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RESEARCH ON TECHNOLOGY OF COMPLEX PROCESSING OF PHOSPHOGYPSUM

Purpose. To conduct systematic studies on the process of obtaining rare earth elements from phosphogypsum by sulfate acid treatment. To determine the concentration of acid and rare earth elements in the filtrate after phosphogypsum excretion in the samples, depending on the ratio of phosphogypsum : acid 1 : 1.5; 1 : 2 and 1 : 2.5. To test purified calcium sulfate as a reagent for the extraction of phosphates from urban liquid waste sludge, to extract organ–mineral fertilizer from purified phosphogypsum and activated sludge from wastewater treatment plants.

Methodology. For research, a laboratory unit for complex processing of phosphogypsum was prepared and the principle of its work was described. The experimental studies were performed using trilon B titration techniques to determine the rare earth element concentration and NaOH titration to determine the acid concentration. A photometric method was used to determine the concentration of inorganic phosphates in the wastewater.

Findings. The content of acid in the filtrate at different ratio of “phosphogypsum: acid” from the enterprise “Dnipro Mineral Fertilizer Plant” and from the waste heaps was revealed. It is established that the concentration of acid increases with the ratio of “phosphogypsum: acid” from 1 : 1.5 to 1 : 2.5, respectively. The obtained organic–mineral fertilizer corresponds to DSTU 7369:2013.

Originality. The regularities of the process of acid treatment of phosphogypsum depending on the origin have been established, and it is found that the concentration of the rare earth elements and acid is higher in phosphogypsum, which is obtained at the Dnipro Plant of Mineral Fertilizers than in phosphogypsum selected from waste heaps. The dependence of the ratio “phosphogypsum: acid”, namely 1 : 1.5; 1 : 2 and 1 : 2.5 on the concentration of acid and rare earth elements in the samples was found. It was established that the presence of activated sludge in anoxic mode for 30 h leads to an increase in the content of phosphates in the aqueous phase by 2.6–2.8 times. Dependences of the process of extraction of phosphates from urban liquid waste sludge by phosphogypsum were obtained. Organic–mineral fertilizer from activated sludge of urban wastewater treatment plants and purified phosphogypsum was obtained, which meets the requirements of DSTU 7369:2013.

Practical value. A laboratory unit has been developed for obtaining purified phosphogypsum from soluble impurities. It is proposed to use purified phosphogypsum as a raw material in agriculture for the organic–mineral fertilizers and composts production, a reagent for the extraction of phosphates from wastewater and in the building materials industry to obtain gypsum binders. The studies made it possible to quantify the concentration of rare earth elements and acids in phosphogypsum, as well as their possible selection as valuable products from the filtrate.

Keywords: *wastewater treatment plants, phosphogypsum, rare earth elements, sulfuric acid, phosphates, organo–mineral fertilizer, filtrate*

Introduction. The chemical industry is one of the most important parts of Ukraine’s economy. The industry has a sufficient raw material base and a complex structure.

The main amount of phosphate fertilizers is produced as a result of sulfuric acid decomposition of phosphate raw materials to obtain 2 main types of intermediates: phosphoric acid, called extractive phosphoric acid, and phosphogypsum waste – phosphogypsum, which is a valuable secondary material resource containing up to 95 % CaSO₄.

In the Dnipropetrovsk region, phosphoric acid is produced at Dniprovskiy Mineral Fertilizer Plant PJSC (Kamianske), the main waste of which is phosphogypsum – calcium sulfate [1].

In the production of extractive phosphoric acid from apatite concentrate by the dihydrate method, the formation of wet fine powder of phosphogypsum is observed [1]. According to the content of the main component of calcium sulfate dihydrate (CaSO₄ · 2H₂O) phosphogypsum is equated to gypsum natural raw materials of the first grade [2]. The reaction of phosphogypsum formation (1) is below



The crystalline precipitate of calcium sulfate is separated from phosphoric acid by filtration. The acid is used in the production of mineral fertilizers, and the sludge is sent to the dumps [3].

There are two main methods of industrial production of orthophosphate acid: extraction and thermal. In practice, the method of acid extraction has become the most common, which uses the decomposition of natural phosphate ore with mineral acids [3].

Phosphogypsum reserves in Kamianske are estimated at 1 million tons.

Fig. 1 shows the main stages of production of phosphoric acid extraction (EFK) [3].

