

## ОСНОВИ ПРИРОДОКОРИСТУВАННЯ NATURAL RESOURCES

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### ENVIRONMENTAL HAZARDS OF THE MINING AND CHEMICAL ENTERPRISES TERRITORY

**Abstract.** *The ecological situation in most mining regions in Ukraine is critical, and the closure of unprofitable mining enterprises, mines and cuts creates environmental problems associated with significant changes in the geological and hydrological environment.*

*The purpose of the work is to assess the environmental hazard of the territory of the Rozdil State Mining and Chemical Enterprise "Sirka".*

*The research was carried out on the territory of Rozdil SMCE "Sirka". Rozdil State Mining and Chemical Enterprise "Sirka" is in the West of Ukraine (Lviv region) of the Dniester River basin. According to the State Register of Potentially Hazardous Objects (PHO) of Ukraine, Rozdil State Mining and Chemical Enterprise "Sirka" belongs to the monitoring facilities of PHO.*

*The X-Ray Diffraction (XRD) method was used experimentally to determine the qualitative and quantitative composition of heavy metals and other inorganic elements in samples, soil pollution with heavy metals. The main threats were identified which should be considered at the stage of liquidation of the mining and chemical enterprise. The main reason for pollution of the water objects of the enterprise territory and the Dniester River is the non-performance of the project on maintenance of ecological balance, monitoring, reclamation of the territory of the land due to lack of financing for the implementation of projects. In this regard, sources of pollution (phosphogypsum, oil tars, lump sulfur, flotation tails, solid waste) constantly affect the environment and over the years the situation is still dangerous. On the example of Rozdil State Mining and Chemical Enterprise "Sirka" the main problems of the monitoring system of the territory of the mining and chemical enterprise at the stage of liquidation are demonstrated. The influence of*

*the mining and chemical enterprise on the state of pollution of the environment: soil, water environment, and waste management status were also assessed.*

*Also, according to the obtained data, in the man-made reservoirs of the enterprise (Lake Hlyboke, Lake Serednie, Lake Chyste, channels), which flow into the Dniester River, an excess of the MPC is seen in many hydrochemical parameters: pH, sulfates, phosphates, ammonium nitrogen, etc.*

**Keywords:** *mining and chemical enterprise; heavy metals; reclamation; environmental hazard; water pollution; soil pollution*

## Introduction

Ukraine belongs to the leading mineral-raw countries of the world with a wide range of minerals. Ukraine – 0.4% of the Earth's surface and 0.8% of the world's population – has about 5% of the world's mineral resources.

The main ecological problems of mining operations for Lviv enterprises are rather specific: the environment is not influenced by the activity of enterprises, but the consequences of their activities in the past, the main issue today is the elimination of these consequences. The main factors of negative influence are the extremely high concentrations of mining enterprises, the important level of production of most deposits, the insufficient amount of financing for work aimed at reducing the environmental impact caused by the exploitation of deposits.

The closure of mining enterprises leads to unforeseen deterioration of the environmental situation, and the scale of this problem causes catastrophic consequences. The neglect during the closure of the mining and chemical enterprises with the requirements of technological and environmental safety leads to significant changes in the quality of underground and surface waters, soil contamination, flooding and waterlogging of the territories, pollution of rivers, sediments of the earth's surface, etc. The problems of waste management of mining enterprises are acute, an imbalance between spent and re-cultivated land in mining enterprises is maintained, and as a result, the risk of physical destruction and chemical pollution of industrial facilities, residential buildings, and communications in the surrounding areas.

Mining complexes as an essential part of economic transformations take in the change of balance of matter, structure and energy of the planetary spheres, exclusively active participation. The main task of environmental safety in the industry soon is to prevent the increase of pollution and depletion of natural objects [1].

**The purpose** of the work is to assess the environmental hazard of the territory of the Rozdil State Mining and Chemical Enterprise "Sirka".

Today, environmental safety issues have covered all countries and continents, touched on the interests, and needs of every inhabitant on the planet, acquired a global, global character.

