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# LIQUID PROCESSING OF GYPSUM INTO AMMONIUM SULPHATE AND CALCIUM CARBONATE

***Abstract:*** *In this research work, experiments were conducted on the processing of phosphogypsum and natural gypsum into ammonium sulfate. In this case, gypsum was converted using a liquid method with ammonium carbonate. The dependence of the conversion process on technological parameters was determined. The experiments were conducted at a stoichiometric ratio of ammonium carbonate of 100, at a temperature of 50 °C, for a period of 5-120 minutes, and the conversion rate was 95.68-96.83%.*

***Keywords:*** *phosphogypsum, natural gypsum, ammonium carbonate, sulfocarbonate suspension, time, temperature, concentration, conversion rate*

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## ЖИДКОСТНАЯ ПЕРЕРАБОТКА ГИПСА В СУЛЬФАТ АММОНИЯ И КАРБОНАТ КАЛЬЦИЯ

***Аннотация:*** *В данной научно-исследовательской работе проведены эксперименты по переработке фосфогипса и природного гипса в сульфат аммония. При этом гипс конверсия осуществлялась жидкостным способом с использованием карбоната аммония. Определена зависимость процесса конверсии от технологических параметров. Опыты проводились при* *стехиометрическом соотношении карбоната аммония 100, температуре 50°C, в течение 5–120 минут, при этом степень конверсии составила 95,68–96,83%.*

***Ключевые слова:*** *фосфогипс, природный гипс, карбонат аммония, сульфокарбонатная суспензия, время, температура, концентрация, скорость превращения*

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# GIPSNI SUYUQLIK USULIDA AMMONIY SULFAT VA KALSIY KARBONATGA QAYTA ISHLASH

***Annotatsiya:*** *Ushbu tadqiqot ishida fosfogips va tabiiy gipsni ammoniy sulfatga qayta ishlashga oid tajribalar oʻtkazildi. Bunda gipsni suyuqlik usulida* *ammoniy karbonat bilan konversiya jarayonlari olib borildi. Konversiya jarayonini texnologik parametrlarga bog'likligi aniqlandi. Tajribalar ammoniy karbonatning 100 stexiometrik me'yorida, 50ºC haroratda, 5-120 daqiqagacha bo'lgan vaqt oralig'ida o'tkazildi,'Bunda konversiya darajasi 95.68-96.83% ni tashkil etdi.*

***Kalit so'zlar:*** *fosfogips, tabiiy gips, ammoniy karbonat, sulfokarbonat suspenziyasi, vaqt, harorat, konsentratsiya, konversiya darajasi*

**Introduction.**

Ammonium sulfate is found in the most common everyday applications due to its unique chemical and physical properties. Ammonium sulfate is used in agricultural fertilizers as a source of nitrogen and sulfur for plant nutrition.

Ammonium sulfate is a compound fertilizer containing nitrogen and sulfur. The nitrogen in ammonium sulfate is retained in the soil due to its low leaching, while sulfur is important for the formation of proteins and amino acids, which increase plant productivity**[1].**

Ammonium sulfate is widely used in areas with alkaline soils. The increasing consumption of fertilizers in an agriculture-based economy is expected to increase the demand for ammonium sulfate, which is recognized by the global farming community, and the market is expected to grow steadily in the coming years due to increased global competition in product production by large multinational companies.

The global market size of ammonium sulfate reached $3.21 billion in 2022 and is expected to reach $6.26 billion by 2032. This means that the annual growth rate from 2022 to 2032 will increase to 6.92%. Farmers around the world are working to increase crop yields. This will serve as a key factor in achieving significant progress in the agricultural industry in the future. In addition, the limited total arable land in the world will increase the consumption of fertilizers. As a result, this is expected to lead to an increase in the revenue of the ammonium sulfate market **[2].**

Today, phosphogypsum reserves in countries producing phosphorus fertilizers are increasing every year. In addition, such waste occupies a large part of the production area and causes serious environmental pollution problems **[3]**. In the process of extractive phosphoric acid production, an average of 5-6 tons of phosphogypsum waste is generated per 1 ton of product **[4]**. About 300 million tons of PG are produced worldwide annually, and its reserves exceed 7 billion tons **[5].** Currently, obtaining valuable products through secondary processing of industrial waste is an urgent problem. With the depletion of existing mineral deposits, there is a need to develop new technologies for processing industrial waste. In this regard, phosphogypsum can be classified as a mineral that does not have mining costs. These factors determine the strong interest of researchers in the problems of studying the properties of phosphogypsum and methods for processing phosphogypsum **[6].**