Depending on the production conditions, process temperature and P₂O₅ concentration, calcium sulfate (phosphogypsum) is released in the form of CaSO₄ · 2H₂O (dihydrate mode), CaSO₄ · 0.5H₂O (semi–hydrate mode) and CaSO₄ (anhydrite mode). Dihydrate and semi–dihydrate regimes have become industrially widespread [3].

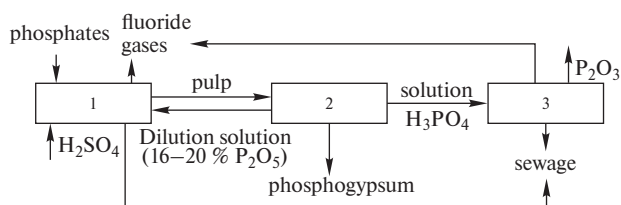


Fig. 1. The main stages of production of phosphoric acid extraction: 1 – extraction; 2 – filtering; 3 – evaporation

The raw material for acid production is apatite and phosphorite ores [3]. Apatites are rocks of volcanic origin with a coarse-grained structure. Therefore, for the production of phosphate fertilizers, the product of preliminary enrichment of apatite ores is used – apatite concentrate containing up to 40 % P_2O_5 [4].

Phosphorites are ores of sedimentary origin, highly dispersed and contain Phosphorus in the form of fluoroapatite and apatite-like minerals of variable composition. Phosphorus content in phosphorites ranges from 16 to 30 % P_2O_5 [4].

Until the mid-1990s, to obtain extractive phosphoric acid in Ukraine Khibiny apatite concentrate was used and the phosphorite one (Syrian, Moroccan or Tunisian phosphorites) was used from the mid-1990s [3].

An important distinguishing feature of the old phosphogypsum dumps available in Ukraine, which were obtained after the processing of Khibiny apatite concentrate, is that unlike other sources of rare earth elements, it does not contain radioactive compounds. The rare earth elements obtained from it are not radioactive and do not require decontamination, which makes their production very profitable.

Depending on the quality of raw materials used and the accepted technology per 1 ton of acid in terms of 100 % H_3PO_4 you can get 4.5–8.4 tons of wet phosphogypsum (or 3.6–6.2 tons in terms of dry matter) [3]. When processing 1 t of apatite concentrate into extraction phosphate acid (EFC), 1.5–1.6 t of phosphogypsum is formed, and per 1 t of P_2O_5 – 4–5 t of phosphogypsum [3].

This waste is a gray fine-crystalline powder, which is whipped into balls with the humidity of up to 25–40 % (depending on the conditions of formation of phosphoric acid). Phosphogypsum (in terms of dry matter) contains up to 94 % $CaSO_4$, as well as impurities of unwashed phosphoric acid, oxides, compounds of strontium and fluorine, various micro-impurities [5].

Table 1 shows the chemical composition of the main components of phosphogypsum obtained from Kolskia apatite and Syrian phosphorites [3].

On the territory of Ukraine, about 90 million tons of phosphogypsum have accumulated [3] in dumps. Storage of industrial waste on a large scale has become a global environmental problem. Development of technologies for complex processing of phosphogypsum dumps is an urgent scientific task. In world practice, a number of technologies have been developed to obtain valuable products based on phosphogypsum. Thus, in particular, it is used in the cement industry as a mineralizer and regulator; in the production of construction products of blocks, panels, as well as composting with organic and organo-mineral fertilizers [3, 6, 7].

Based on the analysis of scientific and technical literature [3, 6, 7], the most promising areas of phosphogypsum use as a valuable large tonnage secondary resource are given below.

In agriculture:

- for chemical reclamation of solonchic soils;
- in a mixture with lime materials for reclamation of acid soils [6];
- composting with organic fertilizers [7].

In the cement industry:

- for use as a mineralizing additive in the firing of cement clinker [6];
- to obtain hydraulic additives;

Chemical composition of apatite and phosphorite phosphogypsum

The name of the chemical in the composition of phosphogypsum	The chemical content, % wt.	
	From the Kolskia apatite	From Syrian phosphorites
Composition (in terms of dry matter):		
$CaSO_4 \cdot 2H_2O$	> 90	> 90
F	0.3–0.4	0.2–1.3
$(P_2O_5)_{com}$	1.0–1.2	< 1.2
$(P_2O_5)_{wat}$	0.5–0.6	< 0.2
Hygroscopic (over crystallization) water	6–20	10–23

- as a regulator of setting speed – instead of natural gypsum [7].

