

Geochemical properties of water under the waste heaps in Chervonohrad mining region

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Abstract. The geochemical properties of water under the waste heaps within the Chervonohrad mining region have been studied. The environmental remediation around the technogenic reservoirs of rock heaps using the bioplateau systems is proposed. In 2017, samples were taken from reservoirs of technogenic origin located at the foot of rock heaps of such coal mines as “Mezhyrichanska”, “Velykomostivska”, “Stepova”, “Zarichna”, “Lisova” and “Chervonohradska”. According to the analysis of the studied parameters, it has been determined that water under the Mezhyrichanska Mine waste heaps is the most polluted. The most dangerous landscape-transforming factor of water under the waste heaps is the transfer of polluting substances into the soil, surface and subterranean waters. Through the use of the Pearson coefficients of correlation, the ratios between pollution parameters have been obtained. The determined correlation coefficients are high, positive ($r = 0.78 - 0.99$) and evidence of the toxic components spread in water under the waste heaps throughout the entire coal mining region. The obtained geochemical data on water under the waste heaps of mines in the Chervonohrad mining region are important in terms of the environmental impact assessment of mining activity on the human body and the biosphere components – the hydrosphere, the phytogenic field. It is necessary to establish environmental monitoring systems and to develop measures for the environmentally safe decommissioning the waste heaps of coal mines.

1 Introduction

The mining industry causes significant technogenic impact on the environment and is a powerful factor in the growth of greenhouse effect and climate change. The research into the influence of the coal industry on the environment is of great interest to many scientists in the world. Many scientific works are devoted to rock heaps of mines that pollute all the components of the human environment – air, surface and subterranean waters, soil and vegetation. Among the scientific works, the works aimed at identification of the environmental and technogenic hazards of rock heaps should be noted [1 – 6], and, those, devoted to the decommissioning of these objects, including by means of biota [7 – 11].

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The issues of geochemical pollution of surface and subterranean waters in the coal mining zone are the subject of many scientific works. Such studies originated in the 70s, 80s of the 20th century [12 – 14]. In particular, in [14], the removal of heavy metals and the deacidizing of mine wastewater with the help of algae and bacteria are considered. It has been shown that growing the artificial algae in artificial systems removes significant amounts of heavy metals and small particles from mine wastewater. The bacterial systems for the ferrous iron oxidation and sulphate reduction are described, which leads to the acidity neutralization. It has been made a conclusion that the combination of bacterial and algal systems with the process optimization, including corrections to nutrients, can provide an appropriate mine wastewater treatment. Metal resistant bacteria can also be important in the rock heaps reclamation.

The use of municipal sludge in the recovery of a mine dump in Colorado is represented in [12]. It has been found that the addition of the sludge promoted the development of vegetation, similar to the process of adding the inorganic nitrogen fertilizers (N) and phosphorus (P), and helped to stimulate microbial activity.

The pollution of surface and subterranean waters with wastewater from the mining and metallurgical industry of Poland is described in work [13]. It has been set that an increase in the concentration of pollutants, mainly heavy metals and chlorine ions, should be considered as hazardous. About 50% of superficial runoff does not even meet the standards of quality class III. Having in consideration the emission of dust and gases, as well as volumes of discharged waste, including wastewater per 1 km², it has been identified 27 environmentally hazardous regions in Poland. Half of these regions are located in the mining and metallurgical areas.

In the scientific work [15], the results of physical and chemical studies of mine water and wastewater from rock heaps are represented. It has been determined that the mine water may be acidic or neutral depending on the concentration of pyrite in the coal. This degrades the quality of water in the region in terms of decrease in pH of surrounding water resources and increase in the level of total amount of suspended solids, total amount of dissolved solids and some heavy metals. It has been determined that in non-acidic rocks the quality of water indicates high hardness and bacterial contamination. The wastewater from waste heaps is enriched in metal concentrations, especially in Fe, Cu, Mn and Ni. High values of mine water hardness reduce its suitability for domestic purposes. This work demonstrates the quality of acidic and non-acidic mineral waters, as well as characteristics of open coal mines filtration. The polluting substances, such as oil products and heavy metals can be found in return flows of rock heaps.