This condition is due to a few circumstances, of which the following should be highlighted:

- the ratio of the scale of manifestation and the degree of environmental impact of the processes and industries that are created by the hand and will of man, with the natural processes that occur in nature;

- in the pollution of the environment a significant share falls on the mineral and industrial complex [1–6].

A comparison of the influence of several types of mineral raw materials on the natural environment of Ukraine shows in table 1.

Table 1 – Comparative characteristics of the influence on the natural environment the development of various types of mineral raw materials of Ukraine [7]

Mining region	Disturbed surface area, km <sup>2</sup>	The volume of mine water flow per day, 10 <sup>1</sup> m <sup>3</sup>	Dangerous geological processes development	Volume of accumulated waste, mln. m <sup>3</sup>	Nature contamination of soils
Donbas (coal)	15000	2.5	Subsidence, flooding, landslides, karst, erosion	1050.0	Complex (heavy metals, petroleum products, chemical compounds)
Lviv-Volynsky (coal)	150	0.06	Subsidence, flooding, karst	0.05	Complex (heavy metals, chemical compounds)
Dniprovskiyi (brown coal)	20	0.24	landslides, flooding	Insignificant	Complex (heavy metals, petroleum products)
Dniprovsko-Donetska Depression (oil and natural gas)	Insignificant	–	Insignificant, local	Non-available	Complex local (petroleum products)
Kryvbas (iron)	170	0.13	Subsidence, flooding, landslides, karst	1.6	Complex (heavy metals, petroleum products, chemical compounds)
Pre-carpathians (sulfur)	150	0.13	Subsidence, flooding, landslides, karst, suffusion	Over 50.0	High contamination (chemical compounds, sulfur, salts)

Deforestation and vegetation violations take place in open areas, during storing on the surface of overburden and dumps of mineral raw materials, during road laying and construction of facilities for the maintenance of mining enterprises.

Changing of the earth's surface occurs when the minerals are discovered in the places where quarries are created, the shaft shafts are located, and during the underground extraction of minerals as a result of the surface subsidence. During the removal of rocks, the surface of the soil subsidences. The formed deposits are filled with water. Such a phenomenon is seen in the Precarpathians region during the development of potassium salts and the extraction of sulfur. The reservoirs that formed there reach a depth of 3 meters.

Mining developments violate soil hydrology, lead to an increase in the runoff of mines and mine waters that carry a significant amount of pollutants: chloride compounds, sulfuric acid, soluble iron salts, manganese, copper, zinc, nickel, and others. Heavy metals are especially dangerous for human health: Cd, Mo, Ni, Zn, Va, Be, as well as metal-poisons – Hg, As, Se, Pb.

The solution of the problems of technological and ecological safety needs:

- implementation of the restructuring of the man-made environment, technical re-equipment of the production complex based on the introduction of the latest scientific achievements, energy, and resource-saving technologies, non-waste and environmentally safe technological processes, the use of renewable energy sources, solving the problems of neutralization and use of all types of waste;

- establishment of effective environmental control over scientific research work on the creation of objects of artificial origin, their design, construction and functioning in order to manage man-made loads, rational use of natural resources and the placement of productive forces;

- realization the classification of regions of Ukraine according to levels of man-made and ecological loads, creation of maps of man-made and ecological loads;

- development of a methodology for determining the degree of environmental risk for the environment caused by man-made objects;

- conducting researches in order to create a system of models of monitoring of objects of observation in industry, energy, construction, transport and agriculture [2, 3].

Violation of soil hydrology leads to a decrease in the yield of cultivated areas next to the mines where mining is carried out. With the open-pit method of development around the quarries, the depression funnel grows, power is reduced by aqueous solutions of the soil layer with all its consequences [4, 5].

According to the State Register of Potentially Hazardous Objects (PHO) of Ukraine, Rozdil State Mining and Chemical Enterprise "Sirka" belongs to the monitoring facilities of PHO [6].

