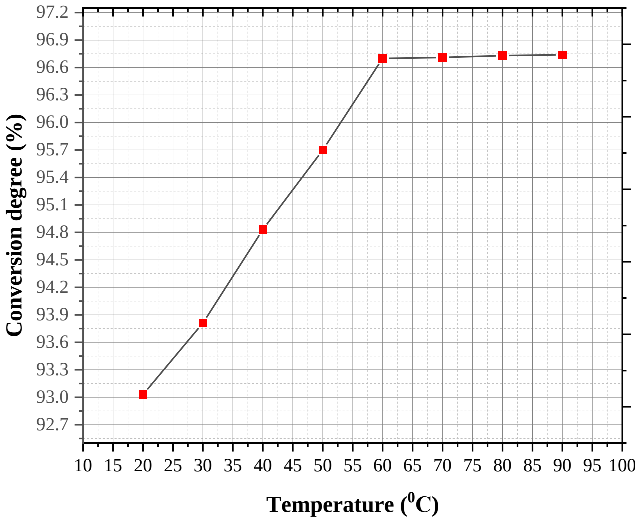


Fig. 4. Calcium sulfate conversion coefficient versus temperature
Рис. 4. Зависимость коэффициента превращения сульфата кальция от температуры

Table 4

The composition of the solid and liquid phases of phosphogypsum conversion products depending on the process temperature (Na_2CO_3 norm – 105%, Na_2CO_3 concentration – 20%, contact time – 30 min)

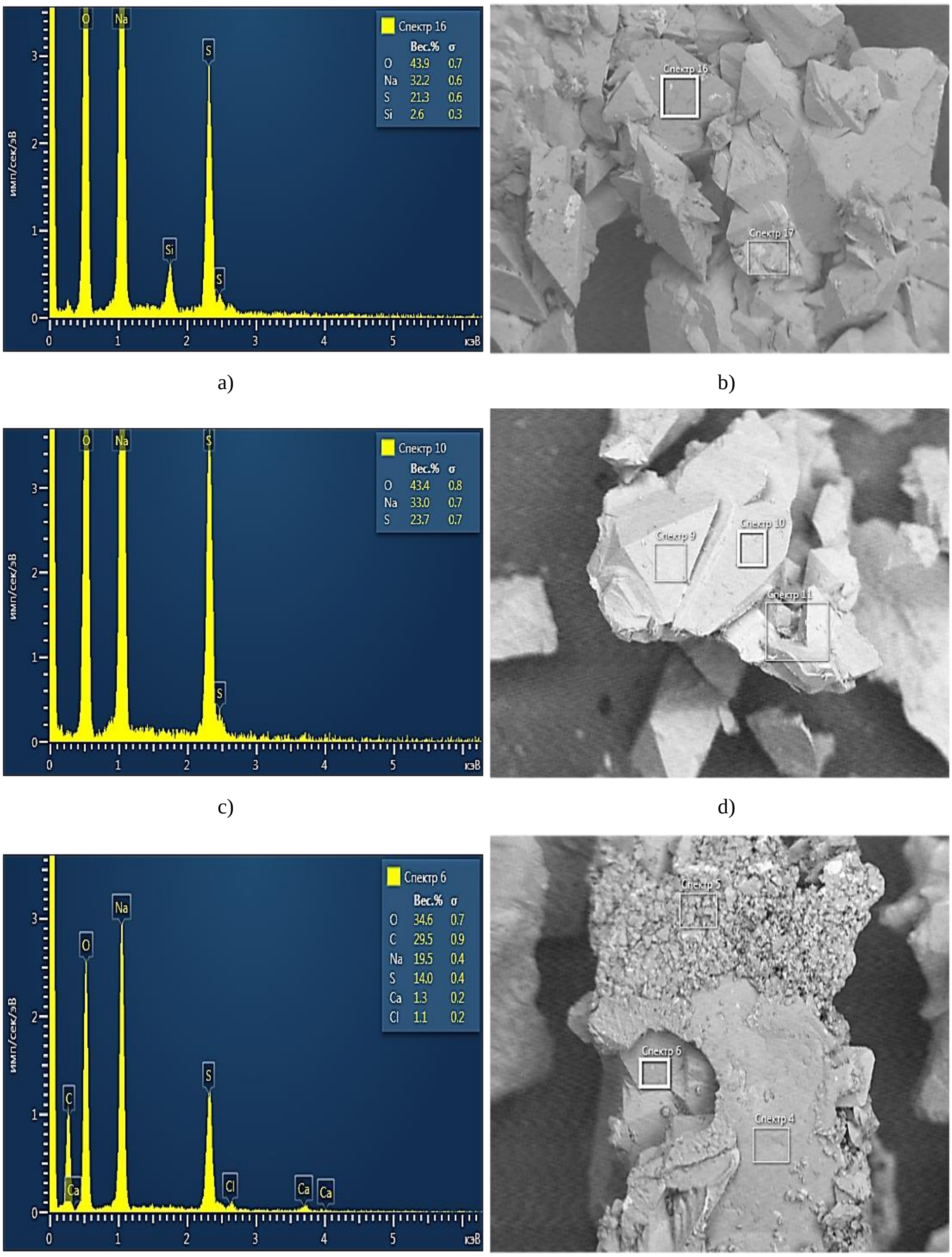
***Таблица 4.* Состав твердой и жидкой фаз продуктов конверсии фосфогипса в зависимости от температуры процесса (норма Na_2CO_3 – 105%, концентрация Na_2CO_3 – 20%, время контакта – 30 мин)**

