

Obtaining ammonium sulfate and calcium carbonate by processing natural gypsum and phosphogypsum

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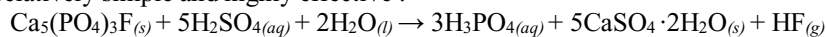
Abstract. Studying the conversion of local natural gypsum and phosphogypsum, categorized as a byproduct of extracting phosphoric acid (EPA), into ammonium carbonate through a liquid-based method. At the same time, the concentration of ammonium carbonate in an aqueous solution was obtained in the range from 10 to 50%. The norms of ammonium carbonate were 100, 105, 110% relative to stoichiometry. The transfer time of ammonium carbonate to the reaction zone was from 5 to 30 minutes, and the conversion time was also studied in the range from 5 to 30 minutes. The conversion process was carried out at a temperature of 30 to 50°C. The optimal time for the carbonate conversion of gypsum was 30 minutes, and the conversion rate was 95.68 and 96.83%.

1. Introduction

About 70 million tons of P₂O₅ are produced annually from phosphate ores. By 2050, this indicator will increase to 220 million tons. On the one hand, this can provide food for the growing population, but on the other hand, it leads to the formation of large amounts of phosphogypsum reserves. Today, phosphogypsum reserves in the world are about 6 billion tons [1-5]. This figure increases by 150 million tons every year. Such indicators indicate that the total amount of phosphogypsum will double by 2025-2045. Among the countries that process phosphoride ores the most and have growing phosphogypsum reserves, we can cite the following as an example [6-9]. The largest US companies are located in Florida, where phosphogypsum reserves exceed 200 million tons, more than 400 million tons in Hubei province, Yunnan, Guangzhou, Sichuan and Anhui provinces of China, about 500 million tons in Russia, 60 million tons in Ukraine, more than 150 million tons in Brazil, 52 million tons in Tunisia and 100 million tons in Spain, 5 million tons in Poland, 18 million tons in the Republic of Belarus, 30 million tons in Kazakhstan and others [10-13].

The problem of using and storing phosphogypsum is very important for many countries in the world. Because it causes many environmental problems, i.e. pollution of water, land and atmosphere. Phosphogypsum contains rare earth elements such as calcium sulfates, silicon, iron, titanium, magnesium, aluminum, manganese, as well as heavy metals and toxic elements [14-16].

CaSO₄·2H₂O, hemihydrate CaSO₄·0.5H₂O and anhydride methods of extractive phosphoric acid production, which are the main factors in the formation of phosphogypsum. Among the above methods, the dihydrate method is the most common and relatively simple and highly effective.



In the production of extractive phosphoric acid, on average, 1 ton of P₂O₅ is obtained, causing the formation of 5-6 tons of phosphogypsum waste [17-19]. More than 85% of the composition of phosphogypsum is CaSO₄. It accounts for 15% of world production due to its high acidity (pH-3) and high moisture content. Phosphogypsum is used to stabilize alkaline soils, obtain building materials, produce agricultural fertilizers, and process as ameliorants [20-23]. Currently, phosphogypsum is becoming a major problem in many factories producing ammophos. Phosphogypsum waste cannot be disposed of in acceptable ways. Transportation and storage of phosphogypsum in special areas requires a large amount of costs and labor [24-26].

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2. Materials and Methods

For laboratory research, phosphogypsum, an EFK waste product produced at "Olmaliq Ammofos-Maksam" JSC, and natural gypsum obtained from the "Shorsuv" mine located in Fergana region were used. Raw materials chemical composition; phosphogypsum P_2O_5 – 0.638%, CaO – 35.4%, SO_3 – 46.7%, Fe_2O_3 – 0.05%, Al_2O_3 – 0.569%, SiO_2 – 2.08%, and in natural gypsum CaO – 35.3%, SO_3 – 41.5%, MgO – 3.0%, Fe_2O_3 – 0.05%, Al_2O_3 – 0.499%, SiO_2 – 0.792%. Initial laboratory experiments used $(NH_4)_2CO_3$ for liquid carbonate conversion of ordinary gypsum and phosphogypsum. In aqueous ammonium carbonate solution, the concentration ranged from 10 to 50%. The rates of ammonium carbonate were 100, 105, 110% relative to stoichiometry. The transfer time of ammonium carbonate to the reaction zone was studied in the range of 5 to 30 minutes and the conversion time was also studied in the range of 5 to 30 minutes. The conversion process was carried out at a temperature from 30°C to 50°C [27-30].