### **Analysis of recent research in the field of environmental safety and monitoring of the territory as a result of the activity of the mining and chemical enterprise**

The study and research of the affected areas because of extraction of minerals, the study of technogenic landscapes, the soil cover was carried out by many scientists, among whom: B.I. Volosetskyi, A.M. Haidin, I.I. Zozulia, O.H. Maryshevych, L.P. Markovych, L.V. Motorina, R.M. Panas, H.I. Rudko, L.Ye. Shkitsa, A. Gąsiewicz, M. Ossowska and others. The issue of studying and studying the land cadastre has been highlighted in studies and publications M.H. Lykhohrud, A.A. Liashchenko, A.H. Martyn, A.M. Mukhovykov, L.M. Perovych, O.S. Petrakovska, M.H. Stupen, R.B. Taratula, A.M. Tretiak, P.H. Cherniaha and other scientists. Problems with the improvement of the ecological state, streamlining of disturbed territories, development of scientifically substantiated recommendations and suggestions on effective use of disturbed lands are still unsolved. The solution of these problems depends essentially on monitoring the state of the environment in the area of activity of mining and chemical works, which will enable to create an objective and reliable model of the state of the environment and react in a timely manner to adverse changes.

## Problem Statement

Now, after the completion of the development of minerals, as a rule, there is a question of developing projects for the construction of disturbed territories. One of the essential elements of such projects is environmental monitoring, which involves identifying and assessing man-made processes and phenomena that can negatively affect the natural environment, lead to accidents and crises. In our opinion, this is a one-sided, only ecological approach, by which it is impossible to foresee or predict the creation of appropriate landscapes in disturbed territories. There is no ecological-landscape monitoring, which involves the formation of ecological and man-made landscapes on disturbed lands, taking into account the former natural landscapes and the present, created by human production activities in Ukraine.

The main sources of environmental hazard after the activity of the mining and chemical enterprise are industrial waste. During 2017, 2542.1 thousand tons of waste was created in the Lviv region (by 8.4% less than in 2016), including 2367.2 thousand tons from the economic activity of enterprises and organizations (93.1% of all and 7.0% less), 174.9 thousand tons in households (6.9% of all and 23.5% less).

The main part of the waste generated in the region in 2017 (99.9% of the total volume) belongs to hazard class IV waste. 2645 tons of waste of I-III class of danger were formed, including I class – 40 tons, II class – 503 tons, III – 2102 tons. In 2017, the total volume of waste utilization of all classes of hazard was 603.0 thousand tons, and compared with 2016 it increased by 24.9%, the volume of utilization of waste I-III classes of danger increased by 65.4%. The share of wastes that were disposed of amounted to 23.7% in the total volume formed in 2017. In 2017, there were 45 plants for utilization of waste with a total capacity of 236.3 thousand tons per year, for combustion for energy purposes were 76 units (161.6 thousand tons per year).

One third (37.0%) of the total volume of wastes generated in 2017 was mining waste and quarry development during the extraction and enrichment of ores and mineral raw materials, 20.4% were waste of medical, veterinary, or agricultural origin, pharmaceutical products, etc.

One of the most dangerous and most widespread environmental pollutants are heavy metals, the source of which may be industrial waste from the mining and chemical enterprise.

Even high-grade mineral ores consist almost entirely of non-metallic materials and often contain undesired toxic metals (such as cadmium, lead, and arsenic). The beneficiation process generates high-volume waste called 'tailings', the residue of an ore that remains after it has been milled and the desired metals have been extracted (e.g., with cyanide (gold) or sulfuric acid (copper)).

To reduce the harmful effects of heavy metals, appropriate rules for their content are introduced:

1. MPC of the gross content of heavy metals in the arable layer of soil and plant mass, mg/kg;
2. MPC of moving forms of heavy metals in soil, mg/kg;
3. Clarke of heavy metals in soil, mg/kg.

Pollution of soil by industrial facilities is a serious potential threat to human health, ecosystems and the economy as a whole. The consequences are not yet clearly identified due to the presence of a large number of dangerous compounds and their various contents in the soil.

The consequences can be as follows:

- the receipt of hazardous substances into the soil, surface and groundwater;
- the absorption of pollutants by plants;
- direct contact of people with contaminated soil;
- inhalation of dust particles or volatile substances;
- fire or discharge of gases in landfills of domestic and industrial waste;
- corrosion of pipes and other elements of underground communications;
- formation of harmful secondary waste;
- conflicts during land cultivation and use [8–13].