One of the ways to process phosphogypsum is to obtain building materials from it, namely wall panels, dry mixes, and various types of cements. However, due to the high acidity of phosphogypsum and the additives in its composition, it cannot be used on an industrial scale. And cleaning it from residual acid and additives is energy-consuming and economically impractical **[7-10]**. Phosphogypsum is used to improve soil, but this form of its processing leads to uncontrolled contamination of the soil with impurities contained in phosphogypsum. Therefore, a thorough study of the effect of impurities contained in phosphogypsum on the effectiveness of its use and the implementation of cheap and effective use of phosphogypsum resources is of great theoretical and practical importance **[11]**. In addition, this use of phosphogypsum, which is a valuable raw material for the production of some basic inorganic substances, such as ammonium sulfate, sodium sulfate, calcium carbonate, calcium sulfoaluminate, and lithium sulfate monohydrate, is economically beneficial **[12]**.

Gypsum conversion technology was first implemented in Germany (Merseburg) at the beginning of the 19th century by BASF. The traditional method of converting natural gypsum and phosphogypsum into liquid is widely used today in India, Japan, Pakistan, Turkey, Italy, and the USA. This method is not yet available in Uzbekistan. In the process of carbonate conversion of gypsum by the liquid method, the high conversion time and energy consumption limit the widespread use of this technology worldwide. That is, it is practically not used in countries with limited and expensive energy resources **[13].**

This article studies the production of ammonium sulfate by the carbonate recycling of phosphogypsum in a liquid process. The process of reducing the gypsum conversion time was studied depending on the main technological parameters.

**Materials and Methods**

The objects of this research were phosphogypsum, a waste product of the EPC produced at "Ammophos-Maxam" JSC, and natural gypsum from the "Shursuv" deposit located in the Fergana region. The gypsum samples were first washed with distilled water, dried, ground to a particle size of 0.16-0.25 mm and had the following composition (mass %): 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 %, 0.41 F, 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 %. The ammonium carbonate $(NH_4)_2CO_3$ used to treat gypsum samples consisted of 44.2% $CO_2$ and 28.4% $NH_3$ by dry mass.

The FG conversion process was carried out using a 50% $(NH_4)_2CO_3$ solution. The ammonium carbonate rate to gypsum was taken as 100% of the stoichiometry to produce ammonium sulfate. The contact time varied between 5-120 minutes. The temperature was studied in the range of 50 $^oC$.

The conversion rate was determined by the authors of the study using various formulas [14, 15].

The following formula was used to determine the conversion rate ($C_{rate}$) of gypsum

$$ɑ = (SO^{2-}{}_4(L)/ (SO^{2-}{}_4(S) \times 100\%$$

where ɑ is the conversion rate, %; $SO^2{}_{-4}$ (L) is the amount of sulfate ion in the solution, g; $SO^2{}_{-4}$ (S) is the amount of sulfate ion in the solid phase, g.

$$C_{rate}=1-\frac{m_1\cdot W_1-m_2\cdot W_2}{m_1\cdot W_1}\%$$

Here, $m_1$ and $W_1$ are the mass fraction and mass of $SO_3$ in the phosphogypsum sample, and $m_2$ and $W_2$ are the mass and mass fraction of $SO_3$ in the washed phosphogypsum sediment sample.

To determine the degree of gypsum conversion, the following was done. After the experiment time, the reaction mass was filtered in a Buchner funnel with a paper filter using a vacuum pump at a pressure of 0.65 atm. The N, CaO, $SO_3$, and $CO_2$ contents of the separated liquid and solid phases were determined using known methods [16].

**Results and discussion.**

The main indicator of the carbonate conversion of gypsum in the liquid method is, of course, its conversion rate. Based on the data obtained, it can be noted that the optimal time is 30 minutes, during which the conversion rate is 95.68 and 96.83%.

