Experimental geoecology

Akhmedzhanova G.M., Malinkina G.V., Kotelnikov A.R. Modeling of solubility and transport of heavy metals (Ni, Cu, Zn, Pb) in natural waters. *UDC 550.84.092*

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Abstract. In order to simulate the interaction of natural waters with mining waste dumps, experiments were conducted on hydrolytic leaching of heavy metal sulfides (ZnS, PbS, FeS, $CuFeS_2$, $(Ni,Fe)_9S_8$) with aqueous solutions of salts and distilled water. The calculated number of sulfides, feldspars and quartz was placed in teflon containers with a lid. The required amount of solutions (0.1 M KCl or 0.2 M NH_4Cl) or distilled water was added. The experiments were carried out under gradient conditions. The temperature in the lower part of the reactor was 70°C, in the upper part – 20°C. The duration of the experiments was 30 days. Data on the content of heavy metals in solutions after the experiments were obtained.

***Keywords**: solubility, heavy metals, experiment*

In order to simulate the interaction of natural waters with mining waste dumps, experiments were carried out on hydrolytic leaching of heavy metal sulfides (ZnS, PbS, FeS, $CuFeS_2$, $(Ni,Fe)_9S_8$) with aqueous solutions of salts and distilled water. The calculated number of sulfides, feldspars and quartz was placed in 30 cm long, 50 ml volume teflon containers with a lid. The required amount of solutions (0.1 M KCl or 0.2M NH_4Cl) or distilled water was added. The experiments were carried out under gradient conditions. The temperature in the lower part of the reactor was 70°C, in the upper part – 30°C (Table 1). The duration of the experiments was 40 days. The analysis of the solution compositions was performed on a Kvant-4 atomic absorption spectrometer.

Table 1. Experimental conditions for modeling ore deposit dispersion halos and metal transport

T=70°C	Fsp + Qz + sulfides	Sand (Qz)	Soil (sand + peat)	T=30°C
Bottom	Lower part of the container	Middle part of the container	The upper part of the container	Top

It is shown that their concentration allows leaching and mobilizing such ore elements as Pb (up to 0.1 – 3.2 µg/ml); Zn – from 0.3 to 4.2 µg/ml; Cu – from 0.1 to 0.45 µg/ml; Ni – from 0.11 to 57 µg/ml. In salt solutions (NH_4Cl and KCl) of relatively low concentration (0.1 – 0.2 M), an increase in the content of petrogenic elements (Na, K, Ca, Mg) is observed. When using salt solutions (NH_4Cl and KCl), the extraction of elements into the solution increases several times. The solubility of ore elements also depends on the composition of the solutions. The results of the experiments are presented in Table 2 and show the possibility of transporting elements under the influence of surface water in weight quantities.

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Table 2. Experiments on the transfer of granite matter and ore elements (modeling of dispersion halos). Contents in solutions in µg/ml (ppm)

Solution	**K**	**Na**	**Ca**	**Mg**	**Fe**	**Zn**	**Pb**	**Ni**	**Cu**	**Position**	**Charge**
NH_4Cl 0.2M	11.400	3.800	42.000	7.600	2.900	0.300	0.000	0.000	0.000	top	Soil
	41.700	8.100	100.000	14.700	0.600	0.300	0.000	0.000	0.000	middle	Sand
	57.600	15.000	320.000	28.200	280.500	4.200	0.000	0.000	0.000	bottom	Qz+Fsp+FeS+PbS+ZnS
	9.200	7.470	28.500	6.100	0.900	0.000	0.000	0.004	0.002	top	Soil
	31.970	4.070	80.600	11.700	0.950	0.000	0.000	0.080	0.110	middle	Sand
	53.700	14.220	581.200	24.830	0.110	0.000	0.000	17.900	0.140	bottom	Qz+Fsp+$(Ni.Fe)_9S_8$+$CuFeS_2$

Continuation of the **table 2.**

Solution	K	Na	Ca	Mg	Fe	Zn	Pb	Ni	Cu	Posi-tion	Charge
H_2O	6.780	4.580	15.300	5.300	5.000	0.280	0.130	0.000	0.000	top	Soil
	16.500	10.000	12.000	6.000	14.900	0.400	0.300	0.000	0.000	middle	Sand
	40.200	10.100	26.800	10.000	13.800	1.720	3.200	0.000	0.000	bottom	Qz+Fsp+FeS+PbS+ZnS
	5.800	3.400	16.200	2.700	12.030	0.000	0.000	0.110	0.140	top	Soil
	16.900	5.900	7.010	2.420	1.680	0.000	0.000	0.040	0.090	middle	Sand
	40.000	11.900	25.100	5.700	1.360	0.000	0.000	0.250	0.260	bottom	Qz+Fsp+ $(Ni.Fe)_9S_8$+Cu FeS_2

End of the **table 2.**

Solution	K	Na	Ca	Mg	Fe	Zn	Pb	Ni	Cu	Posi-tion	Charge
KCl 0.1M	343.000	5.200	24.000	7.620	5.000	0.400	0.080	0.000	0.000	top	Soil
	209.100	10.500	64.400	10.500	7.400	0.300	0.070	0.000	0.000	middle	Sand
	211.200	13.200	226.400	24.500	259.300	0.600	0.450	0.000	0.000	bottom	Qz+Fsp+FeS+PbS+ZnS
	290.000	3.700	10.500	3.230	4.700	0.000	0.000	0.110	0.020	top	Soil
	75.000	12.600	52.300	12.600	4.000	0.000	0.000	0.360	0.010	middle	Sand
	50.500	18.200	901.200	56.500	4.000	0.000	0.000	57.300	0.450	bottom	Qz+Fsp+ $(Ni.Fe)_9S_8$+ $CuFeS_2$