## Site information

The research was carried out on the territory of Rozdil SMCE “Sirka”. Rozdil State Mining and Chemical Enterprise “Sirka” is located in the West of Ukraine (Lviv region) of the Dniester River basin. The enterprise is located between latitudes 49°28'32.20"N and 49°25'53.18N, and longitudes 24° 6'21.46"E and 24° 5'12.22"E (Fig. 1). On the balance sheet of this enterprise are storage technological waters – man-made lakes Hlyboke, Serednie, Kysle, Chyste.

The total area of land use of the Rozdil State Mining and Chemical Enterprise "Sirka" as of 01.01.2015 is 1816.24 hectares (Fig. 1), in particular:

- in the Mykolaiv district – 967 hectares, including:
  - a) on the territory of Krupsk village council – 47.0 hectares;
  - b) on the territory of Berezyna village council – 545.0 hectares;
  - c) on the territory of the Rozdil Settlement Council – 245.4 hectares;
  - d) on the territory of Berezdivtsi village council – 130.0 hectares;
- in Zhydachiv district – 30.3 hectares;
- in Novyi Rozdil city – 818.5 hectares.

Due to the long-term activity (1956–1996) of the Rozdil SMCE "Sirka" on its territory different wastes were formed. They are the sources of environmental hazard:

- lump sulphur – 700 m<sup>3</sup>;
- sulphur ore tailings – 85 million t;
- sediment of recycled waters – 1.29 million m<sup>3</sup>;
- phosphogypsum – 3 million t;
- goudrons (imported from Hungary) – 17 thousand t;
- solid household waste – 560 thousand m<sup>3</sup>.

Rozdil State Mining and Chemical Enterprise "Sirka" used an open method of sulfur extraction. It should be noted that the open pit mining method has higher impact on the morphology and landscape compared to the underground one. The main activity of Rozdil State Mining and Chemical Enterprise “Sirka” is the implementation of environmental works according to the project: “Liquidation of sulfur quarries and restoration of ecological balance and landscape around activity of Rozdil State Mining and Chemical Enterprise “Sirka”.

## Methods of Analysis

Excessive amounts of heavy metals in soils is a very dangerous ecological factor, the effect of which is aggravated by the penetration of compounds of heavy metals into

groundwater, accumulation in plant organisms, negative impact on soil organisms and the cultivation of environmentally hazardous products.

In order to determine the qualitative and quantitative composition of metals and other inorganic elements in the samples, X-Ray Diffraction (XRD) technique was used. The concentration of elements in the sample was determined by X-ray spectrometry using an S2 PICOFOX Bruker X-ray spectrometer - detector type: silicon drift detector, high voltage generator: MNX 50P50 / XCC, X-ray source: metal ceramic air cooled MCB50-0.7G, X-ray optics: multilayer monochromator.

Direct sample preparation.

1. An aqueous solution of a concentrated gallium standard (100  $\mu$ l) in distilled water (10 ml) was prepared.

2. To 20 ml of a gallium standard water solution was added to 1 ml of the sample and mixed well in vortex (5 seconds).

3. Prepared samples were applied to quartz media and analyzed on an X-ray spectrometer. The analysis time was 1000 seconds. The determinations were carried out in Manuel off mode - work at maximum 50W lamp power, 50 keV energy.

4. Results are expressed in units of  $\mu$ l / l [14–17].

## Results of Research

The main threats to be considered at the stage of completion of the exploitation of the deposit are chemical pollution of soils, waters, geophysical disturbance of the stability of the territory [10]. There is the satellite image of the territory of the enterprise and the main sources of ecological danger (Fig. 1).

Heavy metals are present in the soil as natural impurities, and the reasons for increasing their concentrations are related to human activity. The results of measurements were obtained by the following parameters: Strontium, Manganese, Zinc, Lead, Arsenic.

Soil pollution is a result of economic activity in the past and now. Since the content of heavy metals within the limits of maximum permissible concentrations is important, the dynamics of changes in the content of heavy metals in soils is presented in Fig. 3–8. The content of Manganese in soil in 2016 almost reached the MPC (1500 mg/kg) near the dump of phosphogypsum at a distance of 20 m and a depth of 0.2 m.