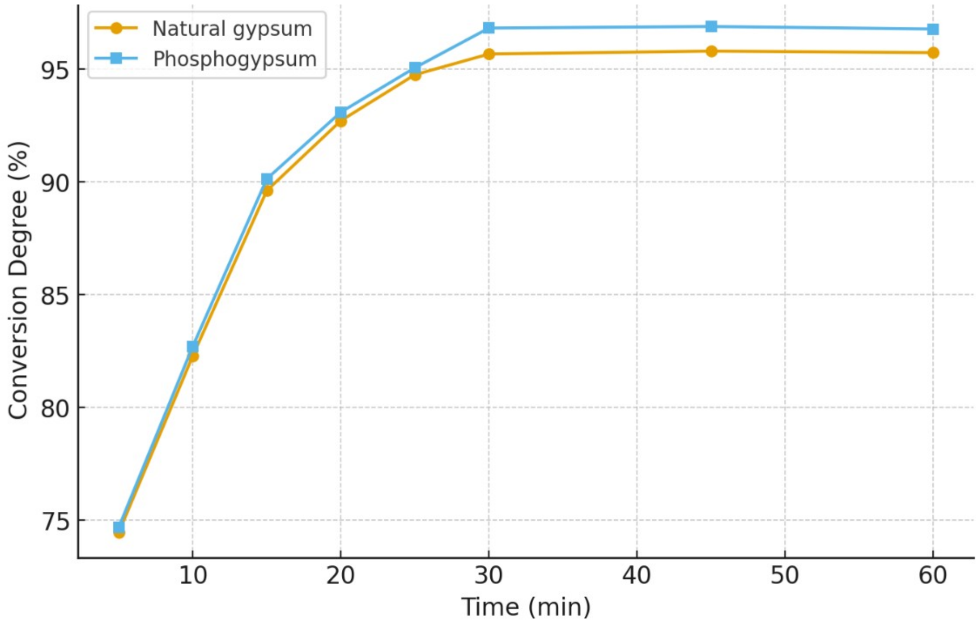


**Figure 1. The dependence of the degree of gypsum conversion on the conversion time and the time of ammonium carbonate introduction**

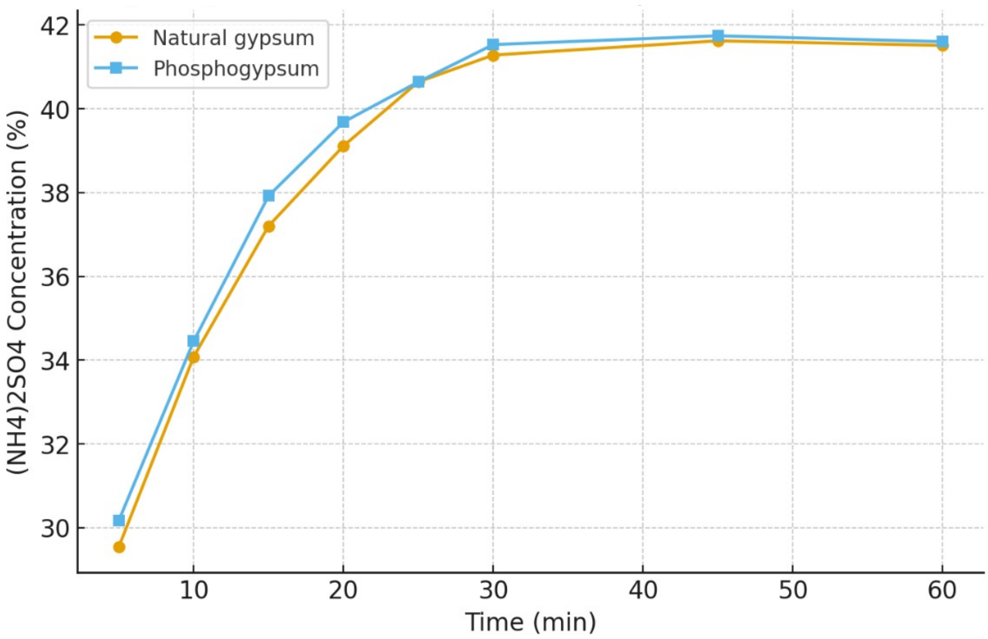


**Figure 2. Dependence of ammonium sulfate concentration in the liquid phase on conversion time and ammonium carbonate introduction time**

Figure 1 shows that the conversion rate for natural gypsum increased from 74.45% to 95.68% and for phosphogypsum from 74.68% to 96.83% within 5–30 minutes. It can be seen that the conversion rate increased with increasing time.

In the initial stage of the reaction, the conversion rate increased rapidly between 5 and 15 minutes, which mainly indicates a high diffusion rate between the solution and the gypsum surface. This indicator slows down after 20 minutes and reaches an almost equilibrium state in 30 minutes.

