# Experimental geoecology

**Kotelnikov A.R.**[1]**, Akhmedzhanova G.M.**[1]**, Krinochkina O.K.**[2]**, Belousova E.O.**[1] **Hydrolytic leaching of schungite at different temperatures (experimental data).** UDC: 550.4.02, 553.9

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**Abstract**. The leaching of shungite samples from the Zazhogino and Maksovo deposits has been experimentally studied. The experiments were carried out in special containers or autoclaves lined with teflon at a temperature of 25-200°C and saturated steam pressure. Distilled water, solutions of hydrogen peroxide, sulfuric acid, and salts (NaCl, KCl) were used as the fluid phase. Intensive leaching of elements is shown even at room temperature. With an increase in temperature and concentration of solutions, the intensity of leaching increases. The results of experiments are compared with the compositions of natural waters of quarries of shungite substance.

*Keywords: experiment, shungite, leaching, fluid phase*

The studied shungite rocks are localized on the Zaonezhie peninsula in South Karelia. The composition of carbonaceous matter is not constant, usually it contains one or another amount of silica and other rock-forming elements. High variability of schungite compositions is shown both in terms of major and minor elements. This may be due to the initial heterogeneity (phase separation) of organic matter (bitumen) and silicate terrigenous-sedimentary matter. Shungite rocks of Zaonezhye accumulate (above clarke content in the earth's crust) such small elements as Sc(1.2), V(2.3), Cr(1.7), Co(1.5), Ni(3.0), Cu(6.1), Zn(2.3) , As(30.1), Mo(5.0), Ag(3.7), Cd(16.4), Sb(2.3), Pb(1.9), U(5.8). The numbers in brackets are the ratio of the content of the element in shungites to the clarke value of this element in the earth's crust. Shungites are used in iron smelting as a reducing agent and as a $SiO_2$-containing flux. Therefore, the scale of production is tens of thousands of tons. Quite a lot of shungite rocks go to dumps. Under the influence of atmospheric moisture and atmospheric oxygen, contained in shungite, sulfides (pyrite, sphalerite, galena, etc.) are oxidized with the formation of sulfuric acid. This acid leaches phosphates containing rare earth elements and strontium, and they go into solution. An analysis of the quarry waters of the Maksovsky site gives the following contents of a number of elements (in mg/l): V – 0.08; Cr – 0.45; Mn – 6.25; Fe – 137.6; Co – 2.23; Ni – 36.67; Cu – 87.76; Zn – 103.15; As – 0.05; Sr – 0.20; Mo – 0.07; Cd – 0.87; In – 0.02; ∑REE – 15.40; Pb – 0.15; U – 1.48. Assuming a quarry area of 1 $km^2$, 658000 $m^3$ of rainwater will be filtered through the entire quarry area per year (based on the norm of precipitation in the Medvezhyegorsk region). This gives a minute flow of about 1000 l/min. Based on these values, it is possible to estimate the annual removal of these elements into the environment (in tons): V – 0.04; Cr – 0.23; Mn – 3.21; Fe – 70.56; Co – 1.14; Ni – 18.80; Cu – 45.0; Zn – 52.9; As – 0.03; Sr – 0.10; Mo – 0.04; Cd – 0.45; In- 0.10; ∑REE – 7.9; Pb – 0.08; U – 0.76. The removal of these elements into the environment causes significant harm to biocenoses. To assess the possibility of processing dumps of schungite rocks and extracting valuable ore elements from them, we conducted experiments on hydrothermal leaching of the schungite substance.

Previously, experiments were carried out on the leaching of shungite at a temperature of 25 and 90°C. It is shown that an increase in temperature enhances the processes of hydrolytic leaching of shungite material. A comparison of the compositions of solutions and the composition of the original shungite is shown in fig. 1. From fig. 1 it can be seen that the composition of the solutions quite well represents the composition of shungites. Therefore, it was concluded that a sufficiently intensive leaching of shungites would allow transferring all toxic elements into solution. To check this, experiments were carried out at 200°C.

EXPERIMENTAL METHOD

*Initial materials.* To study the leaching, blocks of massive shungite from the Maksovo quarry were used. The content of major and minor elements in shungites from Maksovo are shown in tables 1, 2. Leaching experiments were carried out in distilled water, 1M KCl and 0.1M $H_2SO_4$.

*Equipment.* The starting materials were placed in stainless steel autoclaves (1X18H9T) and loaded into two-winding resistance furnaces. The accuracy of maintaining and controlling the temperature is ±3°C. The pressure was determined by the fill factor of the autoclave. The duration of the experiments was 14 days.