The MPC of Strontium in soil is 1000 mg/kg. On the territory of the enterprise there are significant excess of MPC (up to 6 times). Over time, the content of Strontium in the soil does not decrease.

The dynamics of changes in the content of Lead in soils are showed in Fig. 3. MPC of Lead is 30 mg/kg. Excess was detected only in 2017 at a sampling point of 5 m from the dump of phosphogypsum at a depth of 0.40 m. On the surface of the soil there is a tendency to decrease the content of Lead, depending on the distance from the dump of phosphogypsum.



Fig. 1 – Satellite image of Rozdil State Mining and Chemical Enterprise.  
Source: Google Map

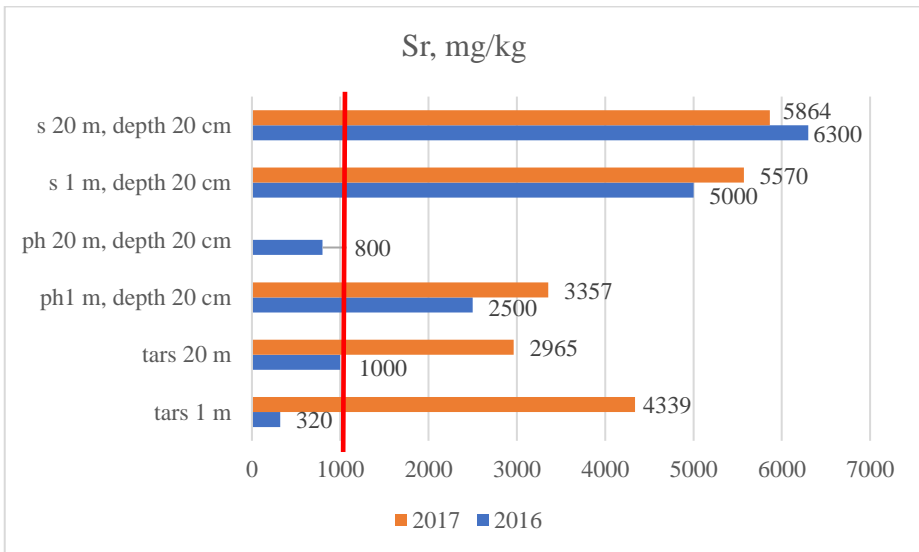


Fig. 2 – Dynamics of changes of Strontium content in soils, where *s* is soil near the tailing's storage, *ph* is soil near the dump of phosphogypsum, *tars* is a soil near the ground with tarts

In 2016, Zinc was not detected in soil samples. Data for 2017 (for Zinc) shown in Fig. 4. MPC of Zinc is 300 mg/kg. Excess was not detected.

In 2016, arsenic was not detected in soil samples, but in 2017 it was (Fig. 5). MPC of Arsenic in soil is 2 mg/kg. There are MPC excess at 4 sampling points. There is an excess of MAC on Arsen 6 times at a distance of 20 m from the tailing's storage.



