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Investigation of technogenic deposits of phosphogypsum dumps

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Abstract. The article contains research materials on the storage of man-made deposits, including phosphogypsum dumps. The consequences of long-term operation of phosphogypsum dumps and their negative impact on the environment have been established. The quantitative content of microelements to the soil within the storage of technogenic phosphogypsum deposit was determined. Graphical dependences of phosphorus, manganese, fluorine, mobile sulfur, zinc, nickel content depending on the depth of sampling and distance from phosphogypsum dumps to settlements and the Goryn River are presented. The directions of processing and utilization of the given waste are offered. The elemental composition of phosphogypsum dumps of PJSC "Rivneazot" has been established, in particular, the presence of a group of valuable rare earth elements.

1 Introduction

Mining is the basis of the economy of any country [1, 2]. Since minerals are exhaustible, there is a need to process existing raw materials, including processed products of other industries [3, 4].

The problem of reduction and utilization of waste from various industries is very acute at the present stage of existence of the population around the world [5, 6].

According to the Rivne Geological Exploration Expedition, about 1,200 stationary landfills for soil and groundwater pollution have been identified in the Rivne region. Among the latter, a man-made phosphogypsum deposit poses a significant threat to human life and health, as well as a negative impact on environmental systems. It was formed as an inevitable multi-ton waste as a result of many years of production of phosphoric acid at PJSC "Rivneazot" [7].

Man-made deposit from phosphogypsum dumps of PJSC "Rivneazot", located in Rivne district at a distance of 1.5 km northeast of the village of Metkiv, and at a distance of 1 km east of the village of Rubche (Fig. 1) [8].

There are a significant number of such man-made phosphogypsum deposits in Ukraine and around the world. Most of them are not used, but only constantly accumulated [9].

Significant areas of agricultural land are allocated for phosphogypsum storage [10, 11]. Thus, phosphogypsum dumps of PJSC "Rivneazot" cover an area of 58 hectares and their total volume is 15.2 million tons [7].

It is known that when stored outdoors, under the influence of atmospheric factors, acid residues and large amounts of impurities, phosphogypsum enters groundwater and affects the ecosystem. Among these impurities are found rare earth elements (REE), the extraction of which does not occur [7, 12, 13].

Fig. 1. Man-made phosphogypsum deposit of PJSC "Rivneazot" (photo taken from open sources).

Rare earth elements are widely used in the production of high-tech products. REE includes chemical elements:

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Sc, Y, La and 14 elements of the lanthanide family. The total demand for these materials in 2013 amounted to 136 thousand tons [14] and now it is about 200.000 tons, which indicates an increase in demand by 47% [15]. New energy-saving fluorescent lamps, which include: yttrium, lanthanum, cerium, europium, gadolinium, terbium, have become widespread. Due to their low toxicity, REE are used in the manufacture of rechargeable La-Ni-H batteries, which will eventually be able to displace lead-acid batteries in automobiles and nickel-cadmium batteries in computers. Elements of the lanthanide family are used in the glass industry to create optical glass in the charge is injected lanthanum oxide (from 5% to 40%) which increases heat resistance and acid resistance, such glass is used for the production of lenses and prisms of telescopes, cameras, film cameras and laboratory glass [16]. Lanthanum nickel hydride is widely used as the basis for high-capacity batteries for hybrid cars, and the cerium dioxide catalyst is widely used in the petrochemical industry.

Therefore, it is already possible to consider man-made deposits of phosphogypsum as a raw material for the extraction of valuable rare earth elements. According to research, phosphogypsum waste contains up to 1% REE.

The use, processing and utilization of phosphogypsum waste is an urgent scientific and applied problem, the solution of which will improve the ecological situation in the storage areas of man-made phosphogypsum deposits and bring significant economic effect for the national economy [17, 18].

2 Materials and methods

The object of the study is the phosphogypsum dumps of PJSC "Rivneazot" and the adjacent territory (Fig. 2). This is a waste of the fourth class of danger, which is represented mainly by phosphorus oxides that accumulate in the dumps of phosphogypsum [7].