In work [16], studies are given to reduce the erosion of the mine dumps surface by vegetation, as well as to regulate wastewater. It has been found that the recovery of vegetation has a different influence on runoff and soil erosion. Over the long run, vegetation can increase soil organic matter, improve the physical properties, and also reduce runoff and erosion to a safe level. This study provides a theoretical basics and technical support for land reclamation, conservation of soil and water resources in environmentally hazardous coal mining areas.

The studies in [17] are devoted to the identification of technogenic environmental pollution by wastewater from the rock heaps of the uranium mine, as well as by a lake formed in the surface mine. It has been set that the concentration of uranium reached 181 µg/l in lake water, 266 mg/kg in water from waste heaps and 377 mg/kg in adjacent soils. The concentration of arsenic was up to 158 µg/l in lake water, 211 mg/kg in water from waste heaps and 223 mg/kg in adjacent soils. It was observed that the greatest concentrations in water of most metals, including As (III), occurred in summer as a result of evaporation. Ecological remediation of the mining area is necessary in order to avoid danger to the population.

Hydrochemical parameters of the Odiel river (Spain), which are formed under the influence of mine water are given in studies [18, 19]. The samples of surface water were taken in 91 different locations throughout the Odiel river basin and analyzed according to field and laboratory methods for dissolving metals and metal-containing compounds. The acid mines drainage affects 37% of the length of the drainage network, indicating a wide geochemical conditions variety. It has been determined that 15% of the total gross flow of dissolved Zn and 3% of the total gross flow of dissolved Cu are transported to the ocean by the river.

In [20], the geochemical studies have been performed of water reservoirs and wetlands in the zone of influence of mines mining Au. Contamination is manifested in the form of low pH (>2) and a high concentration of SO_4^{2-} (in some cases exceeds 7000 mg/dm^3). Water quality is improving at a certain distance from the tailing dump. It was found that pollution at the end of the raining period was higher, which is explained by an increase in the water level and, as a consequence, by an increase in the leakage of subterranean water. In the areas where the water level approaches the surface, the upper soil profiles of 20 cm are highly polluted with heavy metals through capillary rise and evaporation of subterranean water [21]. Ferrous oxide has made an oxidation-reduction buffer controlling the pH of water flow. The rate of oxidation and dilution is slow, but the harmful effect from the addition of polluted water is preserved for more than 10 km outside the source.

The assessment of risks for subterranean water in the zone of the copper-molybdenum quarry influence is described in the work [22]. A study of the risk assessment for subterranean water from pollution by several sources, as well as development of a long-term monitoring program to solve such problems are of great importance. It has been decided that it is necessary to develop a monitoring system for subterranean water which takes into account the direction of migration and the distance of polluting substances depending the subterranean water movement in an artificial flow under the influence of a subterranean water funnel.

In Ukraine, the numerous studies are conducted on the hydrological regime of mining areas [23 – 25]. The scientific works present the research results on the peculiarities of influence on the hydrosphere of mining operations with open-cut and underground methods of mining. The technical solutions for remediation of the hydrosphere after stopping the mining operations have been proposed. The methods of hydrological research into the zone of coal mines influence have been substantiated.

However, the questions of geochemical research of wastewater from coal mine heaps, their accumulation in technogenic reservoirs and their impact on biota have not been thoroughly studied.

2 Purpose and objectives of research

The purpose of the work is to research into the geochemical properties of water under the waste heaps within the Chervonohrad mining region and to specify the main measures to restore the environment around technogenic reservoirs of rock heaps.

As part of the purpose set, the following tasks should be solved:

- to analyze scientific sources for study of water under the waste heaps;
- to take water samples from technogenic reservoirs of rock heaps of coal mines;
- based on the physical and chemical analysis of the samples taken, make a conclusion on the influence of water under the waste heaps on the human body and biota.

The research of samples taken was conducted in the Scientific Research Laboratory of Environment Safety, functioning in Lviv State University of Life Safety (Ukraine) (Certificate of conformity of the measurement control system No. RA127/17 dated November 14, 2017, in effect until November 13, 2021, issued by the SC “Lvivstandartmetrolohiia”).