In the building materials industry:

- for the production of gypsum binders and products based on them – building blocks, mortars and mixtures, slabs for partitions and ceilings [3];

- in road construction as a material for the base backfilling [7];

- in the production of paper and paints as a filler;

- when arranging sea and coastal zones;

- to obtain a high-strength anhydrite binder [3].

In the chemical industry to obtain:

- sulfuric acid or lime [6];

- ammonium sulfate;

- Sulfur [3].

It is also possible to use phosphogypsum to isolate rare earth elements (REE).

Rare earth elements are a group of chemical elements that in different years included up to half of D.I. Mendeleev's table, but its main components have always been lanthanides [8].

Lanthanides or lanthanides make a group of 15 chemical elements of the third group of the periodic table from Lanthanum to Lutetia (from La to Lu). Also rare earth elements include Scandium (Sc) and Yttrium (Y), Cerium (Ce), Neodymium (Nd) [3, 8], which are among the most imported and exported goods in the world [9].

Rare earth elements and their compounds have a number of unique properties that have ensured their widespread use in industry, engineering, metallurgy and green energy production technology [3, 9]. REEs play a significant role in the world of innovative technologies (production of lasers, conductors, magnets) [3]. They are also needed to produce most high-tech products: computers, mobile phones, flat screens, batteries for electric vehicles and wind turbines [3, 9].

Literature review. The methods for processing and using phosphogypsum as a secondary raw material have recently drawn considerable attention of the researchers. Some of them are below.

In chemical technology $(NH_4)_2SO_4$ and $CaCO_3$ can be obtained by conversion of phosphogypsum with the help of carbonate ammonium. The basis of the method is the reaction (2)



that is, ammonium sulfate can be obtained without the use of sulfuric acid.

There is a [10] cost-effective method for processing phosphogypsum, which includes several stages: ammonization, carbonization, calcination and conversion of ammonium sulfate. Further processing of ammonium sulfate was carried out to obtain potassium sulfate and ammonium chloride [10]

The authors proposed [11] the technology for processing phosphogypsum produced as the waste in the production of wet-process phosphoric acid in integrated fertilizer. To obtain the fertilizer at the first stage phosphogypsum is treated with ammonium carbonate to form a slurry. At the next stage, the resulting suspension is mixed with the diluted phosphate with acid. Drying

the resulting pulp is carried out in moderate temperature in the apparatus intensive heating of the “boiling layer” type using waste flue gases with the production of dry granulated product [11].

In the work by the authors [12, 13] the preparation of a binding agent is described. To fulfill this, the phosphogypsum is mixed in the edge with lime and is left for 1–3 days in open warehouses for the neutralization of acidic residues. Next, the neutralized phosphogypsum is subjected to heat treatment in gypsum boilers of periodic action, where, firstly, the evaporation of free moisture happens, and, secondly, dehydration of phosphogypsum takes place. After cooling, the obtained phosphogypsum binder can be used without grinding to manufacture the products.

The [13, 14] method for making synthetic gypsum from phosphogypsum has been studied, which includes washing with water, neutralization with ground chalk, bonding of particles with polyvinyl-acetate emulsion and granulation on the drum-type installations [13, 14], acidic residues are neutralized with ground burnt lime, as the active mineral additives natural zeolite is used. The production of granules from a mixture of components is produced by bilateral pressing in a roller press under pressure of 60–70 MPa with subsequent hardening in the air for 5–7 days [13, 14].

The researchers offered [15] the obtaining of compound fertilizers with the use of phosphogypsum, including its treatment with phosphate solution, filtering and drying of the finished product. The process runs several stages: the first stage is pre-calcined phosphogypsum carbonating treated with alkaline reagent to a pH of 9–10, the second one – the obtained chalk pulp is mixed with half-product of wet-process phosphoric acid production to a pH of 5.4–6 [15].

In the work by the authors [16] the processing of phosphogypsum for the extraction of rare earth elements with a solution of ammonium carbonate and dissolving of precipitated calcium carbonate with nitric acid is proposed. It is characterized in the ratio of solid phase and liquid equal to 1 : 1–1 : 2 with a solution of calcium nitrate, the precipitated calcium carbonate is pulverized; the obtained pulp is treated with nitric acid, the concentration of which is 45–57 % at pH of 5.1–7.1 and flow rates of 1.0 acid – 1.37 dm³/h per 1 kg of calcium carbonate.