Phosphogypsum refers to calcium sulfate dihydrate. It mainly consists of gypsum ($CaSO_4 \cdot 2H_2O$), impurities P_2O_5 (undecomposed phosphate, unwashed phosphoric acid, crystallized P_2O_5 and water) and other inclusions of trace elements, including REE [19, 20].

Phosphogypsum is a polydisperse material that has a grayish-white color. It is represented by aggregates of particles, lumps with interunit cavities. The density of phosphogypsum is 2.2…2.4 g/cm^3, relative humidity 25…30%, bulk density 0.67… 0.93 g/cm^3, porosity 71.5… 76.3 [21, 22].

Hunting canals have been designed to intercept surface runoff and prevent contamination of soils and groundwater around the perimeter of the facility, and a pumping station has been designed to pump water from the site. Water is diverted to the treatment facilities of PJSC "Rivneazot". Currently, the pumping station is out of order. The water in the canals is highly mineralized, as evidenced by the results of research and dry trees in the riverbed, the water pressure in the canals is 0.5 m. To the object from the side of the village Metkiv there is a concrete road that connects PJSC "Rivneazot" and man-made dumps of phosphogypsum [7].

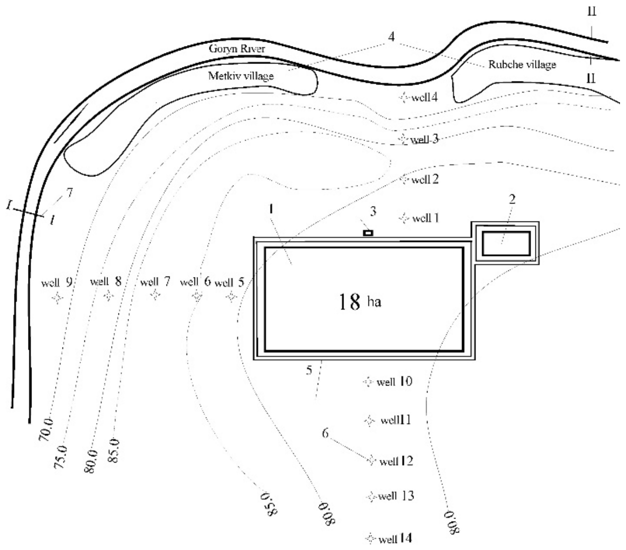

Fig. 2. Experimental area - phosphogypsum dumps of OJSC "Rivneazot": 1 - phosphogypsum dumps; 2 - storage of solid toxic substances; 3 - pumping station; 4 - settlements; 5 - system of channels for interception of surface runoff; 6 - wells for soil sampling; 7 - places of water sampling from the river Goryn, 8 - treatment facilities;w.1 - w.14 - wells for soil sampling; I, II - create for water sampling in the river Goryn.

To determine the content of contamination in soils and in the Goryn River, the study was conducted in two stages: at the first stage, soil and water samples were taken at the Goryn River, and at the second stage, the study results were processed.

To take soil samples, the experimental plot was divided into three sights, which were projected on the lowest points of the terrain. The first line west of the warehouse in the direction of the village. Rubche 1 km long; the second to the south of the object is 1.5 km long; the third to the east of the object towards the forest, 0.9 km long. The total number of wells is 14 pcs.

In Fig. 3 shows a longitudinal section of the target №1.