The Regulations on Scientific Research Laboratory (SRL) are developed on the basis of the normative document “The order of voluntary assessment of the measurement control system. General requirements and procedure. SOU 43.01-04725912-001.2016” (order of the SC “Lvivstandartmetrolohiia” of March 21, 2016, No. 648). The premises and the surrounding medium of the laboratory comply with sanitary standards, rules and labour protection requirements. Testing and support equipment, measuring equipment and materials of the Laboratory of Environment Safety comply with the requirements of normative documents, as well as verified and certified according to DSTU 3215-95, DSTU 2708:2006, GOST 24554-81.

A statistical method of research – the Pearson coefficient of correlation (to assess the interaction of studied parameters) is used in the work, which is calculated by the formula (1):

$$r_{xy} = \frac{\sum_{i=1}^m (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^m (x_i - \bar{x})^2 \sum_{i=1}^m (y_i - \bar{y})^2}} = \frac{cov(x, y)}{\sqrt{s_x^2 s_y^2}}, \quad (1)$$

where \bar{x} , \bar{y} are sample means; s_x^2 , s_y^2 are sample variances, $r_{xy} \in [-1, 1]$.

3 Results and discussion

The samples were taken in 2017 from reservoirs of technogenic origin located at the foot of rock heaps of such coal mines as “Mezhyrichanska”, “Velykomostivska”, “Stepova”, “Zarichna”, “Lisova” and “Chervonohradska”. The complex of parameters under determination, as well as their values are represented in a Table 1.

Table 1. Geochemical parameters of wastewater under the rock heaps within the Chervonohrad mining region.

Parameter	Mezhyrichanska (T1, 21.03.2017)	Velykomostivska (T2, 10.03.2017)	Stepova (T1, 02.11.2017)	Zarichna (T1, 19.05.2017)	Lisova (T2, 15.08.2017)	Chervonohradska (T1, 06.11.2017)	Maximal permissible concentration [26 – 28]
1	2	3	4	5	6	7	8
Transparence, cm	18	18	18	18	18	18	–
Dangling substances, mg/dm ³	33.8	34.2	26.4	32.8	32.6	28.8	380
pH	2	7.3	7.6	7.5	4.7	7.4	6.5
Oxidability, mgO ₂ /dm ³	4.8	3.1	4.8	5.4	7.4	4.6	–
Alkalinity, mg/eq.	0	6.6	6.4	6.5	0	6.5	9
Acidity, mg/eq.	35.6	0	0	0	13.8	0	–
Total hardness, mg/eq.	25.3	4.3	6.2	26.8	26.6	19.6	–
Dry residue, mg/dm ³	6941	922	1119	1865	3842	3814	1000
Calcium, mg/dm ³	474	52	96	384	396	300	–
Magnesium, mg/dm ³	19.2	20.4	16.8	91.2	81.6	55.2	20
Total ferrum, mg/dm ³	2.44	0.15	0.13	0.22	2.8	0.18	0.5

Continuation of the Table 1

1	2	3	4	5	6	7	8
Chlorides, mg/dm ³	136	174	324	248	466	438	350
Sulphates, mg/dm ³	6299	194	180	1080	1624	1250	500
Ammonium, mg/dm ³	1.24	0.32	1.56	0.4	0.86	0.56	30
Nitrites, mg/dm ³	0.11	0.03	0.11	0.08	1.52	0.06	3.3
Nitrates, mg/dm ³	1.06	1.1	1.2	0.57	2.8	0.64	45
Fluorine, mg/dm ³	1.91	0.8	0.32	0.3	0	0.44	1
Oil products, mg/dm ³	0.3	0.3	0.3	0.3	0.3	0.3	10
Phosphates, mg/dm ³	2	2	2	2	2	4.2	10
Copper, mg/dm ³	0.28	0.1	0.1	0.1	0.1	0.1	1.03
Manganese, mg/dm ³	8.94	0.05	0.04	0.12	0.64	0.28	0.13
Aluminium, mg/dm ³	1.58	0.04	0.04	0.04	0.04	0.04	0.53
Chromium (VI), mg/dm ³	0.01	0.01	0.01	0.01	0.01	0.01	0.05