The experimental device is equipped with a stirrer, a thermometer and a reflux condenser. The temperature of the reaction mixture was maintained by heating in a water bath. At the end of the experiment, the reaction mass was filtered in a Buchner vacuum funnel with a paper filter using a vacuum pump of 0.65 atm.

The decomposition of gypsum with ammonium carbonate solution proceeds according to the following reaction:

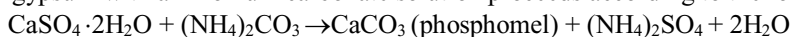


Table 1 shows the results showing the dependence of the time of introduction of ammonium carbonate solution on the gypsum carbonate processing process in the liquid conversion method and the conversion time.

3. Results and Discussion

From the results of Table 1, it can be seen that the mass fraction of ammonium sulfate in the filtrate from natural gypsum conversion is 29.54% at 5 minutes and 100% stoichiometry, and 41.28% at 30 minutes and 100% stoichiometry reached. The mass fraction of ammonium sulfate in the filtrate from phosphogypsum conversion is 30.17% at 5 minutes and 100% stoichiometry, and 30.17% at 30 minutes and 100% stoichiometry and it was 41.53%. It was found that the mass concentration of ammonium sulfate in the obtained filtrate is higher in phosphogypsum than in natural gypsum.

The chemical composition of the liquid and solid phase obtained by carbonate conversion of natural gypsum and phosphogypsum was studied. The obtained results are presented in Table 2.

Table 1. On natural gypsum and phosphogypsum conversion rate and $(NH_4)_2SO_4$ concentration.

$(NH_4)_2CO_3$ input time, min	Conversion time, min	Temperature, °C	$(NH_4)_2SO_4$ in the liquid phase, %	Conversion level %
Natural gypsum				
5	5	50	29.54	74.45
10	10	50	34.08	82.29
15	15	50	37.20	89.62
20	20	50	39.11	92.72
25	25	50	40.64	94.76
30	30	50	41.28	95.68
Phosphogypsum				
5	5	50	30,17	74.68
10	10	50	34.45	82.71
15	15	50	37.92	90.14
20	20	50	39.68	93.10
25	25	50	40.64	95.07
30	30	50	41.53	96.83

As can be seen from the obtained results, the mass fraction of CaO and CO_2 in the solid phase obtained from the conversion of natural gypsum increased from 5 to 30 minutes of conversion time from CaO -39.45% to 51.85%, CO_2 from -29.15 to 40, increasing by 85%. On the other hand, we can see that the mass fraction of undegraded gypsum in the solid phase decreased from 23.48% to 3.98% with increasing conversion time. It was found that the mass fraction of unfiltered ammonium sulfate in the solid phase increased from 1.08% to 3.48%. In the liquid phase, we can see that all components increase in mass fraction with increasing conversion time. For example, it was found that the mass fraction of SO_3 and N in the liquid phase increased from 13.09% to 24.60%, from 4.10% to 8.43%, from 5 to 30 minutes of conversion time. When the experiments were carried out with phosphogypsum, the following results were obtained. For example, the mass fraction of CaO and CO_2 in the obtained solid phase increases from 40.53% to 52.29% of CaO , and from -30.28 to 41.52% of CO_2 as the conversion time increases from 5 to 30 minutes. On the other hand, we can see that the mass fraction of unconverted gypsum in the solid phase decreased from 22.80% to 2.91% with increasing time. It was found that the mass fraction of unfiltered ammonium sulfate in the solid phase

increased from 1.23% to 3.56%. In the liquid phase, we can see that the mass fraction of all components increases as the conversion time increases. For example, it was found that the mass fraction of SO₃ and N in the liquid phase increased from 13.62% to 25.44%, from 4.36% to 8.90%, from 5 to 30 minutes of conversion time. We can see that the results obtained on the basis of phosphogypsum are slightly higher than those obtained on natural gypsum.