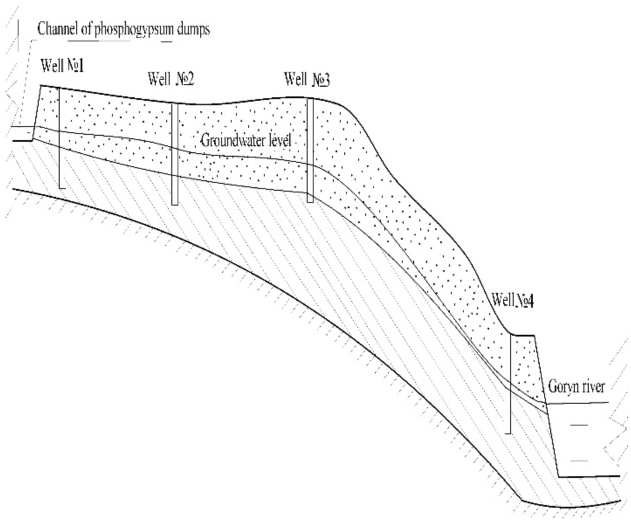

Fig. 3. Scheme of longitudinal section on the target №1:
1 - sand; 2 - loam; 3 - water resistance.

Wells for sampling were drilled by hand drill (geological drill, diameter 50 mm) to a depth of 6 m. Soil samples were taken every meter, starting from the surface with three repetitions of each sample. The distances between the wells in the first three lines are 50, 250, 300, 400 m, respectively. Along the first line there is a decrease of the territory towards the river Goryn. The distances between the wells in the second line, respectively, 50, 250, 300, 400, 500 m

Processing of data of field measurements was carried out jointly with specialists in the laboratory of the State Department of Ecology and Natural Resources in Rivne region [23, 24].

The raw material for the extraction of rare earth elements was phosphogypsum from the dumps of PJSC "Rivneazot" [7, 8, 25]. Sampling points on the territory of the dump were determined for research (Fig. 4).

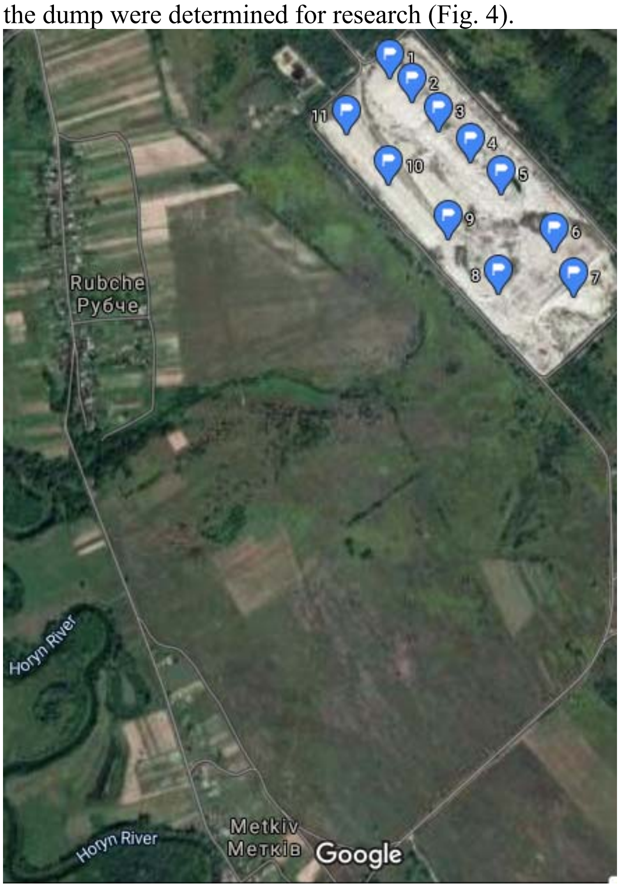

Fig. 4. Location of technogenic deposit and place of phosphogypsum sampling on dumps of PJSC "Rivneazot".

Graphical coordinates of the points were determined using a Garmin GPSMAP 64 navigator: sample 1 (50°44'47.9"N 26°10'53.5"E), sample 2 (50°44'45.8"N 26°10'56.4"E), sample 3 (50°44'43.4"N 26°10'60.0"E), sample 4 (50°44'40.8"N 26°11'04.1"E), sample 5 (50°44'38.2"N 26°11'08.2"E), sample 6 (50°44'33.4"N 26°11'15.3"E), sample 7 (50°44'29.6"N 26°11'17.8"E), sample 8 (50°44'29.9"N 26°11'07.9"E), sample 9 (50°44'34.4"N 26°11'01.2"E), sample 10 (50°44'39.0"N 26°10'53.3"E) , sample 11 (50°44'43.1"N 26°10'47.9"E). A total of 11 samples were taken, with a total of 25 kg.