Grishantseva E.S., Nikolaeva I.Yu., Grigorieva M.L. Study of metal forms in bivalve shells from the Ivankovskoe Reservoir. *UDC 550.47*

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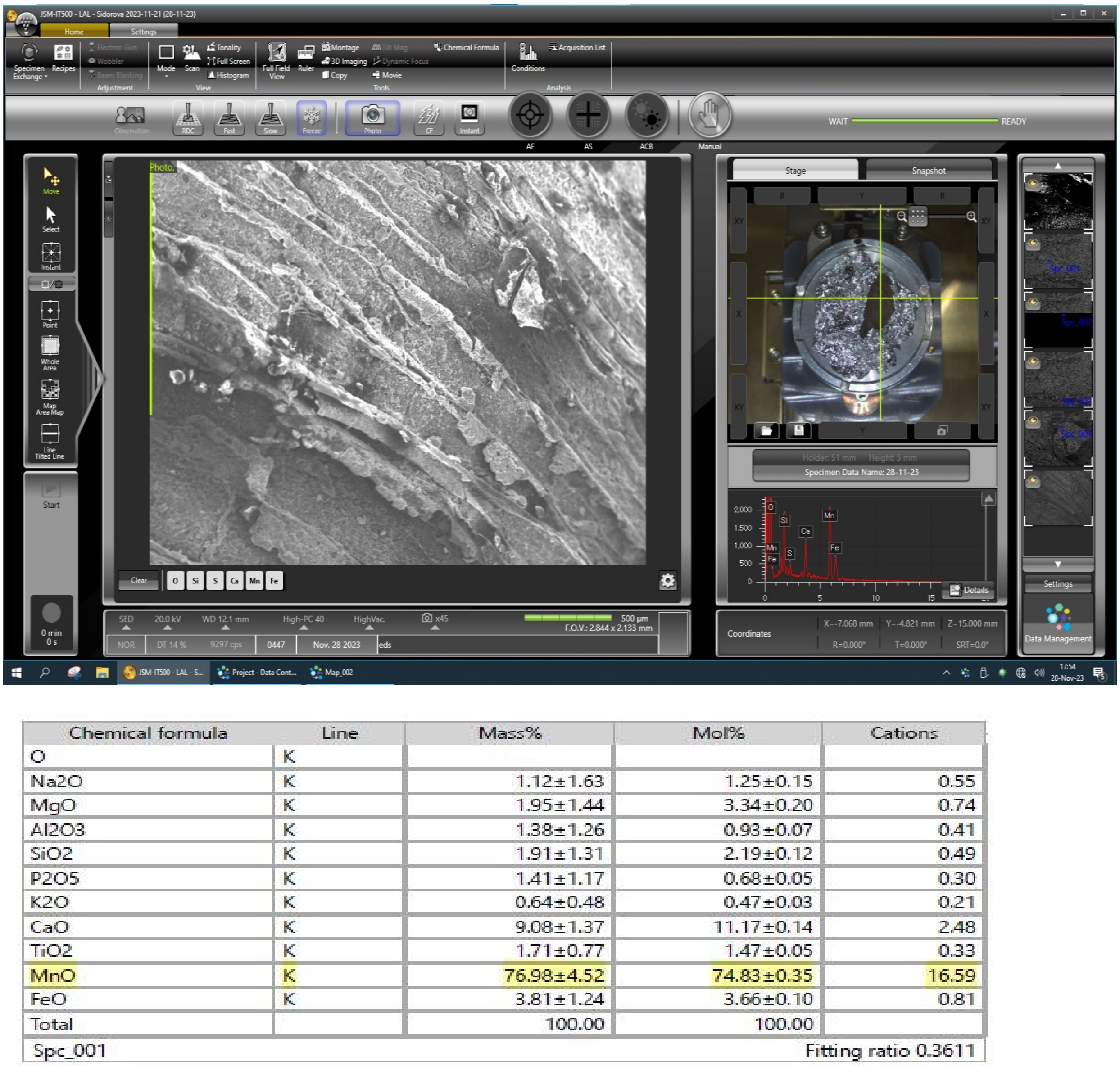
Abstract The paper discusses the results of an experimental study of the forms of metals occurrence in the shells of bivalve mollusks (*Dreissena polymorpha* Pallas) from the Ivankovskovo Reservoir. The study of the forms of metals in hydrobionts is necessary for a quantitative assessment of the contribution of bivalve mollusks to the geochemical migration of metals in the reservoir ecosystem, determining the volumes of passive and active bioaccumulation and identifying their participation in the biogenic sedimentation of chemical elements. To study the physicochemical forms of metal occurrence, a selective chemical extraction method was employed using various reagents to extract exchangeable metal forms, metals in the adsorbed complex, those bound to Fe and Mn hydroxides, and the total content of mobile, migration-capable forms. Metal concentrations in the extracts and shells were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a Supec 7000 instrument. Concentration maps of chemical element distribution on the shell surfaces were obtained using an analytical, multifunctional scanning electron microscope (JSM-IT500) at IGEM RAS.

***Keywords:** bioaccumulation; bivalve mollusks; metal speciation.*

The study aimed to identify the patterns of metal accumulation in freshwater mollusks (Dreissena polymorpha Pallas) and evaluate the proportion of metals accumulated through passive and active bioaccumulation. The accumulation of chemical elements during biomineralization occurs not only through active metabolic processes (i.e., absorption into the organomineral matrix of the shells) but also passively via adsorption onto the shell surfaces (Demina, 2010). The practical significance of this work lies in its potential application for planning environmental monitoring measures for water bodies, including the Ivankovskoe Reservoir—a source of drinking water for Moscow—and contributing to the development of bioindication and biomonitoring methods for aquatic ecosystems.

