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Dmytro Yelatontsev

RESEARCH INTO THE PROCESS OF CARBONATE CONVERSION OF PHOSPHOGYPSUM IN THE WATER MEDIA

For a long time, the problem of phosphogypsum disposal was not given due attention, which led to the accumulation of huge reserves of this environmentally hazardous waste. Transportation of phosphogypsum in dumps and its storage requires significant capital investment and operating costs, as well as the allocation of large land areas. The storage of phosphogypsum harms the environment, as it leads to the entry of significant amounts of toxic substances into groundwater and the atmosphere. The object of the study was phosphogypsum, which is formed during the production of phosphoric acid from apatites and phosphorites. To date, numerous studies have focused on finding effective ways to use phosphogypsum, but its composition usually limits its reuse. The research aims to study the scientific prerequisites for creating an effective control scheme for phosphogypsum by converting it to calcium carbonate. For this purpose, the chemical composition and technological parameters of phosphogypsum conversion from the dumps of «Dnipro Mineral Fertilizer Plant» (Kamianske, Ukraine) were studied. The proposed conversion method involved a reaction between phosphogypsum and aqueous NaOH solution to form $\text{Ca}(\text{OH})_2$, which was converted to CaCO_3 by carbonization in a CO_2 stream. The influence of temperature on the conversion of phosphogypsum into $\text{Ca}(\text{OH})_2$ has been established. The conversion was investigated at 25 °C, 40 °C, and 70 °C for 3 hours. It was found that at the first stage of the process the impurities contained in phosphogypsum were transferred to the precipitate of $\text{Ca}(\text{OH})_2$. As a result of carbonization, low-quality CaCO_3 was obtained, which contained more than 10 % of impurities. Increasing the duration of carbonization to 1 hour allowed to obtain CaCO_3 with content of $\text{Ca}(\text{OH})_2 < 4$ %. The results of the study show that the method of carbonate conversion of phosphogypsum requires further optimization of technological parameters to improve the purity of the finished product.

Keywords: carbonate conversion phosphogypsum, sodium hydroxide, calcium hydroxide, carbon dioxide, carbonization, X-ray phase analysis, mass spectrometry, conversion temperature, mineralogical composition.

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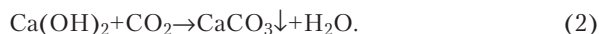
1. Introduction

Production of uranium products on the territory of the former Production Association «Prydniprovsky Chemical Plant» (PA «PChP») in Kamianske (Dnipropetrovsk region, Ukraine) has led to a threatening scale of accumulation of phosphogypsum [1]. As a result of the imperfect construction of phosphogypsum storages on the industrial site of «Dnipro Mineral Fertilizers Plant» (Kamyanske, Ukraine), today there is a gradual release of a significant amount of toxic impurities in the tributary of the Dnieper River [2].

In recent years, numerous researches work in the field of technologies for the direct use of phosphogypsum and its conversion into other products [3–5]. The technical feasibility and technological feasibility of using phosphogypsum in the national economy instead of traditional types of phosphorus fertilizers have been experimentally proven [6]. Despite the wide range of applications of

phosphogypsum, the huge volume of its formation and significant costs for cleaning, as well as competition with industrial counterparts significantly limits the market for phosphogypsum and its products [7].

Among the works that consider methods of conversion of phosphogypsum into marketable products, the most promising should be considered those that involve the integrated use of raw materials and the extraction of all valuable components present in phosphogypsum [8–10]. In particular, in [10] the process of phosphogypsum conversion to CaCO_3 was developed by treatment with sodium hydroxide followed by carbonization in an aqueous medium. The obtained calcium carbonate contains the main part of impurities (rare earth elements, radionuclides), and the mother liquor serves as a source for obtaining valuable sodium sulfate, which can be used in the production of synthetic detergents and glass. Reactions describing the process are expressed by the following chemical equations:



Thus, *the object of research* is selected phosphogypsum – waste generated during the production of phosphoric acid from apatites and phosphorites.

The aim of research is a study the effectiveness of carbonate conversion of phosphogypsum to optimize process conditions.