In the work [2] the authors considered the process of acid refining of phosphogypsum. It was found that with an acid content of 0.2 mol/dm³ and a contact duration of 0.2 hours at a temperature of 90 °C, the content of F is 0.3 %, P – 0.2 %; at an acid content of 0.4 mol/l and a contact duration of 1.5 hours at a temperature of 90 °C, the mass fraction F is 0.1–0.2 %, P is 0.1–0.2 %. It was also found that at pH 1–1.5, the REE content in the filtrate is 1.7 g/dm³, but the extraction of REE in the sediment does not occur, and at pH 2.7 – 3.5 the REE content in the filtrate is equal to 0.1–0.3 g/dm³, and the degree of REE transition to sediment is 82–94 %.

However, the question of establishing the effect of the ratio “phosphogypsum: acid” on the content of rare earth elements and the effect of acid treatment on the residual acid content in the filtrate remained unexplored.

Unsolved aspects of the problem. The effect of the ratio “phosphogypsum: acid”, namely 1 : 1.5, 1 : 2 and 1 : 2.5 on the concentration of rare earth elements and acids in the filtrates.

Purpose. The aim of the work is to study the process of obtaining chemically pure phosphogypsum with simultaneous extraction of rare earth elements and obtaining organo-mineral fertilizer.

As the object of study the phosphogypsum obtained at the Dniprovskiy Mineral Fertilizers Plant was compared to the one obtained from the dumps of Kamianske in terms of the concentration of acid and rare earth elements in the filtrate.

The influence of the ratio “phosphogypsum: acid”, namely 1 : 1.5; 1 : 2 and 1 : 2.5 on the concentration of rare earth elements and acids in the filtrates is defined.

Methods. For the experimental research, a laboratory installation for complex processing of phosphogypsum was made, the scheme of which is shown in Fig. 2.

The study was performed as follows. To container 3, 250 g of phosphogypsum was added and 375, 500 and 625 ml were filled with a solution of 0.6 mol/dm³, respectively, with a solution of sulfuric acid. After that, the container with the pulp was placed on the furnace 4, and heated for 2 hours at a temperature of 95 °C with stirring and bubbling air. After the allotted time, the tap 6 was opened and the precipitate was filtered through the filter 5 and washed with 350 ml of water. The filtrate was sent to prepare a new portion of the solution.

At the end of the experiment, the concentration of acid and rare earth elements in the filtrates was determined by the methods of titration with NaOH and Trilon B.

To determine the concentration of acid in the filtrates the method of titration with NaOH was used.

To 20 ml of the sample, a few drops of phenolphthalein were added and titrated with NaOH 0.1 N.

The acid concentration in the filtrates was determined by the formula

$$\frac{a \cdot 0.1}{b},$$

where *a* is the volume of NaOH tested; *b* is the volume of the sample taken for analysis.

To determine the concentration of rare earth elements in the filtrate, the method of titration with Trilon B 0.05 N was used.

To 20 ml of the sample, 1 drop of thymol blue solution and ammonia solution were added until a yellow color appeared. Then a buffer solution of pH = 6 and indicator mixture were added and titrated with Trilon B 0.05N until the color change of the solution from red to yellow.

The total content of rare earth elements was determined by the formula

$$\frac{c \cdot 3.5}{d},$$

where *c* is the volume of Trilon B tested; *d* is the volume of the sample taken for titration.

The washed precipitates were mixed with 0.5 g of calcium hydroxide and removed as a finished product – purified phosphogypsum.

Subsequently, part of the treated phosphogypsum was used to extract phosphates from urban wastewater and to obtain organo-mineral fertilizer.

To determine the concentration of inorganic phosphates in wastewater, a photometric method (reduction with ascorbic acid) was used, using the following equipment: a colorimeter, a red light filter, cuvettes with a layer thickness of 5 cm. The measurements were performed using a colorimeter photoelectric concentration CPK–2.