Contact time, min	Content, %					Concentration of Na_2SO_4, %
	W_{moist}	CaO	SO_3	Na_2O	CO_2	
Solid phase						
20	22.07	48.9	5.73	4.52	40.1	-
30	22.56	49.1	5.14	3.75	40.9	-
40	22.80	49.9	4.53	3.12	41.6	-
50	22.96	50.4	4.34	2.47	42.0	-
60	23.11	50.9	3.21	2.31	42.3	-
70	23.18	50.9	3.27	2.24	42.4	-
80	23.25	51.0	3.31	2.22	42.4	-
90	23.27	51.1	3.37	2.20	42.5	-
Liquid phase						
15	76.19	0.71	13.9	11.4	0.68	18.46
30	75.91	0.65	14.4	12.0	0.55	19.07
45	74.19	0.61	15.9	12.9	0.48	19.46
60	73.91	0.52	16.4	13.3	0.45	19.77
75	73.42	0.42	17.3	13.9	0.35	20.03
90	73.37	0.41	17.4	13.9	0.34	20.13
105	73.33	0.41	17.5	14.1	0.33	20.18
120	73.25	0.40	17.6	14.1	0.32	20.23

All this leads to an increase in the concentration of the sodium sulfate production solution from 18.46 to 20.23% and thus a decrease in water from 76.19 to 73.25%. This is attributed by an increase in the conversion coefficient from 93.03 to 96.82%.

Since the conversion reaction is endothermic, the temperature favors the dissolution of PG with the generation of calcium carbonate and sodium sulfate. The optimal temperature for the processing process is 80 °C, because a further increase leads to an overrun of heat and power costs.

Physicochemical studies of calcium sulfate conversion products. Samples of conversion products obtained at 30, 60, and 120 min and 80 °C were selected for scanning electron microscopic analysis (SEM) (Figs. 5 and 6).