If the concentration of ammonium carbonate is higher than the stoichiometric norm, the yield of the reaction increases. But an excess amount of ammonium carbonate causes the reaction medium to become strongly alkaline. As a result, this leads to the agglomeration of calcium carbonate and the formation of small crystalline particles of calcium carbonate that cover the surface of calcium sulfate and reduce the efficiency of the product obtained due to incomplete conversion. Table 3 shows the results showing the degree of conversion of gypsum as a function of ammonium carbonate concentration.

The mass fraction of ammonium sulfate in the liquid phase and the degree of conversion of gypsum were determined with 10-50% concentration solutions of ammonium carbonate at 100% stoichiometry in a period of 30 minutes. As the concentration of ammonium carbonate increased during the conversion process, the concentration of ammonium sulfate formed in the liquid phase and the degree of conversion of gypsum increased. In natural gypsum, the mass fraction of ammonium sulfate in the liquid phase over a period of 30 minutes, (NH₄)₂CO₃ with a concentration of 10% and 100% stoichiometry is 11.13% of the norm, and (NH₄)₂CO₃ with a concentration of 50% and a stoichiometry of 100% is 41.28% of the norm, and in phosphogypsum, the mass of ammonium sulfate in the liquid phase share in a 30-minute period, (NH₄)₂CO₃ with a concentration of 10% and 100% stoichiometry was 12.52% of the norm, and (NH₄)₂CO₃ with a concentration of 50% and 100% stoichiometry was 41.53% of the norm.

Table 2. Dependence of the changes in the composition of the solid and liquid phase resulting from the conversion of natural gypsum and phosphogypsum on the conversion time.

Mining time, min	W water, %	Liquid phase, %				Solid phase, %			
		SO ₃	CaO	N	W water, %	SO ₃ ((NH ₄) ₂ SO ₄)	SO ₃ (CaSO ₄)	CaO	CO ₂
Natural gypsum									
5	78.91	13.09	0.12	4.10	31.10	1.08	23.48	39.45	29.15
10	73.14	17.46	0.11	5.54	28.14	1.54	16.57	43.68	32.95
15	70.30	19.42	0.10	6.79	26.48	2.25	9.54	46.83	35.28
20	67.52	21.80	0.09	7.63	25.64	2.78	6.82	48.75	37.46
25	66.24	23.54	0.09	7.96	24.50	3.20	4.81	50.26	39.21
30	64.70	24.60	0.09	8.48	23.71	3.48	3.97	51.85	40.85
Phosphogypsum									
5	78.32	13.62	0.13	4.36	30.78	1.23	22.80	40.53	30.28
10	72.74	18.02	0.11	5.73	27.92	1.60	16.19	43.96	33.09
15	69.85	20.78	0.10	7.29	26.04	2.46	9.22	47.29	35.43
20	66.74	22.55	0.09	7.82	25.30	2.95	6.40	49.58	38.24
25	64.58	24.10	0.09	8.15	24.18	3.30	3.92	51.14	39.48
30	63.83	25.44	0.09	8.90	23.30	3.56	2.91	52.29	41.52

Table 3. Effect of ammonium carbonate concentration on natural gypsum and phosphogypsum conversion rate

(NH ₄) ₂ CO ₃ Concentration, %	(NH ₄) ₂ CO ₃ input time, min	Conversion time, min	Temperature °C	(NH ₄) ₂ SO ₄ in the liquid phase %	Conversion Level %
Natural gypsum					
10	30	30	50	11.13	84.12
20	30	30	50	21.26	88.91
30	30	30	50	29.81	90.95
40	30	30	50	37.12	93.77
50	30	30	50	41.28	95.68
Phosphogypsum					
10	30	30	50	12.52	85.26
20	30	30	50	21.88	89.25
30	30	30	50	31.99	91.64
40	30	30	50	37.89	94.35
50	30	30	50	41.53	96.83

In the next experiments, the X-ray structural composition of the obtained calcium carbonate precipitate and the initial raw ash samples were studied. The composition of the samples was obtained on a XRD-6100 (shimadze, Japan) powder diffractometer manufactured in Japan. CuK was transferred under the influence of a radiation (b -filter, Ni, $\lambda=1.54178\text{\AA}$ current and voltage in the x-ray tube 30mA, 30Kv). In the current, the constant rotation speed of the detector is 4 hr/min, 0.02° minimum ($\omega/2\theta$ -link), and the scanning angle is 4° from to 80° . The samples were analyzed in a chamber with a rotation speed of 30 rpm.