Before the research, a quantitative chemical analysis was performed to determine the elemental composition of raw materials [26, 27].

3 Results and discussion

3.1 Research of phosphogypsum storage landfill

As a result of chemical analysis of water and soil samples taken on the territory of the experimental site, the content of microelements in the experimental samples was determined. The content of nitrates NO_3, fluorine F, mobile phosphorus P_2O_5, mobile sulfur S, zinc, iron, cobalt, nickel, lead, manganese, copper and chromium in soil samples in mg/kg was determined. The pH of the water extract was determined. Graphical dependences of the content of microelements in the soil on the length of the target for each depth of sampling are constructed.

The results are presented for the target №1. It is directed towards the village Rubche and Horyn river, therefore, the obtained data are of the greatest value in terms of impact on soil and groundwater pollution due to the storage of man-made phosphogypsum deposits.

In fig. 5. and fig. 6. graphical dependences of phosphorus and manganese content on the length of the line, respectively, are presented. Samples were taken at a depth of 1 to 6 m.

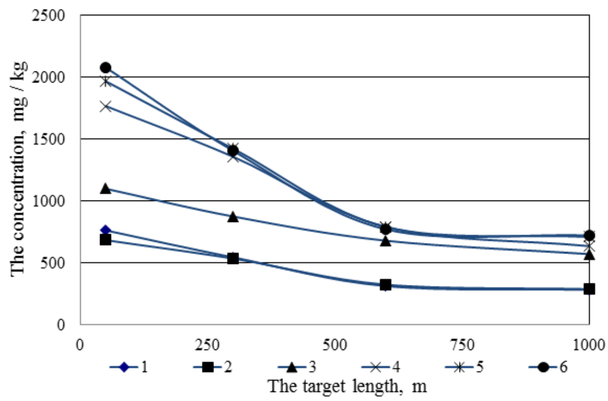

Fig. 5. Dependence of phosphorus content on the length of the target:1 - h =1 m; 2 – h=2 m; 3 – h=3 m; 4 – h=4 m; 5 – h=5 m; 6 – h=6 m.

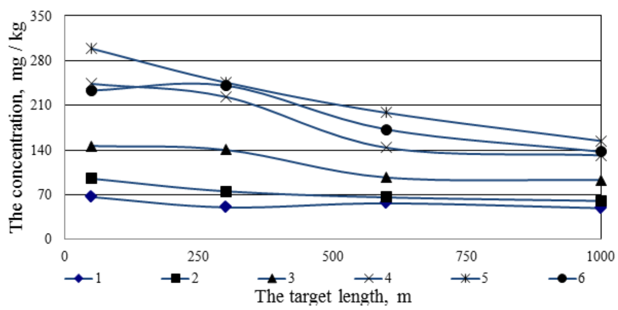

Fig. 6. Dependence of manganese content on the length of the target: 1 - h =1 m; 2 – h=2 m; 3 – h=3 m; 4 – h=4 m; 5 – h=5 m; 6 – h=6 m.

As a result of the analysis of the presented graphic dependences it is established that the concentration of phosphorus varies in the range from 286 to 2078 mg/kg. It is also seen that the concentration of phosphorus in the soil decreases depending on the distance from the phosphogypsum dump, and increases with increasing depth.

The nature of the dependences of the manganese content in the soil is similar to the dependences for phosphorus. Numerical characteristics vary from 48.9 to 298.7 mg/kg.

Studies of the content of microelements from the length of the target at a depth of up to 6 m were also carried out. In Fig. 7 the results are presented at a depth of 3 m, and in Fig. 8 - 5 m.