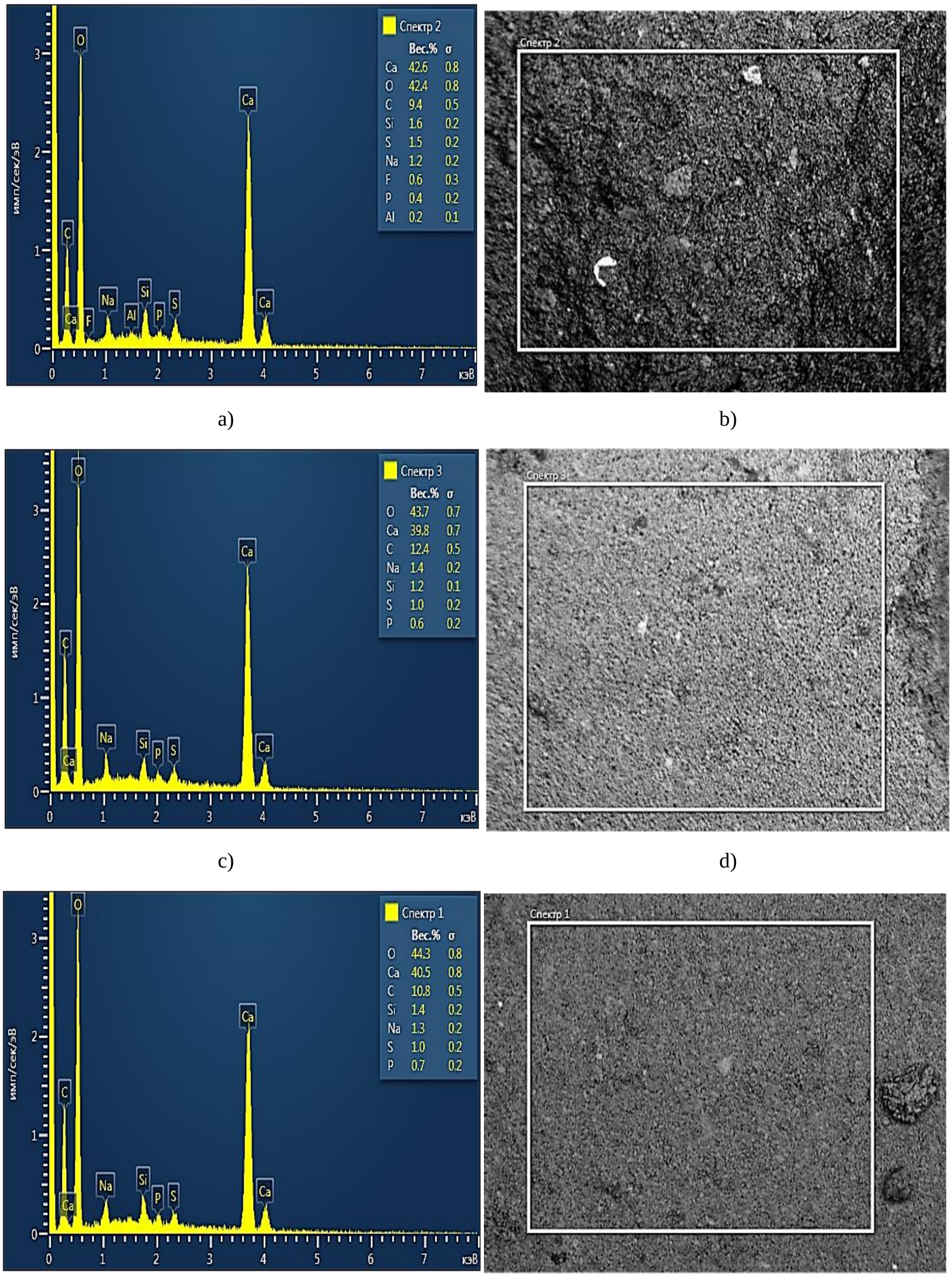
a) b)

c) d)

e) f)

Fig. 5. SEM and spectral image of sodium sulphate crystals obtained from the liquid phase for 30 minutes (a and b), 60 min (c and d), 120 min (e and f)

Рис. 5. СЭМ и спектральное изображение кристаллов сульфата натрия, полученных из жидкой фазы в течение 30 мин (a и b), 60 мин (c и d), 120 мин (e и f)



Спектр 2	Вес.%	σ
Ca	42.6	0.8
O	42.4	0.8
C	9.4	0.5
Si	1.6	0.2
S	1.5	0.2
Na	1.2	0.2
F	0.6	0.3
P	0.4	0.2
Al	0.2	0.1

a) b)

Спектр 3	Вес.%	σ
O	43.7	0.7
Ca	39.8	0.7
C	12.4	0.5
Na	1.4	0.2
Si	1.2	0.1
S	1.0	0.2
P	0.6	0.2