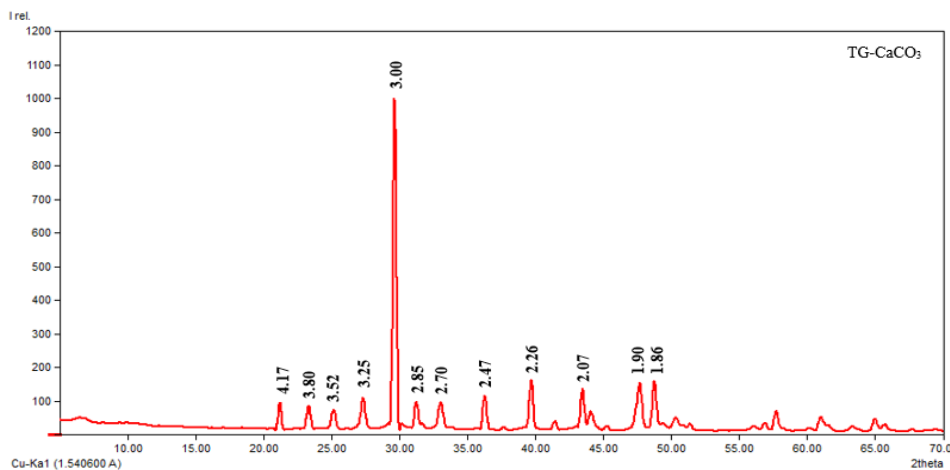


Fig. 1 X- ray image of CaCO_3 obtained on the basis of TG.

The obtained roentgenogram results were analyzed by comparison with the ASTM American catalog and Mihaev's tables of radiometric indicators for determining minerals.

The radiographic components of the initial and final products were compared in order to reveal the substances formed during the liquid gypsum conversion with carbonate and the essence of gypsum conversion.

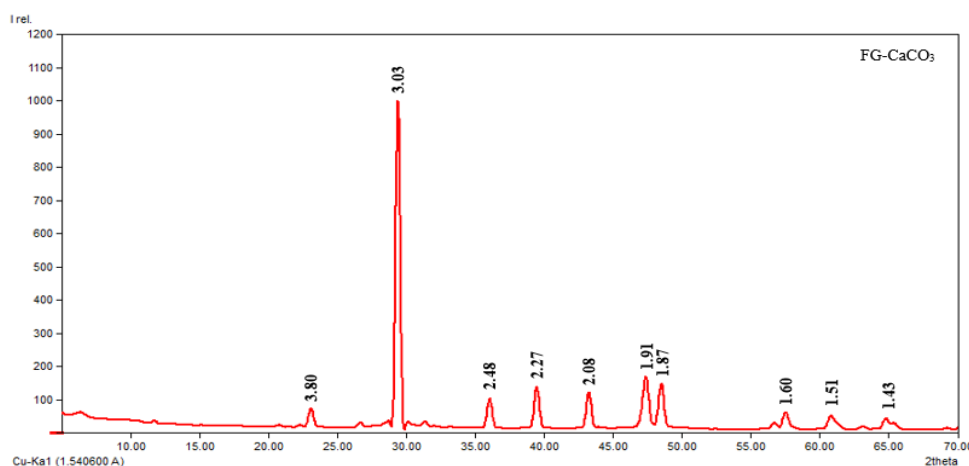


Fig. 2. X- ray image of CaCO_3 obtained on the basis of FG

In Figures 1 and 2, the dried calcium carbonate precipitate obtained by processing natural gypsum and phosphogypsum is shown as TG- CaCO_3 (7.61; 4.25; 3.81; 3.07; 2.87; 2.68; 1, 90 \AA) and diffraction peaks confirming the presence of intense peaks (7.58; 4.25; 3.77; 3.05; 1.89 \AA) of FG- CaCO_3 were observed. The composition of the components related to these diffraction peaks is presented in Table 3. These obtained data were compared with the values related to the intense peaks of CaCO_3 presented in Table 4 .