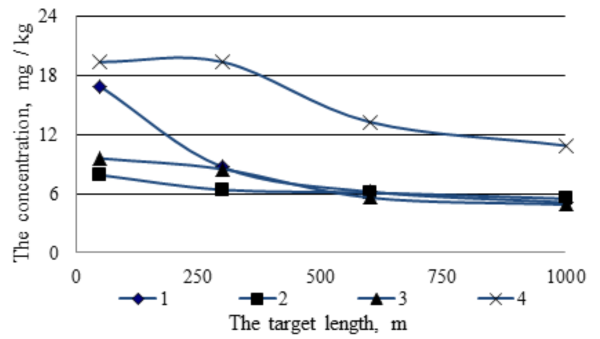

Fig. 7. Dependence of the content of microelements on the length of the target at a depth of 3 m from the soil surface, mg/kg: 1 - fluorine; 2 - mobile sulfur; 3 - zinc; 4 – nickel.

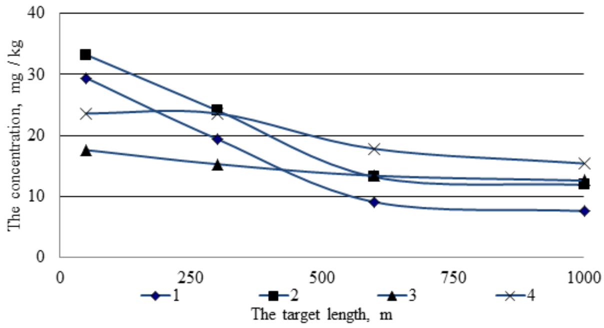

Fig. 8. Dependence of the content of microelements on the length of the target at a depth of 5 m from the soil surface, mg/kg: 1 - fluorine; 2 - mobile sulfur; 3 - zinc; 4 - nickel.

The result of the obtained data showed that the content of such microelements as fluorine, mobile sulfur, zinc and nickel increases with depth, and decreases with distance from the man-made phosphogypsum deposit.

When comparing the data obtained experimentally and the data of the State Department of Ecology and Natural Resources in Rivne region, there is a tendency of significant accumulation in time of harmful chemical elements in the soil. The content of lead, zinc, copper, cadmium, nickel, cobalt, nitrites, manganese, phosphorus exceeds the maximum allowable norms. Thus, in samples taken at a distance of 500 m to the west in 2000, the content of mobile phosphorus in the soil is 332 mg/kg, and in 2019 - 670 mg/kg. As a result, it can be concluded that it is necessary to reconstruct the system of protection of soils and groundwater from pollution by harmful substances on the territory of phosphogypsum dumps near the production site of PJSC "Rivneazot", or the introduction of new more effective methods, which will ensure high-quality interception of pollutants at the outlet of the facility and will not cause an environmentally unfavorable state of the environment. Another way to reduce the negative impact on environmental systems is to develop a project for integrated disposal of phosphogypsum dumps.

3.2 Investigation of man-caused phosphogypsum deposit

From the raw materials obtained for research from phosphogypsum dumps, a quantitative chemical analysis was performed, the results of which are presented in Table 1. For comparison, the results of quantitative chemical analysis of phosphogypsum OJSC "PhosAgro-Cherepovets" (Russia) are presented [28].

Table 1. Quantitative analysis of raw materials from phosphogypsum dumps.