The calcium carbonate $CaCO_3$ crystals formed during the reaction form a thick layer on the surface of the gypsum particles, which reduces the number of active surfaces available. This layer makes it difficult for ions to penetrate into the inner layers. The conversion curve almost flattens out after 25–30 minutes, which is a clear sign of approaching equilibrium.

The concentration of ammonium sulfate $(NH_4)_2SO_4$ in the liquid phase was 29.54% - 41.51% in natural gypsum, and 30.17% - 41.60% in phosphogypsum. After a conversion time of 30 minutes, the concentration of ammonium sulfate $(NH_4)_2SO_4$ remained almost unchanged (Figure 2).

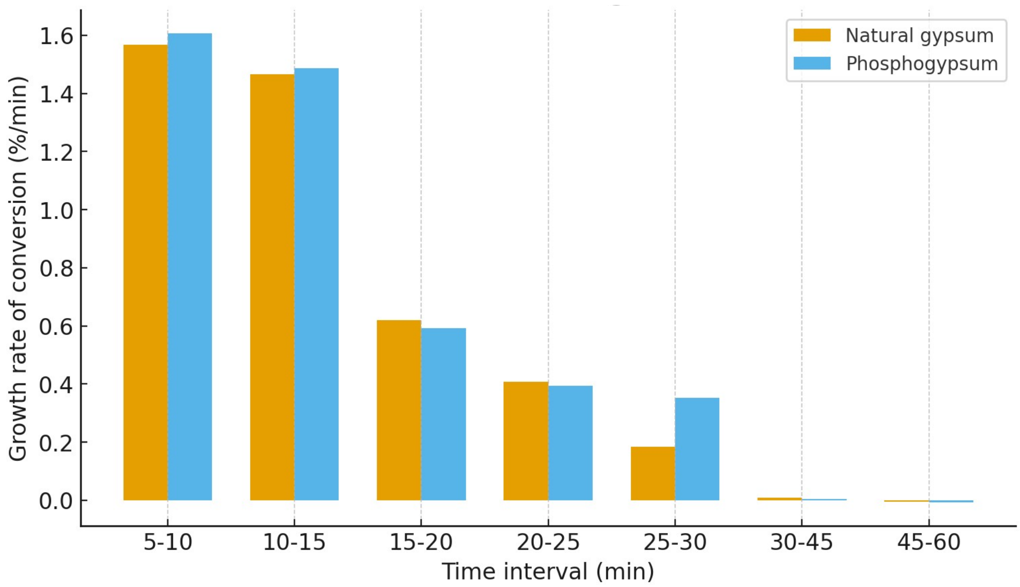


**Figure 3. Growth rate of gypsum conversion over time**

Figure 3 shows the rate of gypsum conversion over time, with a maximum rate of 1.6%/min observed between 5 and 0 minutes. At this stage, the reaction rate is high and ion exchange is active. In the next 10-15 minutes, the rate decreases slightly to 1.5%/min, but is still high. In the 15-20 and 20-25 time intervals, the decrease is more significant, to 0.6 and 0.4%/min. This indicates that the calcium carbonate $CaCO_3$ layer begins to form and the diffusion paths narrow. After 25-30 minutes, the rate is very small, 0.1%/min. Between 30-45 and 45-60, the rate is almost zero and the conversion process reaches equilibrium.

During the experiments, the composition of the liquid and solid phases formed during the conversion process was studied. The mass fraction of CaO and $CO_2$ in the solid phase obtained from the conversion of natural gypsum was CaO-39.45% - 51.85%, and $CO_2$-29.15 - 40.85% with an increase in the conversion time from 5 to 120 minutes. On the other hand, it was found that the mass fraction of undissociated gypsum in the solid phase decreased from 23.48% to 3.98% with an increase in the 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, the mass fraction of $SO_3$ and N was 13.09% - 24.60% and 4.10% - 8.43% with an increase in the conversion time from 5 to 120 minutes. It was found that the results obtained on the basis of phosphogypsum were slightly higher than those obtained on natural gypsum.

**Conclusion.**

As a result of the conducted research, the dependence of the conversion time and the time of introduction of ammonium carbonate in the process of carbonate conversion of gypsum by the liquid method was studied. During the experiments, optimal options for technological parameters were identified. The data obtained as a result of experiments conducted with natural gypsum and phosphogypsum in a 50% aqueous solution of ammonium carbonate and 100% stoichiometry at a temperature of 50°C for 30 minutes were found to be optimal options. Based on these results, a certain amount of energy savings was achieved in the technological process.

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