It has been determined that the pH of the medium (water under the waste heaps) is in the range from highly acidic (“Mezhyrichanska” mine) to alkaline (“Velykomostivska”, “Stepova”, “Zarichna”, “Chervonohradska” mines), with a rate close to neutral (6.5). It should be noted that the water under the waste heaps influences the pH of the soil, and this, in turn, affects the development of forest and agricultural crops. The value of dangling substances does not exceed the maximal permissible concentration (MPC) and is in the range of 26.4 – 34.2 mg/dm³. The value of total ferrum exceeds the MPC for water under the waste heaps of the “Mezhyrichanska” mine (by 4.88 times) and “Lisova” mine (by 5.6 times). The long-term water consumption with a high concentration of ferrum, in addition to liver diseases, blood and allergic reactions, increases the risk of heart attacks, negatively affects the reproductive human function. Ferrum is slowly removed from the human body, has a carcinogenic effect and disrupts the brain functions.

Often, there is a high concentration of nitrates in the wells of the studied region, which causes serious health disorders due to methemoglobinemia, when hemoglobin in a person’s blood loses the ability to carry oxygen to tissues.

The concentration of ammonium in water under the waste heaps is within the normal range (0.32 – 1.24 mg/dm³). The spatial distribution of ammonium, total ferrum, dangling substances and pH is shown in Fig. 1.

The spatial distribution of polluting substances adversely affects all the biota components. The sulphate concentration in water under the waste heaps exceeds the MPC for the “Mezhyrichanska” mine (by 12.6 times), “Zarichna” mine (by 2.16 times), “Lisova” Mine (by 3.25 times), and “Chervonohradska” mine (by 2.5 times). Most of them were found in the water under the waste heaps of the “Mezhyrichanska” mine – 6 941 mg/dm³. The fluorine concentration in water under the waste heaps exceeds the MPC only for the “Mezhyrichanska” mine (by 2 times). The highest phosphate concentration was found in the water under the waste heaps of the “Chervonohradska” mine (4.2 mg/dm³), but it does not exceed the MPC, which is 10 mg/dm³.

Chlorides are mostly concentrated in water under the waste heaps of the “Lisova” mine and “Chervonohradska” mine, exceeding the MPC by 1.33 and 1.25 times, respectively. An excess of chlorides in compounds with other organic substances leads to oncology diseases of a human.

The main disadvantage of drinking water – excessive hardness, that is, the excess of calcium and magnesium salts, hydrocarbonates, sulphates and ferrum. If a person is constantly drinking this water, there is a risk of kidney stones and gallstones formation.

The high level of water hardness leads to urolithic illness. In particular, water with hardness greater than 10 mg-eq./dm^3 increases the risk of endemic goitre. Water with high level of hardness leads to the development of dermatitis in humans.