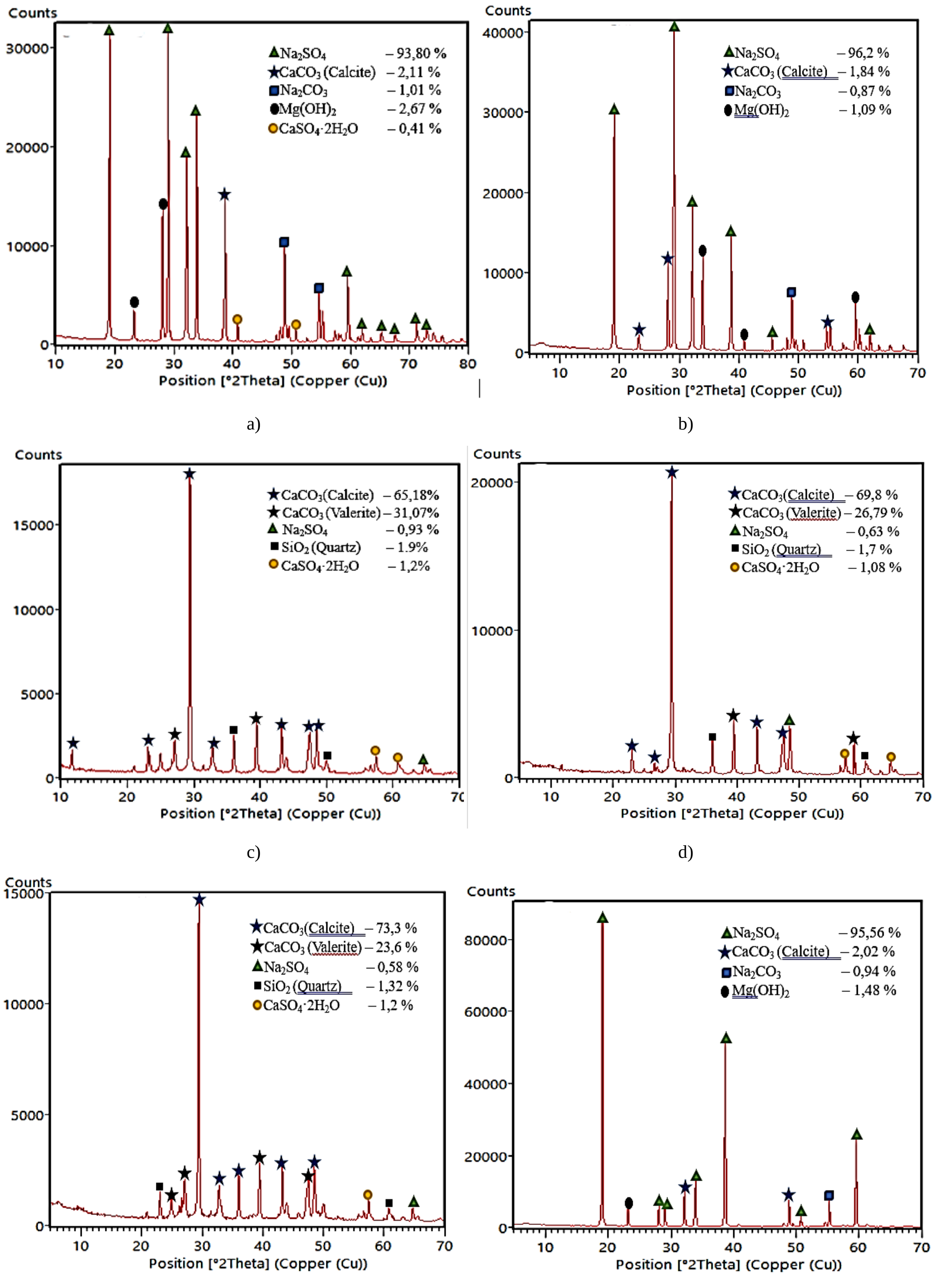
c) d)

Спектр 1	Вес.%	σ
O	44.3	0.8
Ca	40.5	0.8
C	10.8	0.5
Si	1.4	0.2
Na	1.3	0.2
S	1.0	0.2
P	0.7	0.2

e) f)

Fig. 6. SEM and spectral images of precipitation obtained from the solid phase for 30 min (a and b), 60 min (c and d), 120 min (e and f)

Рис. 6. СЭМ и спектральные изображения осадков, полученных из твердой фазы в течение 30 мин (a и в), 60 мин (c и d), 120 мин (e и f)



a) b)

c) d)

e) f)

Fig. 7. XRD patterns of sodium sulfate crystals (a, c, e) and calcite precipitation (b, d, f) obtained for 30, 60, and 120 min
Рис. 7. Рентгенограммы кристаллов сульфата натрия (a, c, e) и осадков кальцита (b, d, f), полученные в течение 30, 60 и 120 мин

To do this, the samples recovered from the solid phase were dried, and the liquid phase was evaporated to obtain sodium sulfate crystals. The precipitate from the solid phase and dry crystals from the liquid phase were subjected to SEM and XRD analysis. The microscopic morphology of the evaporated products is represented mainly by various shapes, hexagonal, tubular and needle-shaped, rhombic crystals, as well as scaly irregularities (Fig. 5). Traces of adsorbed impurities are visible on the surface of the crystals. The elemental composition shows a high content of Na, S, O, which corresponds to a semiquantitative composition of 94.5, 96.29, and 93.85% Na_2SO_4, respectively, at contact times of 30, 60, and 120 min.