Sampling of hydrobionts was conducted in July 2024 at the Ivankovskoe Reservoir (Volga River) at three sites with varying hydrodynamic conditions and anthropogenic impacts: Melkovo, near the Konakovskaya GRES, and Korcheva. The analysis of trace elements in the shells and soft tissues of bivalve mollusks, as well as in extracts for metal speciation, was performed using ICP-MS (Supec 7000) at the Department of Geochemistry, Faculty of Geology, Moscow State University. The distribution of chemical elements on the shell surfaces was studied using a JSM-IT500 scanning electron microscope at IGEM RAS. Figure 1 shows the scaly structure of the shell surface and the mass content of chemical elements in the outer layer.



Chemical formula	Line	Mass%	Mol%	Cations
O	K			
Na2O	K	1.12±1.63	1.25±0.15	0.55
MgO	K	1.95±1.44	3.34±0.20	0.74
Al2O3	K	1.38±1.26	0.93±0.07	0.41
SiO2	K	1.91±1.31	2.19±0.12	0.49
P2O5	K	1.41±1.17	0.68±0.05	0.30
K2O	K	0.64±0.48	0.47±0.03	0.21
CaO	K	9.08±1.37	11.17±0.14	2.48
TiO2	K	1.71±0.77	1.47±0.05	0.33
MnO	K	76.98±4.52	74.83±0.35	16.59
FeO	K	3.81±1.24	3.66±0.10	0.81
Total		100.00	100.00	
Spc_001				Fitting ratio 0.3611

Fig. 1. Shell surface image and chemical element spectrum obtained using the JSM-IT500 electron microscope

Experimental determination of metal forms on bivalve shells was performed using parallel extraction methods. Exchangeable metal forms were extracted with $MgCl_2$ for 1 hour on a shaker (solid-to-liquid ratio 1:10). Mobile, migration-capable metal forms were extracted using the Toxicity Characteristic Leaching Procedure (TCLP) with 0.11N acetic acid for 5 hours (ratio 0.5 g : 20 ml). Metals bound to organic matter and sulfides were extracted with 30% H_2O_2 + HNO_3 (ratio 1g : 20 ml). Metals in the adsorbed complex were extracted with 25% acetic acid for 1 hour on a shaker (ratio 1g : 10 ml). The results are presented in Table 1.

Table 1. Relative content of different metal forms in mollusk shells (as a percentage of the total content). Note: below LOD — below the method's detection limit

Element	Exchangeable forms	Adsorbed complex	Mobile, migratory forms	Complexes with organic matter and sulfides
V	29-46	0.5-1.3	1.8-3.8	*Below lod*
Cr	1.5-40	1.7-6	1.6-5	*Below lod*
Mn	2-5	1.1-3.9	0.3-0.9	0.6-1.2
Fe	1-2	1.6-4.9	0.1-0.2	0.1-0.3
Cu	1.2-11	4.6-16	0.9-2.9	0.2-2.1
Zn	1.6-16	7-8	1.9-3.7	1.7-8

The predominant mass of metals (from 65 to 98%) inside the organisms of bivalve mollusks is concentrated in the shells, which serve as a kind of reservoir-storage of the studied microelements. The study of the shells by the electron microscopy method allowed us to establish that the surface layer consists mainly of MnO. The conducted experimental studies allowed us to determine a low level of accumulation of elements on the shells by the mechanism of passive bioaccumulation. Extraction of mobile forms of most metals did not exceed 16% of their total content. The content of adsorbed, mobile and complexed with organic matter metals does not exceed 8%. In the section of the reservoir with a high anthropogenic load, located near the Konakovskaya GRES, an increase in the proportion of exchangeable forms of V, Cr, Zn on the shells of mollusks was found, which can serve as a diagnostic feature when conducting monitoring environmental studies.

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Reference

Demina L.L. *Biogenic* Migration *of Trace Elements in the Ocean:* Abstract of the Doctor of Geol. and Miner. Sciences Dissertation. - Moscow, 2010. - 46 p.

Salavatova D.S., Fiaizullina R.V., Bychkov D.A. Mercury in minor rivers of moscow (on the example of the Setun' and Ramenka rivers). *UDC 550.41 550.424*

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Abstract. Various components of the natural environment of the minor rivers Setun' and Ramenka were studied: water, suspension, bottom sediments, adjacent soils, snow cover, air and vegetation. When entering natural waters, ionic forms of mercury can transform into thermodynamically more stable and migratory mobile ones. In this regard, coexisting mercury species in the river waters were separated: dissolved zero-valent, dissolved ionic, associated with organic ligands, adsorbed on suspension and gross. It was shown that mercury in the minor rivers Setun' and Ramenka is transported mainly in a suspended state. Mercury concentrations in the soils of the Ramenka river are an order of magnitude higher than the content in the soils of the Setun' river, reaching 540 ppb.

Keywords: *mercury; mercury species; mercury in minor rivers; mercury in vegetation; mercury in bottom sediments; mercury in soils; mercury in snow cover; mercury in the air*

In the conditions of a large metropolis, mercury is a universal indicator of technogenic impact. Minor rivers, being an important element of natural water systems, determine the general ecological situation in the upper parts of large river basins. Historically, the assessment of the content of pollutants in surface waters was made only on the basis of the analysis of water samples. However, the content of priority pollutants in the upper layers of bottom sediments and in suspension often exceeds their concentrations in water. Therefore, various components of the natural environment of the minor rivers Setun' and Ramenka were studied.