As a result, it was found that these values corresponded with the values of the obtained samples. Also, in the course of X-ray analysis of CaCO_3 , these samples obtained based on the conversion of gypsum with ammonium carbonate contain a small amount of undecomposed gypsum and intense peaks representing the presence of a very small amount of ammonium sulfate remaining with calcium carbonate crystals during the filtration of sulfocarbonate

suspension $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (2.47; 1.90; 1.43 Å) and $(\text{NH}_4)_2\text{SO}_4$ (3.26; 2.70; 2.47; 1.90; 1.86 Å). The small amount of calcium sulfate remaining in the sample is explained by the fact that the gypsum conversion rate is 96-97%.

Table 4. X-ray analysis of the obtained CaCO_3 samples

Sample TG CaCO_3		Sample FG CaCO_3		CaCO_3 _ 5-8586		$\text{CaSO}_4 \cdot \text{H}_2\text{O}$		$(\text{NH}_4)_2\text{SO}_4$	
dA	I/I ²	dA	I/I ²	dA	I/I ²	dA	I/I ²	dA	I/I ²
4.17	13	3.80	8	3.86	12	-	-	-	-
3.80	9	3.00	100	3,035	100	-	-	-	-
3.52	6	2.48	13	2,845	3	-	-	-	-
3.25	10	2.27	17	2,495	11	2.47	2	3.264	1
3.00	100	-	-	2,285	18	-	-	-	-
2.85	11	2.08	19	2,095	18	-	-	2.704	5
2.70	8	1.91	18	1,913	17	1.90	4	-	-
2.47	13	1.87	7	1,875	17	-	-	2.476	3
2.26	20	1.60	3	1,601	8	-	-	-	-
2.07	17	1.51	5	1,518	4	-	-	-	-
1.90	16	-	-	1,422	3	1.43	4	1.904	1
1.86	18	-	-	-	-	-	-	1.867	1