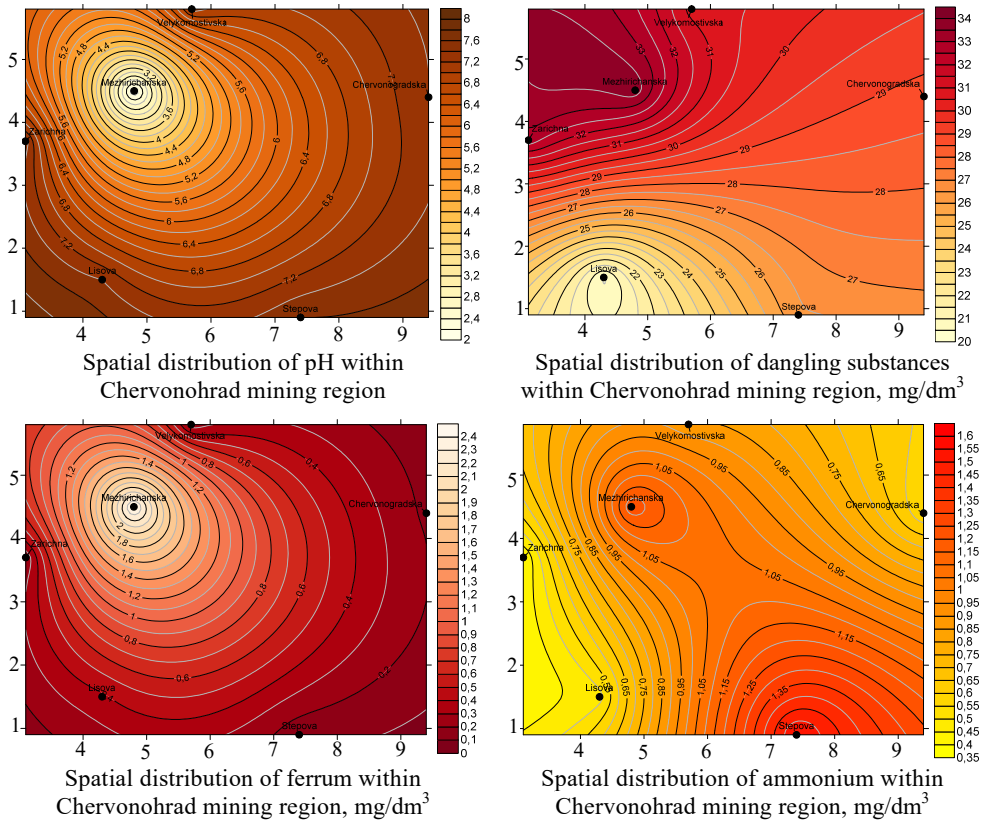


Fig. 1. Concentration of ammonium, total ferrum, dangling substances and pH in water under the waste heap.

The spatial distribution of sulphates, fluorine, phosphates and chlorides is shown in Fig. 2.

According to the analysis of the studied parameters, it has been determined that water under the waste heaps of the Mezhyrichanska Mine is the most polluted. The construction of this mine began in 1954, and it was put in commission in September, 1959. Its design capacity – 750 thousand tons. The set productive capacity as of 01.01.2010 is 500 thousand tons per year, and as of 01.01.2018 – 300 thousand tons per year. The area of mining allotment of a mine is 12 hectares, the land allotment – 64 hectares.

The most dangerous landscape-transforming factor of water under the waste heaps is the transfer of polluting substances into the soil, surface and subterranean waters. Through the use of Pearson coefficients of correlation, the ratios between pollution parameters have been obtained. The determined correlation coefficients are high, positive ($r = 0.78 - 0.99$) and evidence of the toxic components spread in water under the waste heaps throughout the entire coal mining region (Table 2).