The objects of this study were minor rivers of Moscow: Setun' and Ramenka (Fig. 1). Ramenka is the largest right tributary of the Setun', 9 km long, located in the South-West Administrative District of Moscow. The catchment area is 45 km^2. The source of the Ramenka river is located in the cascade of Vorontsov ponds on the Teplostanskaya erosion hill, the mouth is to the southwest of the New Rublevsky bridge. The Ramenka is partially enclosed in an underground collector, but mostly flows in the open channel. The Setun' is a lower right tributary of the Moskva river, 38 km long, located in the west of Moscow. The catchment area is 190 km^2 (Nasimovich, accessed 02.06.2025). The source of the Setun' is a pond near the Salaryevo village, the mouth is the Moskva river below the Berezhkovsky bridge. It should be noted that the Setun' flows mainly in an open channel and along a preserved valley, unlike many other Moscow rivers. Two sampling points were selected: 1) the first point 55°42'54.1"N; 37°30'05.6"E was located in the Ramenka river valley (500 m upstream from the mouth); 2) the second point 55°43'16.4"N; 37°29'59.3"E – in the river valley. Setun' (200 m below the confluence of the Ramenka). At the sampling sites, ecological and geochemical monitoring observations were carried out on the mercury content in various components of the natural environment: water, suspended matter, bottom sediments, adjacent soils, snow cover, air and vegetation. Over the period from 2023 to 2025, 10 field trips were made to collect samples at each point with an average frequency of 3 months.

Water samples were collected in high-density polyethylene bottles with a volume of 5 liters, the containers were pre-rinsed three times with the sampled water, and then filled with it "to the lid", thereby minimizing the contact of water with air.

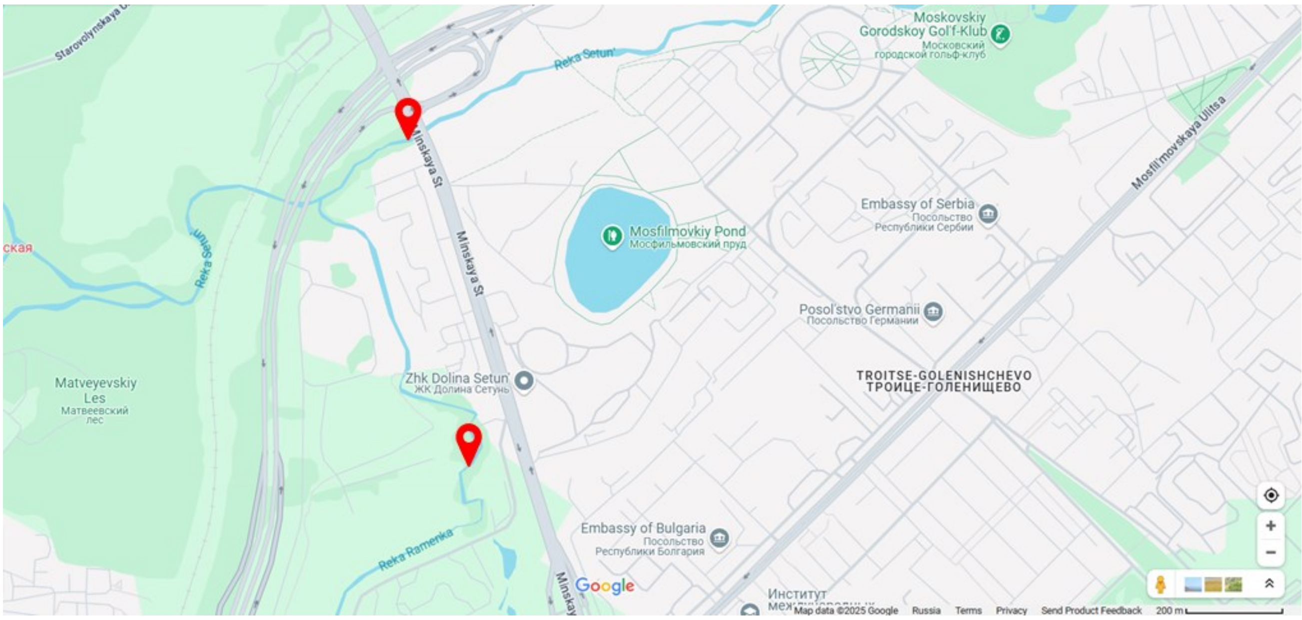

Fig. 1. Sampling sites in the Setun' and Ramenka rivers

Water samples were filtered through an acetate-cellulose membrane ("Vladipor", Vladimir) both in situ and after transportation to the laboratory for comparison of results.

It is known that in mercury analysis, different conditions of its transfer to the gas phase allow to separate the forms of mercury in the sample (Laperdina, 2000). Therefore, the sample was analyzed directly without a reducing agent, which ensured the release of the atomic form of mercury; with a reducing agent (tin chloride) – ionic and bound into weak complexes; and the use of a bromide-bromate mixture as an oxidizer allowed to convert organic forms of mercury into ionic ones.

The suspension was isolated by filtering a large volume of water through an ash-free "blue ribbon" filter, after which the filters were dried in a desiccator.

Snow samples were thawed at room temperature, further actions are similar to those carried out with river water.

Bottom sediments and soils were collected in zip-bags, dried at room temperature, sieved through an aluminum sieve (1 mm), quartered and ground to the state of analytical powder. Among the diversity of plants, three species were selected that were found at both points: ground elder (*Aegopodium podagraria*), dandelion (*Taraxacum officinale*) and stinging nettle (*Urtica dioica*). In addition, fern (*Polypodiophyta*) was selected three times, but was found only near the Ramenka river. In the laboratory, the plants were washed, dried at room temperature and crushed.