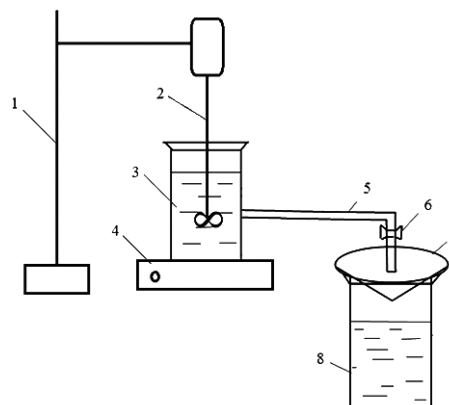


Fig. 2. The scheme of the laboratory unit for complex processing of phosphogypsum:

1 – tripod; 2 – vertical stirrer; 3 – the capacity of the pulp; 4 – oven; 5 – connecting tube; 6 – the crane; 7 – filter; 8 – capacity with filtrate

The content of dissolved phosphates (PO_4^{3-}) in mg/dm^3 was found by the formula

$$x = \frac{c \cdot 50}{v},$$

where c is phosphate concentration, which was found on the calibration curve, mg/dm^3 ; v is the volume of the sample taken for determination, ml; in this case $v = 2$.

The method for obtaining organo-mineral fertilizer was as follows.

In the laboratory, the reactor with a volume of 1 dm^3 was fed with activated sludge from urban treatment plants and the purified CaSO_4 in the form of a solution in the amount of 150/500 ml of sewage sludge was added to it. The mixture of reactive components was maintained for 4 days.

After settling, the precipitate was filtered off from the liquid phase. The filtered precipitate was analyzed for the content of macro- and microelements of the elements, its chemical composition was determined to test the possibility of use as an organo-mineral fertilizer.

Results. After obtaining the purified phosphogypsum, the concentration of acid in the filtrates was determined.

The graph of the concentration of acid on the ratio "phosphogypsum: acid" in the filtrate of both samples is below (Fig. 3).

It was found that the acid concentration increases with increasing ratio "phosphogypsum: acid" from 1 : 1.5 to 1 : 2.5, respectively. This can be explained by the fact that soluble impurities of phosphoric and sulfuric acids may remain in the composition of the initial phosphogypsum and due to washing the precipitate with water, their presence can lead to an increase in the concentration of acid in the filtrate.

It was found that in the phosphogypsum sample, which was selected at the enterprise "Dnieper Mineral Fertilizer Plant", the concentration of acid is higher compared to phosphogypsum from dumps. Under the influence of climatic factors and precipitation on the dumps, the upper layer of phosphogypsum is naturally washed away from acidic and dissolved impurities.

Next, the content of rare earth elements was determined depending on the ratio of "phosphogypsum: acid" in the samples.

Based on experimental studies, it was found that depending on the ratio "phosphogypsum: acid" the concentration of rare earth elements in the filtrate in both samples increases with increasing acid in the ratio of "phosphogypsum: acid" 1 : 2, but with increasing ratio to 1 : 2.5 the concentration of rare earth elements decreased.

These results can be explained by the fact that when the ratio of "phosphogypsum: acid" as 1 : 2.5 increases, the dissolution of REE compounds takes place, especially the hydrated orthophosphates and their precipitation from solution due to the secondary formation of insoluble REE compounds.

More efficient separation of rare earth elements is observed in the filtrate after acid processing of phosphogypsum of the enterprise "Dniprovskiy Mineral Fertilizer Plant". Table 2 shows the mass of purified phosphogypsum in the samples at different ratios of "phosphogypsum: acid".

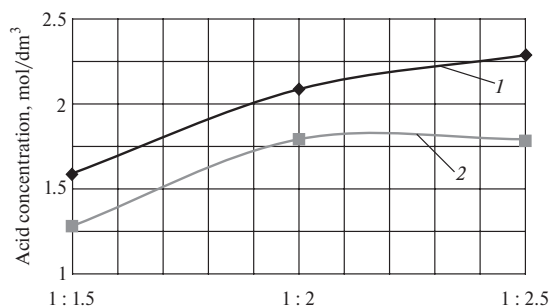


Fig. 3. Dependence of acid concentration on the ratio "phosphogypsum: acid" at 368 K and duration of processing 2 hours: 1 – from DZMD enterprise; 2 – from the stockpile

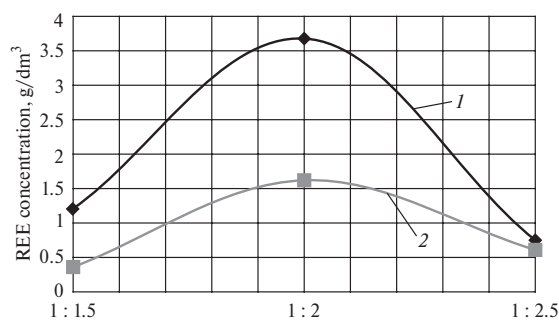


Fig. 4. Dependence of REE concentration on the ratio "phosphogypsum: acid" at duration of processing 2 hours and the temperature of 368 K:

1 – from DZMD enterprise; 2 – from the stockpile

It was found that when treating phosphogypsum with sulfuric acid in different ratios "phosphogypsum: acid", namely 1 : 1.5, 1 : 2 and 1 : 2.5 its mass in the treated state decreases with increasing acid content in it.