2. Methods of research

2.1. Phosphogypsum conversion technique.

200 cm³ of the initial NaOH solution with a concentration of 3 mol/dm³ was poured into a 500 cm³ flask with 5 necks and placed in a water bath at the selected temperature. A pH electrode, a temperature probe, and a mechanical stirrer were inserted into the flask through three of the five available necks. The other two mouths of the flask were closed with plastic plugs. The NaOH solution was stirred continuously until a constant pH of the solution and the selected temperature. 50 g of the phosphogypsum sample was added to 200 cm³ of NaOH solution at the selected temperature. The suspension was stirred at 750 rpm for 3 h, after which the liquid phase was separated by filtration using «blue tape» filter paper. The precipitate was then washed 4 times with 50 cm³ of distilled water to remove unreacted salts and dried at 75 °C for 3 hours.

2 g of the obtained Ca(OH)₂ was dispersed in 40 cm³ of running water at room temperature. The solution was stirred at 750 rpm for 1 h to obtain a homogeneous solution of Ca(OH)₂ and to ensure constant pH and temperature of the solution 25 °C inside the flask. After stirring, the solution of Ca(OH)₂ in the flask was purged with gaseous CO₂ at a flow rate of 285 cm³/min for 30 minutes. The resulting precipitate was washed three times with distilled water in portions of 50 cm³, dried at 75 °C for 3 hours, and weighed before further analysis.

2.2. Methods of research of chemical composition of raw materials and products. To determine the main oxide elements that may be present in the samples, analysis was performed by mass spectrometry with inductively coupled plasma (ISP-MS) using the device Agilent-7500CE 3M (USA) according to standard methods [11].

X-ray phase analysis was performed on a diffractometer DRON-3M (RF), the identification of mineral phases was carried out following the files of the American Society ASTM using software DIFFRACplus TOPAS for quantification with an accuracy of ±1 %.

3. Results of research and discussion

3.1. Investigation of the effect of temperature on the yield of Ca(OH)₂. For each temperature, the reaction was performed in duplicate, the average values were plotted against time.

Reactions between phosphogypsum and NaOH were studied at selected temperatures (25 °C, 40 °C, and 70 °C), and pH changes over time are shown in Fig. 1.

The pH of the NaOH solution at 25 °C before the addition of phosphogypsum was 13.5. After the addition of 50 g of phosphogypsum, the pH rapidly decreased to 13.38, indicating that OH⁻ ions in solution began to react with Ca²⁺ ions due to the dissociation of CaSO₄ contained in phosphogypsum to form a precipitate of Ca(OH)₂. After the addition of phosphogypsum, the pH value was constantly reduced throughout the experiment (3 h). This may indicate that the process was not completed after 3 h of reaction at room temperature and that some phosphogypsum remained unreacted.

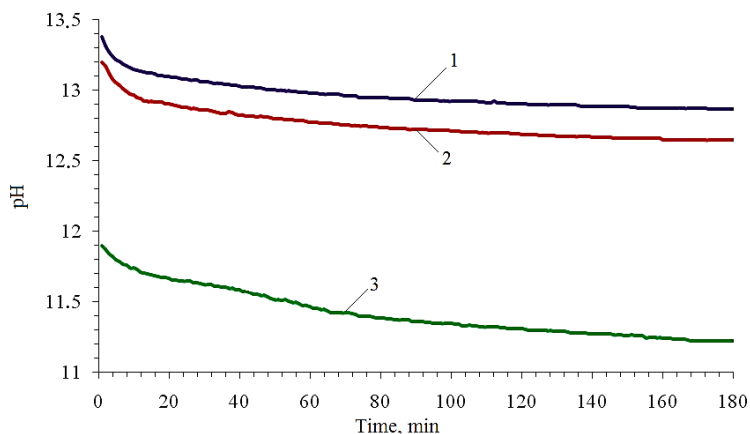


Fig. 1. The dependence of the pH of the reaction medium on temperature: 1 – 25 °C; 2 – 40 °C; 3 – 70 °C

At 40 °C, the pH of the NaOH solution before the addition of phosphogypsum was equal to 13.26. After the addition of phosphogypsum, there was an immediate decrease in pH and even after 3 hours of the reaction, the stabilization of pH values did not occur. This may mean that the conversion has not yet been completed.