Element	Phosphogypsum of OJSC "PhosAgro-Cherepovets", wt.%	Phosphogypsum PJSC "Rivneazot", wt.%
Sulfates	54.4	52.5
Aluminum oxide	0.2	0.15
Boron oxide	0.0092	0.01
Cadmium	0.00032	0.003
Cobalt	-	0.0012
Chrome	0.002	0.018
Copper	0.0014	0.0018
Iron oxide	0.025	0.034
Potassium oxide	0.055	0.064
Magnesium oxide	0.17	0.187 th most common
Manganese	0.0012	0.013 th most common
Molybdenum	0.00016	0.0056
Sodium oxide	0.27	0.294
Nickel	0.00016	-
Lead	0.00098	-
Strontium oxide	2.04	1.4
Vanadium	-	0.0014
Zinc	0.0018	0.002
Titanium oxide	0.014 ± 0.3	0.016
REE oxides:		
Cerium oxide	0.27	0.26
Oxide dysprosium	0.0042	-
Europe oxide	0.0023	-
Gadolinium oxide	-	0.0015
Lanthanum oxide	0.17	0.205
Neodymium oxide	0.12	0.116
Praseodymium oxide	0.018	0.02
Samaria oxide	-	0.0012
Terbium oxide	0.0014	0.0014
Yttrium oxide	0.016	0.015
REE concentrate	0.6019	0.629

In fig. 9 the content of REE oxides of light group of technogenic phosphogypsum deposit of PJSC "Rivneazot" is presented.

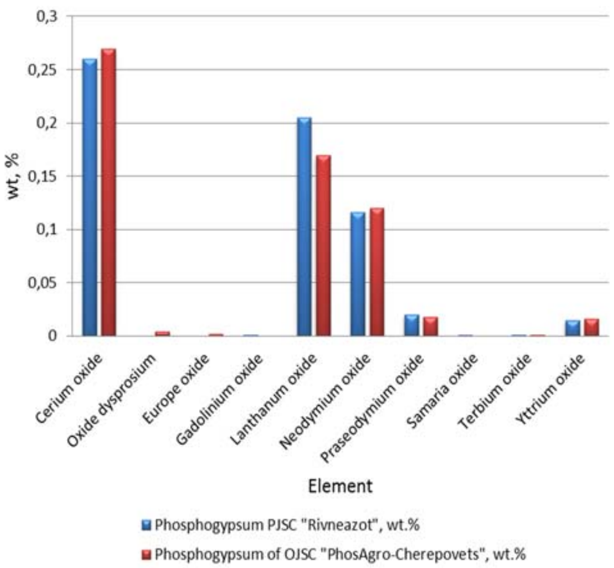

Fig. 9. Oxides of rare earth elements of the light group.

As can be seen from Table 1 and Fig. 9 in the dumps of phosphogypsum PJSC "Rivneazot" presents 8 rare earth elements. The main mass fraction is REE oxides of the light group. These include four elements: lanthanum, cerium, neodymium, praseodymium, the different content of which in concentrates of enrichment determines their commercial value.

3.3 Areas of use of phosphogypsum

The main areas of use of phosphogypsum in the national economy include [29, 30]:

- agriculture, as fertilizers and for reclamation of acid soils;
- use as pavements;
- as creation of X-ray protective designs;
- use as mineralizing additives in the firing of cement clinker;
- in the construction industry, for the production of building materials, production of gypsum binders and production of hydraulic additives;
- as a filler: in the production of paper instead of kaolin, in the paint and varnish industry and in the production of plastics, glass, ammonium nitrate instead of traditional materials (heat-treated phosphogypsum instead of sodium sulfate, etc.);
- mines of coal and other industries - to fill the fastening space and calculation of security strips;
- extraction of rare earth elements.

Conclusions

Solving the problem of processing or utilization of waste that forms man-made deposits of phosphogypsum is an important application, the solution of which will significantly improve the ecological state of the environment.

The research was carried out on the example of a man-made phosphogypsum deposit of PJSC "Rivneazot", located in Rivne region.

According to research, the parameters of micronutrient distribution in the soil around phosphogypsum dumps have been established. The content of lead, zinc, copper, cadmium, nickel, cobalt, nitrites, manganese, phosphorus exceeds the maximum allowable norms. The concentration of these trace elements in the soil decreases with distance from the dumps.

The main areas of use of phosphogypsum in the national economy are agriculture, the manufacture of X-ray protective structures, the extraction of rare earth elements.

According to the results of quantitative chemical analysis, it was found that phosphogypsum dumps contain 0.629% of REE oxides.

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