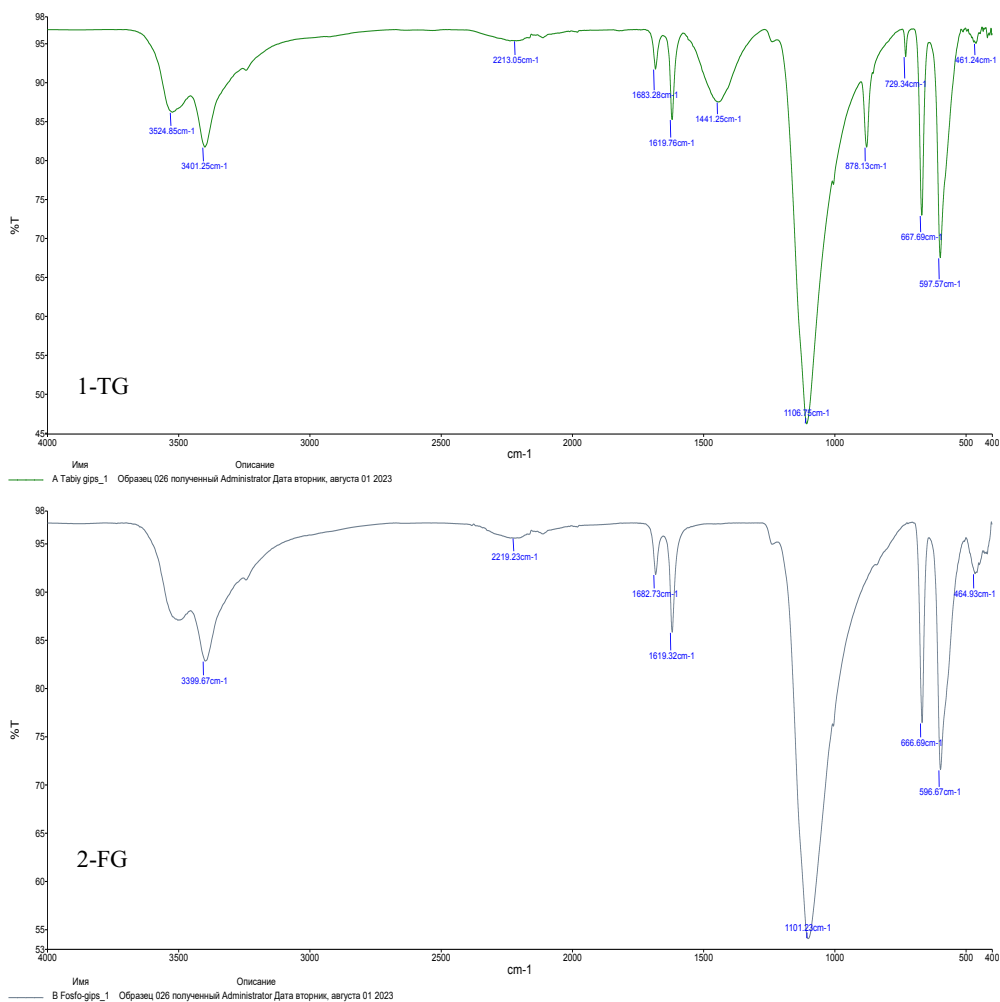


Fig. 3. IR-spectrum graphical representation of natural gypsum and phosphogypsum samples.

The accuracy of quantitative determination of compounds using IR-spectroscopic analysis is low, therefore, in chemistry, this method is mainly used for qualitative determination of compounds. Regardless of the type of molecular skeleton, the absorption lines of the functional groups of the molecule appear at certain values of the wave numbers, which are called characteristic wave frequencies. These characteristic frequencies provide important information about the substance under investigation. The fact that the vibration spectra have a high quality is a unique physical characteristic of this substance. Therefore, IR spectra are widely used to identify chemical compounds and mixtures in individual compounds, to study the mechanisms of chemical reactions. Infrared absorption spectra were determined by IR Tracer-100 spectrophotometer of "SHUMADZU" company (400-4000 cm^{-1}).