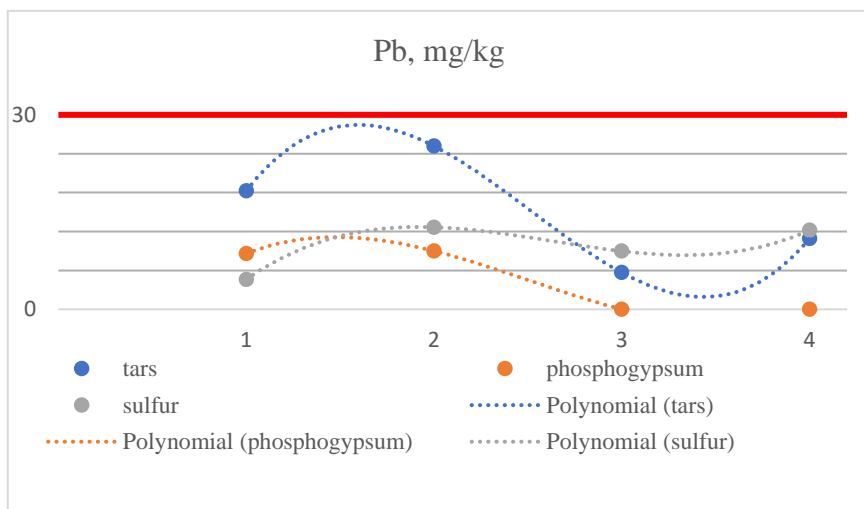


Fig. 3 – Dynamics of changes of lead content in soils, 2017, where sulfur – is soil near the tailing’s storage, phosphogypsum – is soil near the dump of phosphogypsum, tars – is a soil near the ground with tarts

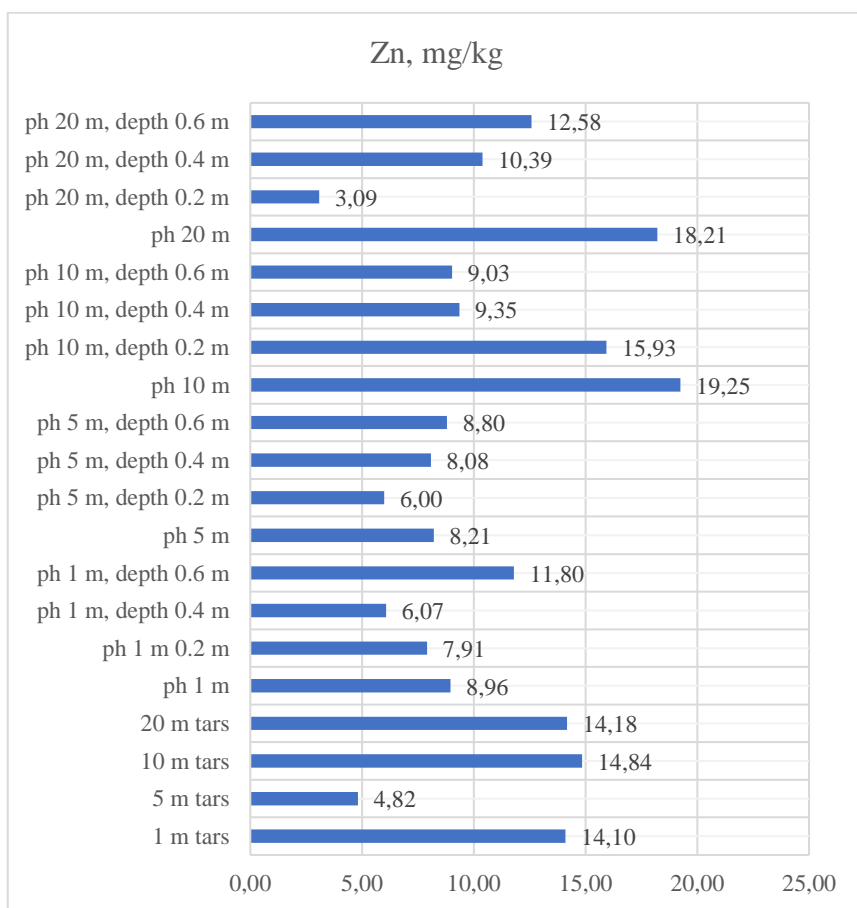


Fig. 4 – Spread of Zinc in soils, 2017, where ph – is soil near the dump of phosphogypsum, tars – is a soil near the ground with tarts