The obtained purified phosphogypsum was used to extract phosphates from urban wastewater. The effect of phosphogypsum additive on the efficiency of phosphate extraction from the aqueous phase of activated sludge after the anoxide regime, the initial content of which was $55.28 \text{ mg}/\text{dm}^3$, was studied. During the activated sludge stay without access to oxygen (anoxide mode) there are stressful conditions (hypoxia), which ultimately leads to release of biogenic elements into aqueous phase. The dynamics of changes in the concentration of phosphates in the aqueous phase from the duration of finding of activated sludge in anoxic conditions is shown in Fig. 5.

Studies have shown that the dephosphatization process of the activated sludge mixture after the secondary settling tank proceeds according to the same patterns as from the tank, i. e. in the period up to 20 h of anoxide regime the phosphate content in the aqueous phase remains constant and from 22 to 28 h begins to increase sharply from 6.5 to $17 \text{ mg}/\text{dm}^3$ and from 19.5 to $55.28 \text{ mg}/\text{dm}^3$. Dephosphating of the activated sludge from the tank after the secondary one before discharge to the sludge sites is more appropriate, both in terms of further reagent treatment of municipal liquid waste with maximum phosphate content to obtain phosphorus-containing components for fertilizer production, and in terms of improving environmental safety near silt maps due to safe discharge of silt waters and prevention of eutrophication of reservoirs. The kinetics of phosphate removal from wastewater by phosphogypsum after anoxic dephosphorization is presented below (Fig. 6).

The results of the study revealed a high (95.5 %) efficiency of phosphate extraction from urban wastewater and ensuring of the maximum allowable concentration ($3.5 \text{ mg}/\text{dm}^3$) with the introduction of $2 \text{ g}/\text{dm}^3 \text{ CaSO}_4$.

To study the process of obtaining organomineral fertilizer, the activated sludge of the left-bank sewage treatment plants of Kamianske was selected, which receives liquid waste only from the population and the Oril Leader poultry farm and does not pose a threat from the point of view of heavy metals.

When developing technologies for obtaining fertilizers from waste and analysis of their quality and the possibility of

Table 2

The influence of the ratio "phosphogypsum: acid" on the mass of purified phosphogypsum in the samples

Samples	The initial mass of phosphogypsum, g	Ratio "phosphogypsum: acid"		
		1 : 1.5	1 : 2	1 : 2.5
DZMD	250	167	161	156
stockpile	250	224	201	190

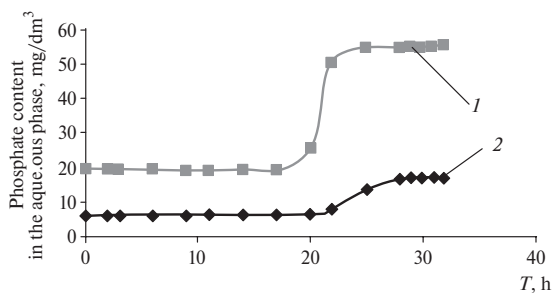


Fig. 5. Dynamics of change of the phosphate concentration in the aqueous phase from the duration of finding of activated sludge in anoxic condition:

1 – AM from the tank before discharge to the sludge sites; 2 – AM sludge chamber after the secondary settling tank

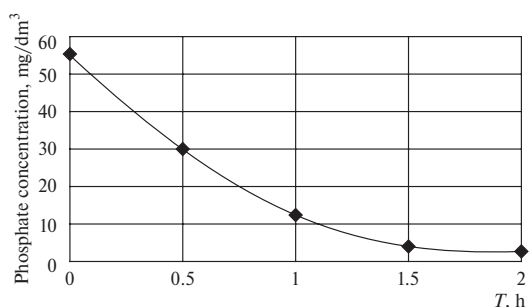


Fig. 6. Kinetics of phosphate removal from wastewater by phosphogypsum

use for growing crops one refers to DSTU 7369–2013 “Wastewater. Requirements for wastewater and its sediments for irrigation and fertilization”, which has been valid since 01.01.2014.