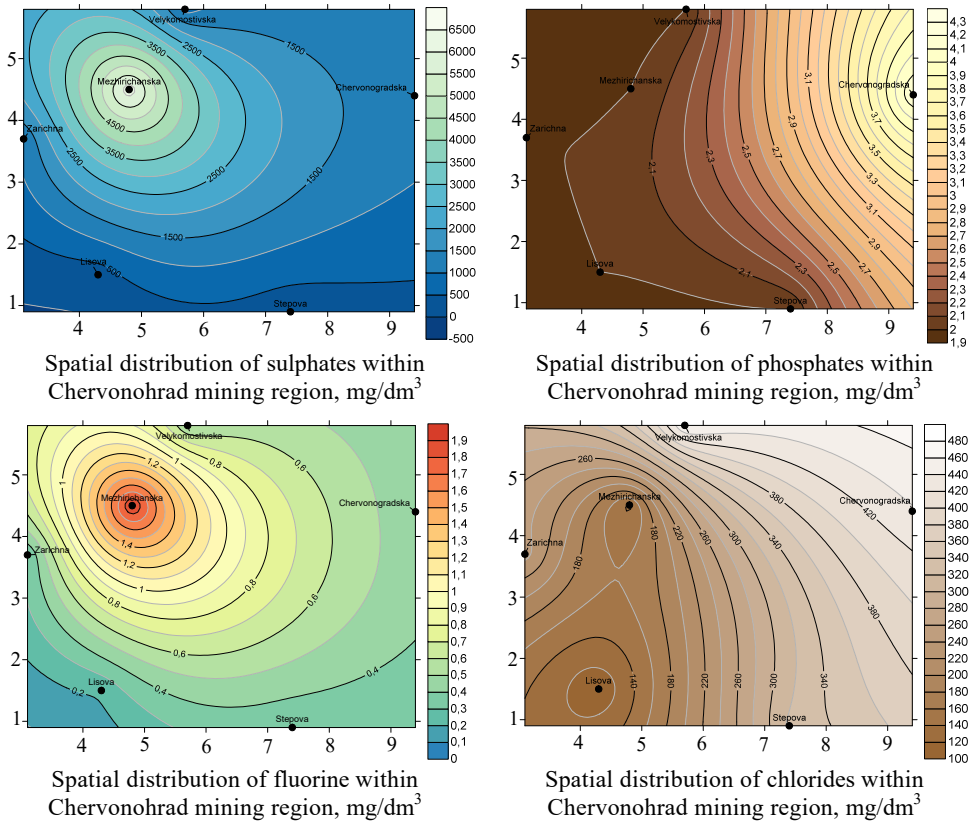


Fig. 2. Concentration of sulphates, fluorine, phosphates and chlorides in the water under the waste heaps.

Table 2. Pearson coefficients of correlation between the studied parameters of pollution.

r	Mezhyrichanska	Velykomostivska	Stepova	Zarichna	Lisova	Chervonohradska
Mezhyrichanska		0.834812	0.788636	0.961378	0.931892	0.899526
Velykomostivska			0.993223	0.935861	0.975816	0.98975
Stepova				0.91079	0.953882	0.971051
Zarichna					0.988139	0.971812
Lisova						0.996146
Chervonohradska						

One of the most environmentally safe and economically feasible methods for neutralizing toxic components in water under the waste heaps are the bioplateau systems. The bioplateau systems are widely used throughout the world for various wastewater treatment. In particular, in the USA, the systems for mine water treatment are quite widely used on reed plantations. The bioplateau of reed for domestic wastewater treatment is described in the Netherlands [29], Japan [30], China [31], for surface runoff treatment in Norway [32], Australia [33] and other countries. The resistance of reeds to high concentrations of polluting substances made it easy to use it also for wastewater treatment in the UK [34].

However, for the studied region, when designing the bioplateau systems, it is necessary to take into account microclimatic, edaphic and landscape-transforming factors. This is the prospects of our future research.

4 Conclusions

The geochemical properties of water under the waste heaps within the Chervonohrad mining region have been studied. The environmental remediation around the technogenic reservoirs of rock heaps using the bioplateau systems is proposed.

It has been determined that the pH of the medium (water under the waste heaps) is in the range from highly acidic (“Mezhyrichanska” mine) to alkaline (“Velykomostivska”, “Stepova”, “Zarichna”, “Chervonohradska” mines). The wastewater under the rock heaps influences the pH of the soil, and this, in turn, affects the development of forest and agricultural crops. The concentration of total ferrum exceeds the MPC for water under the waste heaps of the “Mezhyrichanska” mine (by 4.88 times) and “Lisova” mine (by 5.6 times). It is dangerous that ferrum is slowly removed from the body, has a carcinogenic effect and disrupts the brain functions. The sulphate concentration in water under the waste heaps exceeds the MPC for the “Mezhyrichanska” mine (by 12.6 times), “Zarichna” mine (by 2.16 times), “Lisova” mine (by 3.25 times), and “Chervonohradska” mine (by 2.5 times). The fluorine concentration in water under the waste heaps exceeds the MPC only for the “Mezhyrichanska” mine (by 2 times).

The determined correlation coefficients are high, positive ($r = 0.78-0.99$) and evidence of the toxic components spread in water under the waste heaps throughout the entire coal mining region.

The obtained geochemical data of water under the waste heaps of mines in the Chervonohrad mining region are important in terms of the environmental impact assessment of mining activity on the human body and the biosphere components – the hydrosphere, the phytogenic field. It is necessary to establish environmental monitoring systems and to develop measures for the environmentally safe decommissioning the waste heaps of coal mines.

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