At 70 °C, the pH of the NaOH solution before the addition of phosphogypsum was 11.90. After the addition of phosphogypsum after 3 h of interaction, the pH decreased and reached a stable value of 11.23 at the 165th minute of the reaction. However, 15 min is not enough to claim that the reaction between phosphogypsum and NaOH at 70 °C was complete.

The precipitates formed at different temperatures between the gypsum and NaOH samples were filtered, washed, dried, and weighed. The mass of each precipitate is shown in Table 1.

Table 1

The mass of precipitates formed at different temperatures

Temperature, °C	Mass of precipitate, g
25	23.11
40	22.34
70	22.42

According to stoichiometric calculations, 21.52 g of Ca(OH)₂ can theoretically be formed from 50 g of pure gypsum sample (CaSO₄·2H₂O) dispersed in 200 cm³ of 3M NaOH solution. At the same time, by dispersing 50 g of hemihydrate (CaSO₄·0.5H₂O) in 200 cm³ of 3M NaOH, 25.55 g of Ca(OH)₂ can be obtained. The experimentally

obtained amounts of precipitates formed from phosphogypsum slightly exceed the expected theoretical mass required for the formation of pure $\text{Ca}(\text{OH})_2$. Because the molecular weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is greater than $\text{Ca}(\text{OH})_2$, the increased weight of the product, compared with stoichiometrically calculated, may indicate incomplete conversion of gypsum to $\text{Ca}(\text{OH})_2$. This confirms the results obtained during the pH measurement, indicating that part of the phosphogypsum did not react after 3 h of reaction.

The content of the main elements in the precipitates of $\text{Ca}(\text{OH})_2$ formed at different temperatures is summarized in Table 2.

The calcium content (expressed as CaO) in each of the samples $\text{Ca}(\text{OH})_2$ (64–77 %) is twice the amount of CaO contained in the initial phosphogypsum before conversion (33.3 %).

Other elements are present in the form of impurities that were previously contained in the untreated phosphogypsum and passed into the precipitate of $\text{Ca}(\text{OH})_2$. It was previously reported [10] that in the process of conversion there is a transfer of impurities from phosphogypsum to calcium hydroxide.

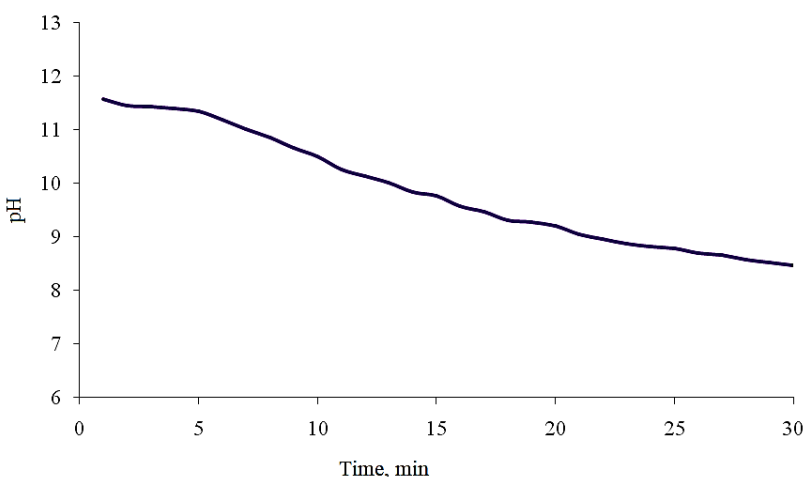


Fig. 2. The dependence of pH during the carbonization of the precipitate $\text{Ca}(\text{OH})_2$ by gaseous CO_2

The mineralogical composition of the carbonized sludge was analyzed by radiography. The results of the analyzes are expressed in mass percent (wt. %), Summarized in Table 3.