Subsequently, filters with suspension, bottom sediments, soils and vegetation were decomposed (extracted) in aqua regia, after which mercury analysis was carried out.

The concentration of total mercury in water was determined by the atomic absorption method with Zeeman correction of non-selective absorption on a mercury analyzer RA-915M ("Lumex", St. Petersburg) using RAPID software. The measurement method is based on the reduction of Hg cations in the sample with a tin (II) chloride solution, the transfer of atomic mercury to the analytical cell of the analyzer with a stream of purified air (the "cold vapor" method) and the measurement of the atomic absorption of mercury at a resonance wavelength of 253.7 nm. The mercury concentration in the sample was determined by the value of the integral analytical signal based on the calibration characteristic previously established using the State Standard Sample.

The mercury content in the air was determined in the concentration monitoring mode on an RA-915M atomic absorption spectrometer for 20-30 minutes.

Mercury concentrations in the Setun' river water were below the detection limit (<0.3 ppt for the dissolved atomic form; <2 ppt for the dissolved ionic form; <2 ppt for the total dissolved), with the exception of two samples collected in March 2023 and 2024. In them, the concentrations of dissolved ionic mercury were 3.5±0 ppt and 2.4±0.5 ppt; total dissolved mercury – 6.9±0.8 ppt and 5.4±1.9 ppt, respectively.

Mercury concentrations in the Ramenka river water samples were also mainly below the detection limit throughout the entire sampling period (dissolved atomic and ionic forms). The concentrations of the total dissolved form of mercury were 10.7±3.6 ppt and 30.2±2.9 ppt in March and January, respectively.

Mercury concentrations in suspension were above the detection limit in all measurements and varied in the range of 7.8-23.7 ppt for the Setun' river; 2.5-23.5 ppt for the Ramenka river. Thus, mercury in the studied rivers is transported mainly in a suspended state.

Figure 2 shows the measured mercury content in soils, bottom sediments and vegetation at both sampling points by dates. The graphs show that mercury concentrations in the soils of the Ramenka river are an order of magnitude higher than those in the soils of the Setun' river, reaching 540 ppb. It is worth noting that these contents do not exceed the maximum permissible concentrations of 2.1 ppm (HS 2.1.7.2041-06…, 2006). As for bottom sediments, mercury content in samples from both rivers, collected on the same day, is comparable, or slightly higher in the sediments of the Setun' river.

Among all vegetation types, the best mercury concentrators are ground elder ($C_{\mathrm{Hg}}^{\max}$ = 61.5 ppb) and fern ($C_{\mathrm{Hg}}^{\max}$ = 110 ppb), collected near the Ramenka river.

Mercury contents in the air at both points are in the range of 0.5-3.3 ng/m^3 and correspond to background values in the surface layer of the atmosphere, which are 0.2-10 ng/m^3 (Jonasson, Boyle, 1972; Lamborg et al., 2002; Lindqvist et al., 1991; Schroeder et al., 1998).

Mercury concentrations in melted snow were below the detection limit. Contents in suspended snow particles varied in the range of 7.7-8.2 ppt in March 2024 at both points.

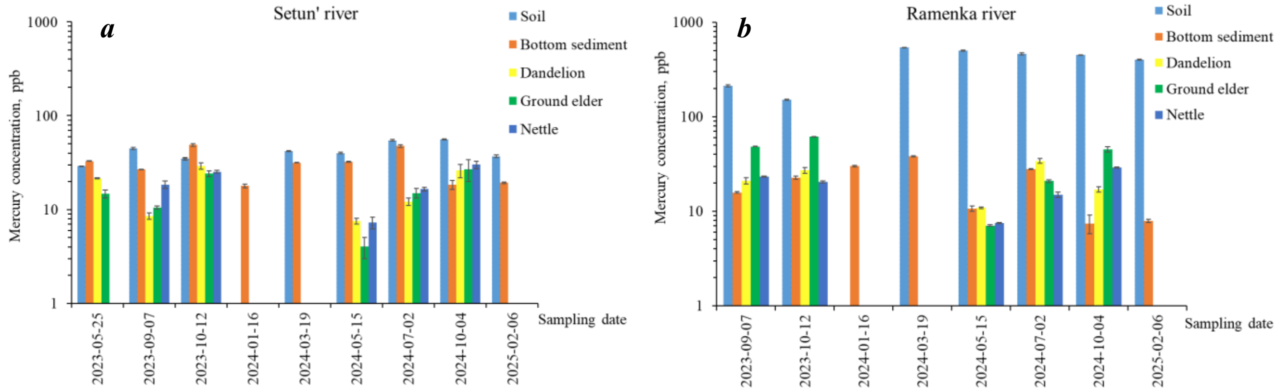

Fig. 2. Mercury content in soils, bottom sediments and vegetation (ordinate axis on a logarithmic scale). a – Setun' river, b – Ramenka river

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References

HS 2.1.7.2041-06 Maximum permissible concentrations (MPC) of chemical substances in soil: Hygienic standards. Moscow: Federal Center for Hygiene and Epidemiology of the inspectorate for customers protection, 2006. – 15 p.

Jonasson I. R., Boyle R. W. Geochemistry of mercury and origins of natural contamination of the environment // Can. Min. Metall. Bull.: Canada, 1972. V. 65(717). P. 32-39.

Lamborg C. H., Fitzgerald W. F., O'Donnell J., Torgersen T. A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients // Geochim. Cosmochim. Acta, 2002. V. 66(7). P. 1105–1118.

Laperdina T. G. Determination of mercury in natural waters. – Novosibirsk: Nauka, 2000. – 222 p.