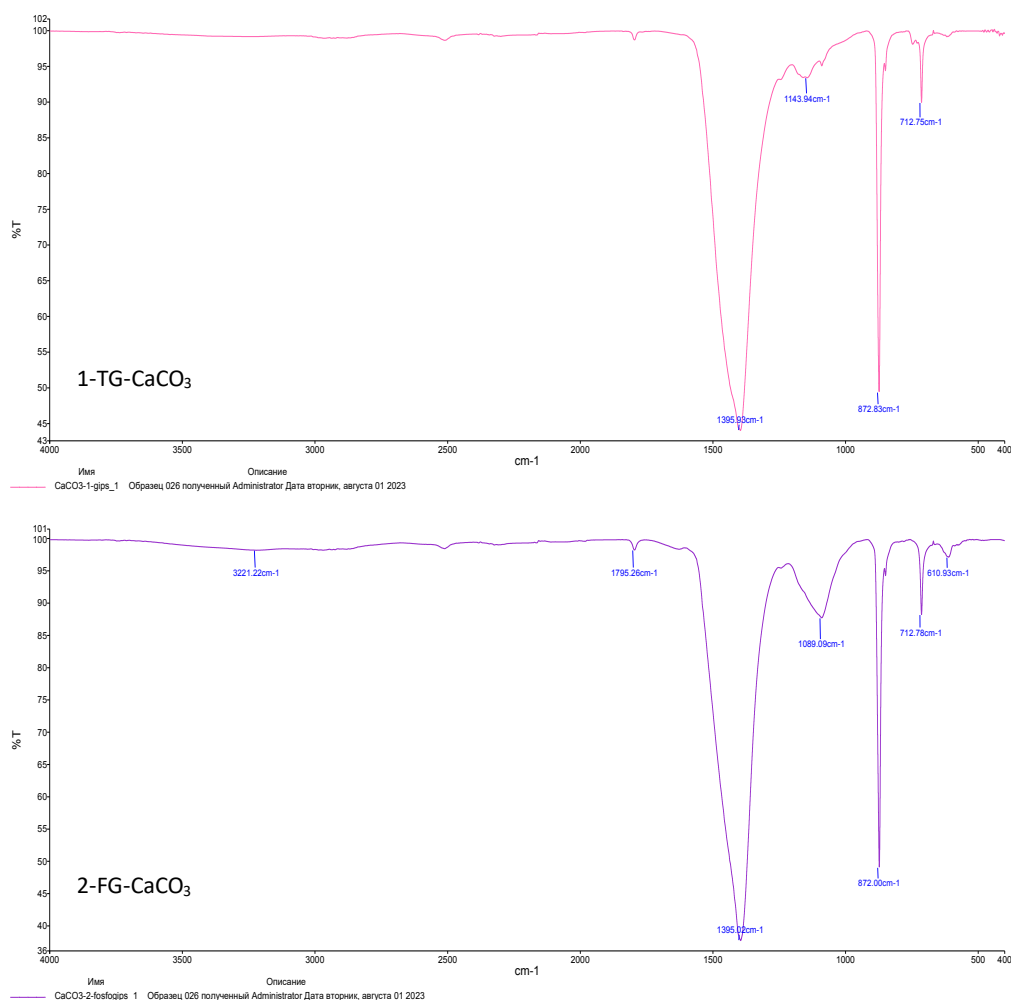


Fig. 4. IR-spectrum graphical representation of the obtained calcium carbonate samples

Based on the analysis of the literature, the infrared absorption spectra of initial gypsum samples and obtained calcium carbonate were studied.

IR-spectrum absorption lines of gypsum samples (TG and FG) presented in Figure 3 showed that the following vibration frequencies in the range of 3700-3400 cm^{-1} belong to water and OH - group. In the frequency range of 1130-1080 cm^{-1} and 680-610 cm^{-1} , S-O bond of SO_4^{2-} group was found. Partial shift of water (3399.67 cm^{-1}) and SO_4^{2-} frequency lines was observed in IR-spectra of phosphogypsum sample. The obtained results confirmed that gypsum is composed of functional groups that make up the main component.

(TG-CaCO₃, FG-CaCO₃) obtained on the basis of conversion of gypsum samples with an aqueous solution of ammonium carbonate have the following vibration frequencies 1450-1390 cm^{-1} and showed that CO_3^{2-} belongs to the 2- group in the range of 880-800 cm^{-1} . We can see from the analysis results presented in Figure 4 that the main component of the wet residue remaining in the solid phase during the filtration of the sulfocarbonate suspension is composed of calcium carbonate.

Natural gypsum and phosphogypsum can be obtained as a crystalline or granulated product from a 33-35% ammonium sulfate solution recycled with carbonate. It is also used in the production of non-sticky AC and sulfate-nitrate ammonium based on liquid ammonium nitrate and ammonium sulfate and in the production of other types of complex fertilizers. In the process of obtaining other types of complex fertilizers from ammonium sulfate conversion solution, its physical and chemical properties, i.e., rheological properties (density and viscosity), boiling point, and saturated vapor pressure are important. In the process of carbonate processing of gypsum in the liquid method, calcium carbonate precipitate is formed in addition to ammonium sulfate. The chemical composition and physicochemical properties of the washed-dried calcium carbonate precipitate are important for its use as a by-product in the production of building materials. The physical and chemical properties of the samples were determined in our next research.

Table 5. Saturated vapor pressure of ammonium sulfate conversion solution, kPa

Temperature, °C	Solution concentration, %				
	15.0	25.0	35.0	40.0	43.0
20	2.23	2.16	2.04	1.92	-
30	4.04	3.92	3.69	3.49	-
40	7.01	6.81	6.42	6.07	5.89
50	11.72	11.40	10.74	10.14	9.85
60	18.93	18.39	17.06	16.30	15.92
70	29.62	28.78	27.15	25.22	24.89
80	45.03	43.76	41.28	38.95	37.75
90	66.64	64.76	61.08	57.63	56.00
100	96.30	93.56	88.26	83.27	80.91
110	136.10	132.27	124.78	117.70	114.37

Saturated vapor pressure of ammonium sulfate solution was determined in a special laboratory device. The obtained results are presented in Table 5.

Water vapor in liquids is determined by the temperature of this solution and the mass concentration of the salts in it. As the concentration of ammonium sulfate in the solution increases, we can see that its saturated vapor pressure decreases. For example, at a temperature of 20°C, it was determined that the concentration of the solution decreased by 2.23 kPa at 15% and by 1.92 kPa at 43% concentration.

4. Conclusions

One of the parameters influencing the conversion process of phosphogypsum and natural gypsum with ammonium carbonate in liquid method was studied. Based on the principle of operation of the technological system, during the gypsum conversion, stepwise introduction of ammonium carbonate solution into the reaction zone was ensured. In this case, 30 minutes of ammonium carbonate solution was considered to be the optimal time to enter the reaction zone. The conversion rate of gypsum is 95.68 and 96.83%.

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