Table 3

Mineralogical composition of sediment

Mineral	Molecular formula	Content, wt. %
Calcite	CaCO_3	87
Portlandite	$\text{Ca}(\text{OH})_2$	4
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	6
Quartz	SiO_2	3

Table 2
The chemical composition of $\text{Ca}(\text{OH})_2$ precipitates formed during the conversion of phosphogypsum at different temperatures

Component	Content, wt. %		
	25 °C	40 °C	70 °C
SiO_2	0.727	1.149	0.901
TiO_2	0.021	0.029	0.018
Al_2O_3	0.216	0.361	0.237
Fe_2O_3	0.438	0.313	0.268
MnO	0.006	0.004	0.004
MgO	0.080	0.098	0.073
CaO	67.356	77.563	64.731
Na_2O	0.212	0.336	0.937
K_2O	0.036	0.056	0.007
P_2O_5	2.291	2.879	2.262
Losses during roasting	21.664	23.728	22.597
Moisture	2.264	1.610	0.818

3.2. Study of the process of carbonization of $\text{Ca}(\text{OH})_2$.

In Fig. 2 shows the change in pH of the precipitates of $\text{Ca}(\text{OH})_2$ obtained by the interaction of phosphogypsum and NaOH at 25 °C, during carbonization.

After dispersing $\text{Ca}(\text{OH})_2$ in water, the pH of the solution before purging with CO_2 was 12.3. After the introduction of CO_2 into the suspension, the pH value began to decrease rapidly, and after 30 min of the process reached 8.47. The decrease in pH is the result of the formation of a precipitate of CaCO_3 . However, as can be seen from Fig. 2, after 30 min of bubbling, the carbonization of $\text{Ca}(\text{OH})_2$ is still not complete.

As can be seen from Table 3, calcite is the main mineral phase of the sediment. Today, it is believed that low-quality CaCO_3 has a purity below 90 %, and high-quality – more than 95 % [4]. An insufficiently high content of CaCO_3 , confirms that the process of carbonization of $\text{Ca}(\text{OH})_2$ precipitates derived from phosphogypsum has not been completed.

Therefore, an attempt was made to convert 5 g of phosphogypsum into CaCO_3 using 20 cm^3 of NaOH solution; the ratio of solid to liquid (S:L)=1:4. Radiographic analysis revealed the formation of stable calcite, with a small amount of unreacted portlandite. No gypsum crystals were found in the sediments, which suggested its complete transformation.

The CaCO_3 precipitate formed at room temperature using 5 g of phosphogypsum and 20 cm^3 of NaOH solution was further characterized because the complete conversion of phosphogypsum to CaCO_3 was obtained. Calcite was found to be the dominant mineral phase (> 96 %) of the precipitate. Subsequently, a study of mass balance was performed using three samples of the formed precipitates to determine the percentage of calcium phosphogypsum, which was transformed into calcite. The results of this study are summarized in Table 4.

From the Table 4 shows that from 5 g of phosphogypsum (containing 1.97 g of calcium) dispersed in 20 cm^3 of NaOH solution, 2.75 g of CaCO_3 is formed, which corresponds to the average degree of conversion of phosphogypsum to CaCO_3 56.08 %. This means that a significant part of calcium (43.92 %) remains unreacted.

Table 4

The degree of conversion of calcium into calcite

A portion of phosphogypsum, g	The mass of calcium in 5 g of phosphogypsum, g	Theoretical mass CaCO ₃ , which can be formed from 1.97 g of Ca, g	The experimental mass of CaCO ₃ , g	Degree conversion of phosphogypsum into CaCO ₃ , %
5	1.97	4.91	2.86	58.25
			2.67	54.38
			2.73	55.60

4. Conclusions

In the process of carbonization in an aqueous medium, phosphogypsum was converted to Ca(OH)₂ in 3 h of interaction with a solution of 3M NaOH. The degree of conversion at 25 °C of phosphogypsum was 96 %. It was found that the impurities contained in phosphogypsum are converted into Ca(OH)₂.

The main phase of the sediment was calcite. However, 30 min of carbonization was not enough for complete carbonization of Ca(OH)₂ derived from phosphogypsum resulting in low-quality CaCO₃ (impurity content – 13 %).

To increase the efficiency of the conversion process, it is recommended to increase the reaction time to 4 h for a more complete conversion of phosphogypsum to Ca(OH)₂, as well as to increase the duration of carbonization to 1 h.

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