Table 3 shows the chemical composition of the organomineral product from phosphogypsum and activated sludge, in terms of dry matter compared to DSTU 7369:2013.

After analyzing Table 3, we can conclude that the resulting multicomponent fertilizer mixture contains a sufficient amount of nutrients: Nitrogen, Phosphorus, Potassium. At the same time, the content of heavy metals does not exceed the maximum allowable norms and the obtained indicators comply with DSTU 7369:2013.

Conclusions. The laboratory installation for complex processing of phosphogypsum with obtaining a purified calcium sulfate and subsequent extraction of rare earth elements was developed.

The regularities of the acid treatment process of phospho-

Table 3

Chemical composition of organomineral product from phosphogypsum and activated sludge, in terms of dry matter compared to DSTU 7369:2013

Name of Indicators	Indicators	DSTU 7369:2013 group 1
Mass fraction of organic matter, %	20.24	no less 40
Mass fraction of nutrients, %		
Nitrogen total	6.20	no less 1.5
Phosphorus total	1.44	no less 0.7
Potassium	5.95	–
Calcium	31.50	–
Trace elements, mg/kg		
Silicon	50	–
Magnesium	55	–
Borium	426	–
Cuprum	147	100–300
Nickel	55	50–75

gypsum depending on origin were established and it was found that the concentration of rare earth elements and acids in calcium sulfate, which is produced at the enterprise “Dniprovskiy plant of mineral fertilizers”, is more than in phosphogypsum selected from the stockpile.

The dependence of the ratio of “phosphogypsum: acid” 1 : 1.5, 1 : 2 and 1 : 2.5 by acid concentration and rare earth elements in the samples was revealed.

The concentration of acid increases with the increase in the ratio of “phosphogypsum: acid” from 1 : 1.5 to 1 : 2.5, respectively.

The optimal ratio “phosphogypsum: acid” 1 : 2, in which there is the maximum content of rare earths in the filtrate was proposed.

Thus, the studies have revealed that there might be further extraction of rare earth elements as a valuable product from the filtrate after precipitation of pure phosphogypsum.

It is established that the stay of the activated sludge in an anoxic mode for 30 h leads to the increase in phosphate in the aqueous phase by 2.6–2.8 times. The dependence of the extraction process of phosphates from urban liquid waste phosphogypsum was revealed.

The organomineral fertilizer was received from the cleaned phosphogypsum and activated sludge of municipal wastewater treatment plants, which meets ISO 7369:2013.

In the future, it is proposed to use purified phosphogypsum as a raw material to receive organomineral fertilizers in agriculture, a reagent for precipitation of phosphates from municipal wastewater and raw materials for the production of gypsum binders in the construction industry.

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Дослідження технології комплексної переробки фосфогіпсу

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Мета. Провести системні дослідження процесу одержання рідкісноземельних елементів із фосфогіпсу шляхом сульфатнокислотної обробки. Визначити концентрації кислоти й рідкісноземельних елементів у фільтратах після виділення фосфогіпсу у зразках у залежності від співвідношення «фосфогіпс : кислота» 1 : 1,5, 1 : 2 та 1 : 2,5. Випробувати очищений кальцій сульфат в якості реагенту для вилучення фосфатів із мулу міських очисних споруд, отримати з очищеного фосфогіпсу та активного мулу очисних споруд органо-мінеральне добриво.

Методика. Для досліджень складена лабораторна установка комплексної переробки фосфогіпсу та описано принцип її роботи. Експериментальні дослідження виконували з використанням методик титрування трилоном Б для визначення концентрації рідкісноземельних елементів і титрування NaOH для визначення концентрації кислоти. Для визначення концентрації неорганічних фосфатів у стічній воді використано фотометричний метод.

Результати. Виявлено вміст кислоти у фільтраті при різному співвідношенні «фосфогіпс:кислота» на підприємстві «Дніпровський завод мінеральних добрив» і з відвалів. Встановлено, що концентрація кислоти підвищується зі збільшенням співвідношення «фосфогіпс : кислота» від 1 : 1,5 до 1 : 2,5 відповідно. Отримане органо-мінеральне добриво відповідає ДСТУ 7369:2013.