Micrographs of the precipitation show the morphology of calcium carbonate with the presence of agglomerates in tubular and hexagonal forms with sizes of at least 2 μm (Fig. 6-a). In addition, the morphology of calcium carbonate agglomerate is represented by small scales with a small area. The average diameter of flake microparticles is 2 μm, the thickness is less than 1 μm (Fig. 6-b, c) [26-34]. The semi-quantitative composition of the solid phase shows a high content of Ca, C, O and impurities such as Na, Fe, Al, P, S and Si. An approximate quantitative composition is in the order of 78.3, 96.5 and 90% $CaCO_3$, corresponding to contact times of 30, 60 and 120 min.

The correlation between the composition of sediment and evaporated products from the liquid phase was identified in more detail by XRD analyses (Fig. 7). The results of the quantitative composition of the XRD analyses correlate with the data of the transcription programs such as Profex and Match! Phase Analysis Report version 2019.

In crystals from the liquid phase, sodium sulfate was identified mainly with diffraction bands at 3.07, 4.64, 2.64 Å; 4.63, 2.32, 1.55 Å and 3.06, 4.63, 2.77 Å related to the thenardite morphology. In turn, the shape of the crystals is orthorhombic with unit cells a = 5.8500 Å, b=12.2900 Å, c=9.7500 Å. The practical density of sodium sulfate crystals is 2.660 g/cm^3, and the calculated density is 2.691 g/cm^3.

Thus, the crystalline products from the liquid phase mainly consist of sodium sulfate in the amount of 93.80; 95.56 and 96.20%, respectively, for 30, 60 and 120 min. The rest are impurities of sodium carbonate, calcium, *etc*., which do not exceed 7%.

Solid phase with diffraction peaks 3.03; 2.27, 2.09 Å; 3.03, 2.28, 1.87 Å, and 3.03, 2.28, 1.87 Å belongs to the morphological change of calcium carbonate – calcite and valerite. In them, calcite crystallizes in a trigonal system (hexahedral axes) with unit cell a = 4.9840 Å, c = 17.1210 Å with calculated densities of 2.707 g/cm^3. Approximate quantitative phase composition shows that the precipitate from the solid phase is represented by calcium carbonate (calcite and valerite) in the amount of 97.25; 96.59 and 96.90%, respectively for 30, 60 and 120 min. In addition to calcium carbonate and calcium sulfate, residues of sodium sulfate and carbonate, silicon oxide, and traces of lanthanides are also present as impurities, but in very small quantities. Balance calculations show that 596, 602, and 609 g of Na_2SO_4 are obtained from 1 kg of PG, respectively, with a conversion time of 30, 60, and 120 min.

From a technological point of view, the optimal conditions for PG conversion were established as follows: sodium carbonate concentration – 20%, sodium carbonate consumption norm – 20 % of the stoichiometry for the formation of calcium carbonate and sodium sulfate, contact time – 60 min and process temperature – 80 °C. Under such conditions, the gypsum conversion coefficient in PG is 96.71%, and the product, sodium sulfate, has a purity of 95.5 %, while calcite contains 96.59% calcium carbonate. Sodium sulfate needs to be recrystallized, whereas precipitation calcium carbonate follows to treat in order to obtain REE concentrate which will be aim of the future studies.

CONCLUSIONS

The possibility of alkaline conversion of phosphogypsum depending on the concentration and norm of sodium carbonate, the duration of contact and the temperature of the process has been studied. It has been established that the concentration and norm of sodium carbonate under the influence of high temperature effectively increase the conversion coefficient of PG. The most optimal condition for the conversion of phosphogypsum, in which the conversion ratio of gypsum is 95.56%, and sulfate and carbonate is obtained with a purity of at least 96% at the followings: sodium carbonate concentration – 20%, contact time – 60 min, temperature – 80 ^oC and sodium carbonate consumption norm – 105%.

Crystallization product obtained after evaporation of the liquid phase can be recommended for the production of synthetic detergents, an ingredient for the textile industry or an additive for the glass industry and glaze in the ceramic industry. A by-product of conversion calcium carbonate precipitation can be recommended as the main component of a building material, raw material for cement, plaster material for finishing work, filler for bit polymers. It should be noted that the deep processing of this precipitate makes it possible to obtain rare earth metals, which are in great demand in the market of electronics and batteries for household appliances.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

The authors declare the absence of a conflict of interest warranting disclosure in this article.

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