Lindqvist O., Johansson K., Aastrup M., Andersson A., Bringmark L., Hovsenius G., Haakanson L., Iverfeldt A., Meili M., Timm B. Mercury in the Swedish environment—recent research on causes, consequences and corrective methods // Water Air Soil Pollut., 1991. V. 55(1–2). P. 1–261.

Nasimovich Yu.A. Rivers, lakes and ponds of Moscow // Dark forest [Electronic resource] URL: https://web.archive.org/web/20200219185650/http://temnyjles.ru/Nasimovich_kraevedenie/reki.shtml (date of access: 2025/06/02) Schroeder W. H., Anlauf K. G., Barrie L. A., Lu J. Y., Steffen A., Schneeberger D. R., Berg T. Arctic springtime depletion of mercury // Nature, 1998. V. 394. P. 331–332.

Zharikov A.V., Malkovsky V.I. An experimental study of the permeability of granite-gneisses samples from Yeniseyskiy site of the Nizhnekanskiy massif, Krasnoyarsk region. *UDC 621.039.7*

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Safe isolation of high level radioactive waste (HLW) in an underground depositary strongly depends on the mobility of radionuclides in the host rocks. The significant part of the HLW intended for storage in the Russian Federation is immobilized in a Na-Al-P glass matrix. Due to glass-water interaction, up to 90% of the actinides contained in the matrix pass into the water in a poorly soluble colloidal

form. These mobile particles are absorbed poorly by rocks, but can be retained mechanically, what is controlled by the rock matrix permeability. We performed some permeability determinations on granite-gneiss samples obtained from the core of the exploratory well drilled in the Yeniseyskiy site, where building of an underground depository for HLW is proposed. The measurements were carried out using a modified pulse decay method. The permeability values of granite gneisses of the Yeniseisky site, located within the framework of the Nizhnekansky massif, (10^{-21} – 10^{-20}) m^2 are comparable with those obtained earlier for the granitoids from the Itatsky and Kamenny sites, located directly in the Nizhnekansky massif.

***Keywords**: high level waste, glass matrix, groundwater, radionuclides, colloids, migration, gneiss, granite-gneiss, permeability, mechanical retardation*

One of the most important tasks when choosing a site for the location of an underground depository for high-level radioactive waste is the search for a massive of monolithic undisturbed low-permeability rocks [Laverov et al., 1991]. However, the experience of geological studies shows that in the upper parts of the earth's crust, up to considerable depths, the rock discontinuities of different scales occur necessarily and there mobile fluids are present: from fracture zones to large faults. The solution of the problem can be to search for a block of monolithic rocks with low permeability (because this rock property governs the rate of fluid mass transfer), and the sizes that would be sufficient great to prevent an pollution escape by groundwater into the biosphere even in the long term in case of the probable loss of protective properties by engineering barriers. Currently, a project is being considered to create an underground depository in the Yeniseisky site located in the Krasnoyarsk region, in the Nizhnekansky massif framing (Fig. 1). The site is mainly composed of Archean granito-gneisses crossed by later dolerite dikes, the discontinuities also occur there Fig. 2.

Downward filtration at the Yeniseysky site develops over a network of connected fractures between the isolated blocks not involved in this high-pressure deeply circulating flow" [Kochkin et al., 2017]. In this regard, it is necessary to ensure that the size of the monolithic blocks, where the HLW will be placed, is sufficient for their long-term safe isolation from the regional groundwater flow.

A significant portion of the radioactive waste in the Russian Federation intended for storage is immobilized in Na-Al-P glass matrix. In case of glass-water interaction, up to 90% of the actinide imitators pass in water into colloidal form. Colloidal particles are poorly soluble and sorbed by rocks, and therefore are considered to be the potentially most mobile and hazardous form of radionuclide waste transport. However, these particles can be mechanically retained by the rocks, what is determined by rock matrix permeability and filtration channels cross-section [Malkovsky et al., 2022].

This paper presents the results of permeability determinations in the granite-gneiss samples selected from the core material obtained at the depth of 496 m during the drilling of an exploration well at the Yeniseysky site.

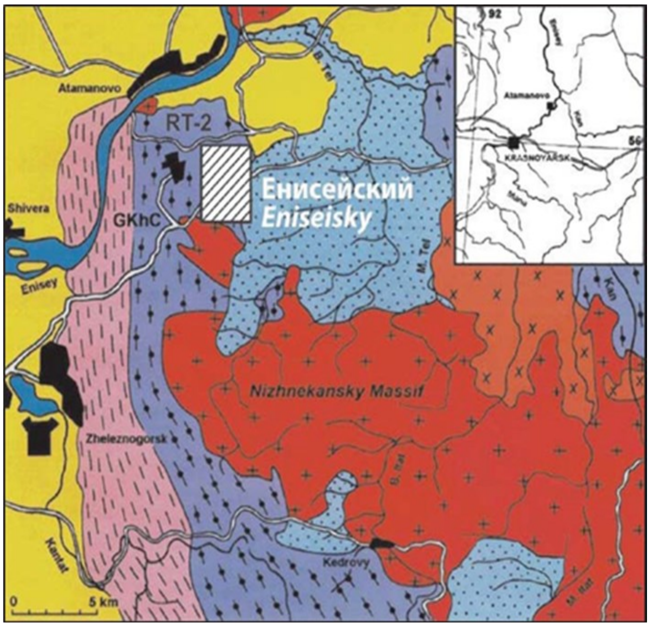

Fig. 1. Geological map of the Krasnoyarsk Mining and Chemical Combine (MCC) area and the position of the Yeniseisky and alternative sites: Itatsky and Kamenny [Minaev et al., 2023].
1 – gneiss complex; 2 – gneiss-shale complex with amphibolites, marbles and quartzites; 3 – granitoids of the Nizhnekansky complex; 4 – sedimentary rocks; 5 – Quaternary sedimentary deposits.