Наукова новизна. Встановлені закономірності процесу кислотної обробки фосфогіпсу в залежності від походження, та виявлено, що у фосфогіпсі, який одержують на підприємстві «Дніпровський завод мінеральних добрив» концентрація рідкісноземельних елементів і кислоти більша, ніж у фосфогіпсі, що відібрано з відвалів. Виявлена залежність співвідношення «фосфогіпс : кислота», а саме 1 : 1,5, 1 : 2 та 1 : 2,5 від концентрації кислоти й рідкісноземельних елементів у зразках. Встановлено, що перебування активного мулу в аноксидному режимі протягом 30 годин призводить до збільшення вмісту фосфатів у водній фазі у 2,6–2,8 разів. Одержані залежності процесу вилучення фосфатів із мулу міських очисних споруд фосфогіпсом. Отримано органо-мінеральне добриво з активного мулу міських очисних споруд і очищеного фосфогіпсу, що задовольняє вимогам ДСТУ 7369:2013.

Практична значимість. Розроблена лабораторна установка для отримання очищеного фосфогіпсу від розчинних домішок. Запропоноване використання очищеного фосфогіпсу в якості сировини в сільському господарстві для одержання органо-мінеральних добрив і компостів, реагенту для вилучення фосфатів зі стічних вод і у промисловості будівельних матеріалів для отримання гіпсових в'язучих. Проведені дослідження дозволили кількісно оцінити концентрацію рідкісноземельних елементів і кислоти у фосфогіпсі, а також можливе їх виділення в якості цінної продукції з фільтрату.

Ключові слова: очисні споруди, фосфогіпс, рідкісноземельні елементи, сульфатна кислота, фосфати, органо-мінеральне добриво, фільтрат

Исследование технологии комплексной переработки фосфогипса

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Цель. Провести системные исследования процесса получения редкоземельных элементов из фосфогипса путем сульфатнокислотной обработки. Определить концентрации кислоты и редкоземельных элементов в фильтрате после выделения фосфогипса в образцах в зависимости от соотношения «фосфогипс : кислота» 1 : 1,5, 1 : 2 и 1 : 2,5. Испытать очищенный кальций сульфат в качестве реагента для удаления фосфатов из ила городских очистных сооружений, извлечь из очищенного фосфогипса и активного ила очистных сооружений органо-минеральное удобрение.

Методика. Для исследований составлена лабораторная установка комплексной переработки фосфогипса и описан принцип ее работы. Экспериментальные исследования выполняли с использованием методик титрования трилоном Б для определения концентрации редкоземельных элементов и титрования NaOH для определения концентрации кислоты. Для определения концентрации неорганических фосфатов в сточной воде использован фотометрический метод.

Результаты. Выявлено содержание кислоты в фильтрате при различном соотношении «фосфогипс:кислота» на предприятии «Днепропетровский завод минеральных удобрений» и из отвалов. Установлено, что концентрация кислоты повышается с увеличением соотношения «фосфогипс : кислота» от 1 : 1,5 до 1 : 2,5 соответственно. Полученное органо-минеральное удобрение соответствует ДСТУ 7369:2013.

Научная новизна. Установлены закономерности процесса кислотной обработки фосфогипса в зависимости от происхождения, и выявлено, что в фосфогипсе, который получают на предприятии «Днепропетровский завод минеральных удобрений» концентрация редкоземельных элементов и кислоты больше, чем в фосфогипсе, отобранном из отвалов. Выявлена зависимость соотношения «фосфогипс : кислота», а именно 1 : 1,5, 1 : 2 и 1 : 2,5 от концентрации кислоты и редкоземельных элементов в образцах. Установлено, что пребывание активного ила в аноксидном режиме в течение 30 часов приводит к увеличению содержания фосфатов в водной фазе в 2,6–2,8 раз. Получены зависимости процесса извлечения фосфатов из ила городских очистных сооружений фосфогипсом. Получено органо-минеральное удобрение из активного ила городских очистных сооружений и очищенного фосфогипса, удовлетворяющего требованиям ДСТУ 7369:2013.

Практическая значимость. Разработана лабораторная установка для получения очищенного фосфогипса от растворимых примесей. Предложено использование очищенного фосфогипса в качестве сырья в сельском хозяйстве для получения органо-минеральных удобрений и компостов, реагента для удаления фосфатов из сточных вод и в промышленности строительных материалов для получения гипсовых вяжущих. Проведенные исследования позволили количественно оценить концентрацию редкоземельных элементов и кислоты в фосфогипсе, а также возможное их выделение в качестве ценной продукции из фильтрата.

Ключевые слова: очистные сооружения, фосфогипс, редкоземельные элементы, серная кислота, фосфаты, органо-минеральное удобрение, фильтрат

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