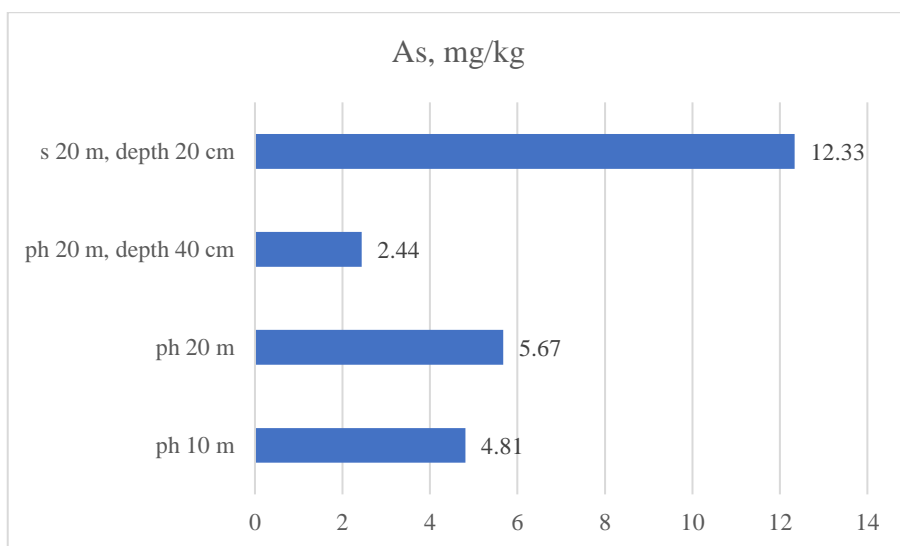


Fig. 5 – Spread of Arsenic in soils, 2017, where sulfur – is soil near the tailing’s storage, ph – is soil near the dump of phosphogypsum

Quarries lakes were being flooded from 2003 to 2010. At the site of the North Rozdil quarry was established a cascade from Lake Chyste, Lake Serednie and Lake Hlyboke. Area of Lake Chyste – 10 hectares, depth – 15 m, area of Lake Serednie – 45 hectares, depth – 12 m. Lake Hlyboke has depth to 30 m, area of the lake – 82 hectares. For leakage of water from the lakes into the Dniester there is a channel in length 3 km. The total area of the catchment of quarry lakes of the enterprise is 6 km<sup>2</sup>.

Fig. 1 demonstrates satellite image of water sampling place. Samples were taken in lakes created on the site of quarries (Lake Chyste, Lake Serednie, Lake Hlyboke, Lake Kysle) and in the channel Hlyboke-Dniester.

In addition to the soil environment, data on pollution of the water environment was obtained. The water environment is contaminated by components of salt composition, ecological and sanitary indicators, indicators of toxic and radiation action (table 2). Just as heavy metals pollute the soil environment, they also affect water. Since the company is in the stage of liquidation, but still poses a threat to the environment, it is therefore essential to create a monitoring system. The organization of the monitoring system at the sites of mining production, depending on the types of environmental impact should be considered from their sources, as each source may have several types of influence on the components of the environment [11, 12, 18–20].

According to the data, in the surface water layer of all the Rozdil lakes, the excess of normative indicators for mineralization (MPC – 1000 mg/m<sup>3</sup>) and sulfates (MPC – 100 mg/m<sup>3</sup>) are recorded and in the Lake Kysle and Lake Serednie are the excess of MPC by phosphates (MPC – 0 mg/m<sup>3</sup>), in the lake. The pH in Lake Kysle is 5.25 in the norm from 6.5 to 8.5.

In the channel of Lake Hlyboke-Dniester there is an excess of the MPC on such indicators: the pH is 6.05 (MPC – from 6.5 to 8.5), sulfates – 1665.3 mg/dm<sup>3</sup> (MPC – 100 mg/m<sup>3</sup>), ammonia nitrogen – 4.6 mg/dm<sup>3</sup> (MPC – 0,5 mg/m<sup>3</sup>), mineralization – 2498.6 mg/dm<sup>3</sup> (MPC – 1000 mg/m<sup>3</sup>). The discharge of contaminated sewage in the Dniester River is a violation of Art. 44, 70, 95 of the Water Code of Ukraine.