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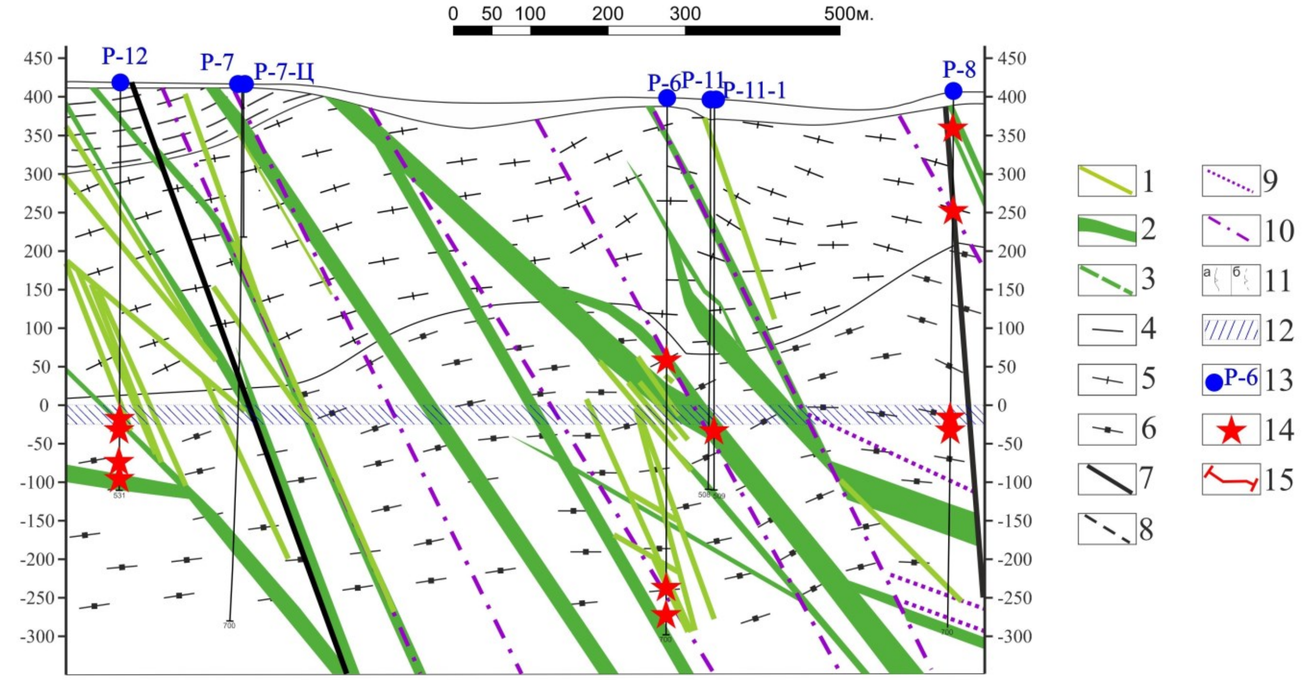

Fig. 2. Geological section of the Yeniseysky site [Minaev et al., 2023].

Legend 1 –dikes of gabbro-diabases and diabase porphyries; 2 -3 - dikes of methadolerites and gabbro-diabases; 4 – biotite and bicuspid gneisses and schists with rare interlayers of sillimanite-cordierite shales; 5 – biotite plagiogneisses with rare interlayers of garnet-biotite gneisses and sillimanite-cordierite shales; 6 – biotite-cordierite gneisses and crystalline schists with layers of biotite and biotite-hypersthenic gneisses; 7-9 – tectonic disturbances represented by crushing zones; 10 –breccia zones; 11 – Early Precambrian migmatized metamorphic rocks; 12 – target horizon of depository location; 13 – deep wells and their numbers; 14 – sampling points for detailed laboratory testing; 15 – the line of the geological section.

The measurements were carried out using a modified pulse decay method [Malkovsky et al., 2009]. One of the sections of the cylindrical sample is connected to a closed reservoir, while the other one is freely open to the atmosphere. At the initial moment of time, conventionally taken as zero, argon is supplied in the reservoir, resulting in an increase in the volume's pressure by Δp. Due to argon filtration through the sample to atmosphere, the pressure in the closed reservoir $p_{in}(t)$ gradually decreases from $p_{in}(t) + \Delta p$ to atmospheric p_{atm}. The sample permeability is determined by the rate of pressure reduction. The distribution of argon pressure in the sample satisfies the equation

$$\varphi\rho\frac{\partial p}{\partial t} = \frac{\partial}{\partial z}\left[\frac{\rho k_w}{\mu}\left(1+\frac{b}{p}\right)\frac{\partial p}{\partial z}\right], \qquad (1)$$

where t– time; z– distance from the input section of the sample along its axis; ρ, μ– density and dynamic viscosity of argon; k_w – permeability of the sample for water; b – Klinkenberg parameter.

The initial and boundary conditions for equation (1) are as follows

$$t = 0, p = \begin{cases} p_{atm}, z > 0, \\ p_{atm} + \Delta p, z = 0 \end{cases}; \; z = 0, p = p_{in}(t); \; z = L, p = p_{atm} \qquad (2)$$

where L– the length of the sample, $p_{in}(t)$ - the dependence determined by the condition of the argon mass balance in the input reservoir

$$V\frac{d\rho(p_{in})}{dt} = -\frac{S k_w}{\mu(p_{in})}\left(1+\frac{b}{p_{in}}\right)\frac{\partial p}{\partial z}\bigg|_{z=0}, \qquad (3)$$

S, V – the cross-section of the sample and the input reservoir volume.