Table 2 – Results of the hydrochemical monitoring, 2017

Indicator	Actual concentrations, mg/dm <sup>3</sup>				
	Lake Serednie	Lake Chyste	Lake Kysle	Lake Hlyboke	Chanel Lake Hlyboke-Dniester
Hydrogen index	7.65	7.65	5.25	7.3	6.05
Sulfates	1755.8	1044.2	1200.8	1628.6	1665.3
Chlorides	241.4	63.2	113.8	122.4	–
Mineralization	3019.5	1684.9	2701.4	2502.4	2498.6
Ammonium nitrogen	5.2	0.9	6.9	2.8	4.6
Nitrate ions	1.8	0.5	6.9	0.4	–
Phosphates	1.1	0	729.3	0	–

The main reason for pollution of the water objects of the enterprise territory and the Dniester River is the non-performance of the project on maintenance of ecological balance, monitoring, reclamation of the territory of the land due to lack of financing for the implementation of projects. In this regard, sources of pollution (phosphogypsum, oil tars, lump sulfur, flotation tails, solid waste) constantly affect the environment and over the years the situation remains dangerous.

To achieve the ecological safety of the territory of the mining and chemical enterprise at the stage of liquidation it is necessary:

- to liquidate sulfur mines, to restore the ecological balance in the landscape of the Rozdil SMCE "Sirka";
- to liquidate Rozdil SMCE "Sirka" with the provision of technological and ecological safety in the zone of influence of the enterprise;
- carry out environmental monitoring of the territory of liquidated quarries and the state of the environment of reclaimed areas.

The system of monitoring of the territory of the mining and chemical enterprise at the stage of liquidation will allow to increase the level of environmental safety of the territory of the enterprise and the surrounding settlements and timely react to adverse changes.

At present, the theoretical and methodological approaches to environmental monitoring of a mining enterprise in the liquidation stage, as well as its material and technical and financial support have not been developed. This problem is only at the initial stage of the solution. The need for a scientific substantiation of the monitoring system in the area of former mining activity, where the mosaic of technogenesis is very complex, requires the use of various theoretical positions, concepts and methodological tools, and interdisciplinary studies of various sciences [17–22].

## Conclusion

Therefore, the parameters of soil pollution by heavy metals in the territory of the Rozdil State Mining and Chemical Enterprise "Sirka" from 2016 to 2017 were analyzed in the work y use of the experimental method. The example of Rozdil State Mining and Chemical Enterprise "Sirka" demonstrates the main problems of the monitoring system of the territory of the mining and chemical enterprise at the stage of liquidation. The influence of the mining and chemical industry on the state of environment pollution (soil, water environment and waste management status) was also assessed.

Prevention, control and restoration of contaminated water objects of the mining and chemical enterprise is a difficult task. Experimental research has established that there is the excess of the normative indicators for mineralization and sulphates in the surface water layer of all man-made lakes of the enterprise. There is the excess of the normative indicators for mineralization, sulphates and phosphates in Lake Kysle and Lake Serednie. In 2017 the pH is 5.25 in Lake Kysle, the normative level should be between 6.5 and 8.5. A significant excess of Strontium MPC (up to 6 times) was established. Over time, the contents of the element do not change, because strontium forms a low-solubility, sedentary forms of sulphates, carbonates, phosphates. At the distance of 20 m from the tailing's storage is the excess of the MPC by Arsenic by 6 times.

The necessity of constructing a monitoring system for the territory of the Rozdil SMCE "Sirka" at the stage of liquidation is substantiated. It was established that monitoring of the territory of the mining and chemical enterprise at the stage of liquidation will allow increasing the level of environmental safety of the territory of the enterprise and the surrounding settlements.

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**ЕКОЛОГІЧНА НЕБЕЗПЕКА ТЕРИТОРІЇ ГІРНИЧО-ХІМІЧНИХ ПІДПРИЄМСТВ**

**Анотація.** У роботі розглянуто основні екологічні проблеми гірничо-хімічних підприємств України, які знаходяться на стадії ліквідації. Експериментальним шляхом за допомогою методу рентгенівської дифракції визначили якісний і кількісний склад важких металів та інших неорганічних елементів у пробах, показники забруднення ґрунтового середовища важкими металами. Встановлено основні загрози, які слід розглядати на стадії ліквідації гірничо-хімічного підприємства. Оцінено вплив гірничо-хімічного підприємства на стан забруднення довкілля: ґрунтів, водного середовища та стан поведження з відходами.

**Ключові слова:** гірничо-хімічне підприємство; важкі метали; рекультивация; екологічна безпека; водне середовище; забруднення ґрунтів

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