Equation (1), was integrated using the semi-implicit Crank-Nicolson method [Roach, 1980] taking into account conditions (2) and (3).

The argon density in the considered pressure and temperature range satisfies the equation of state for ideal gas. The viscosity was calculated using approximation relations for the viscous virial coefficients for argon [Zubarev et al., 1989].

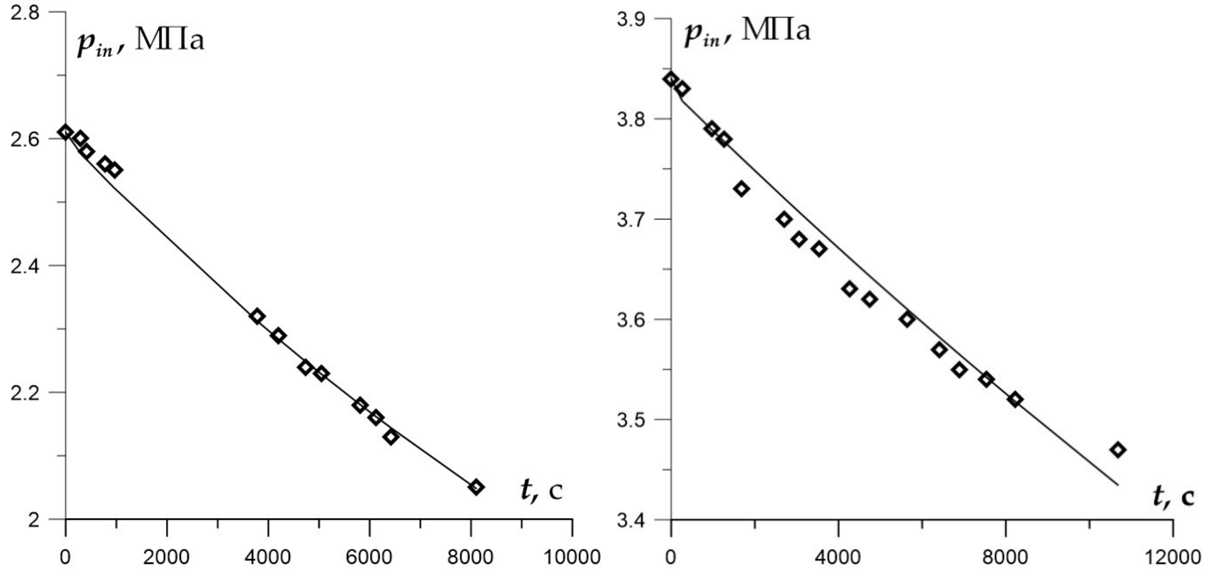

Fig. 3. Comparison of calculated and measured pressures for both studied samples.

The unknown k_w and b values were determined from the condition of the minimum function $F(k_w,b) = \sum_{i=1}^{N} [p_{in}(t_i) - p_i]^2$, where p_i –are the measured values $p_{in}(t_i), i = 1, \dots, N$

As a result of calculations the following values were obtained for the studied samples: (1) k_w= 2.29•10^{-20} m^2, b= 0.137 MPa; (2) k_w= 5.57•10^{-21} m^2, b= 0.0164 MPa. The comparison of the measured and calculated pressure values in the inlet reservoir at these values k_w and b for both samples is shown in Fig. 3 and demonstrates satisfactory agreement.

The measured values are comparable to those obtained earlier for granitoids from the Itatsky and Kamenny sites, which are located directly in the Nizhnekansky massif [Zharikov et al., 2014].

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References

1 Kochkin, B.T., Malkovsky, V.I., Yudintsev, S.V. Scientific basis for safety assessment of geological isolation of long-lived radioactive waste. 2017. IGEM RAS, Moscow (in Russian).

2 Laverov N.P., Kantsel A.V., Lisitsin A.K., Omel'yanenko B.I., Pak A.A., Sel'tsov B.M., Filonenko Yu.D. The Main Tasks of Radioecology in Connection with the Disposal of Radioactive Waste. // Atomic Energy. 1991. V. 71. No. 6. Pp. 521-534 [in Russian].

3 Malkovsky V.I., Yudintsev S.V., Zharikov A.V. Radiocolloid Retention in the Nizhnekanskii Rock Massif // Doklady Earth Sciences. 2022. V. 503. P. 226–231. DOI: 10.1134/S1028334X22040109.

4 Malkovsky V.I., Zharikov A.V., Shmonov V.M. New Methods for Measuring the Permeability of Rock Samples for a Single-Phase Fluid // Izvestiya, Physics of the Solid Earth. 2009. V. 45. No. 2. P. 89–100.

5 Minaev V.A., Poluektov V.V., Murashov K.Yu. Research report “Updating models of geological and structural-tectonic conditions of the site”. / Report under contract No. 1040-3 dated 18.05.2022. Moscow: IGEM RAS, 2023.

6 Roache P.J. Computational Fluid Dynamics Albuquerque: Hermosa Publishers, 1976 446 p.

7 Thermophysical Properties of Technically Important Gases at High Temperatures and Pressures: A Handbook, Ed. by Zubarev V.N., Kozlov A.D., Kuznetsov V.M., et al., Moscow: Energoatomizdat, 1989 [in Russian].

8 Zharikov A.V., Velichkin V.I., Malkovsky V.I., Shmonov V.M. Experimental study of crystalline rock permeability: implications for underground radioactive waste disposal. // Water Resources. 2014. V.41. P. 881–895. doi:10.1134/S0097807814070136