**Lithophile elements**  **Rare earth elements**
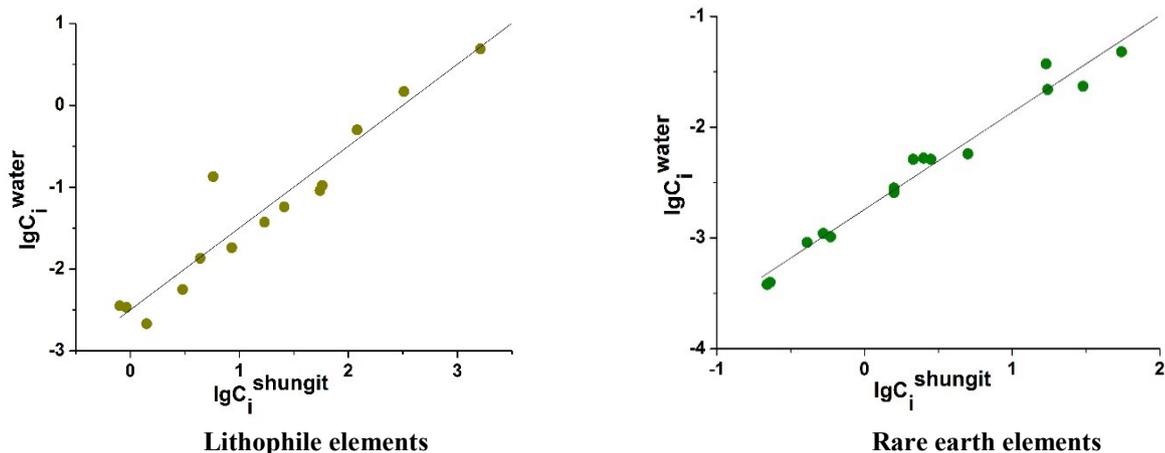
**Fig.1.** Correlation of the compositions of solutions obtained by leaching schungites with the initial composition of schungites.

**Table 1.** Average composition of shungite rocks in the Maksovo quarry

| Oxide | $C_i$, wt% | Variation | $S_x$ | Oxide | $C_i$, wt% | Variation | $S_x$ |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 60.01 | 57.24 - 62.73 | 1.9 | CaO | 0.76 | 0.19 - 2.30 | 0.60 |
| $TiO_2$ | 0.18 | 0.03 - 0.27 | 0.09 | $Na_2O$ | 0.57 | 0.01 - 1.40 | 0.40 |
| $Al_2O_3$ | 4.04 | 2.80 - 5.67 | 0.80 | $K_2O$ | 1.07 | 0.45 - 1.69 | 0.35 |
| FeOt | 2.98 | 1.81 - 7.76 | 1.6 | $P_2O_5$ | 0.25 | 0.06 - 1.15 | 0.30 |
| MnO | 0.04 | 0.01 - 0.09 | 0.02 | S | 0.30 | - | - |
| MgO | 0.73 | 0.32 - 1.57 | 0.33 | C | 28.81 | 11.60 - 40.19 | 9.5 |

**Table 2.** Average content of trace elements in shungite from the Maksovo quarry (g/t)

| Element | $C_i$, wt% | Variation | $S_x$ | Element | $C_i$, wt% | Variation | $S_x$ |
|---|---|---|---|---|---|---|---|
| V | 454.3 | 360 - 629 | 151.4 | As | 63.3 | 30 - 90 | 30.5 |
| Cr | 102.7 | 80 - 120 | 20.5 | Rb | 42.7 | 22 - 75 | 28.3 |
| Mn | 259.0 | 92 - 570 | 269.5 | Sr | 6.6 | 4 − 9.7 | 2.8 |
| Ni | 161.3 | 52 - 297 | 124.6 | Cd | 1.2 | 1 − 1.5 | 0.25 |
| Cu | 283.3 | 110 - 590 | 234.3 | Pb | 12.3 | 7.0 − 17.0 | 5.0 |
| Zn | 85.3 | 49 - 137 | 45.9 | U | 14.3 | 9.9-19.1 | 3.5 |

**Table 3**. Degree of leaching of elements $[(m_i^{fl}/m_i^{sh})*100]$ [1)]

| | L46 | | | L47 | | | L94 |
|---|---|---|---|---|---|---|---|
| Elm | $H_2O$ | 1M KCl | 0.1M $H_2SO_4$ | $H_2O$ | 1M KCl | 0.1M $H_2SO_4$ | 0.1M $H_2SO_4$ |
| Na | 3.7 | 15.7 | n.d. | 4 | 24 | 5.8 | 2.20 |
| Mg | 0.1 | 2.8 | 1 | 0.4 | 1 | 0.3 | 0.5 |
| K | 1.3 | n.d. | n.d. | 0.2 | 2 | n.d. | n.d. |
| Ca | 1.8 | 19 | 1.3 | 0.2 | 0.5 | 0.5 | 0.5 |
| Mn | 1.6 | 24 | 100 | 0.1 | 0.8 | n.d. | 100 |
| Cu | 0.8 | 80 | 50 | 5.2 | 0.3 | 40 | 14 |
| Zn | 6.0 | 100 | 100 | 93.3 | 100 | 100 | 100 |
| Rb | 2.8 | 100 | n.d. | 0.3 | 3 | n.d. | 0.00 |
| Sr | 3.2 | 18 | 100 | 7.0 | 8.4 | 20 | 100 |
| Cd | 0.7 | 22 | 20 | 1.6 | 0.6 | 5 | 9 |

1) conventions: $m_i^{sh}$– weight of the element in the original shungite sample; $m_i^{fl}$ – the mass of the element in the entire volume of the solution; L46, L47, L94 – samples of natural shungite; n.d. – not defined.

*Analysis of products of experience.* After the experiments, the solutions were analyzed by the AAS method for the content of Na, Mg, K, Ca, Mn, Cu, Zn, Rb, Sr, and Cd. Based on the analyzes, the degree of leaching of various elements $(m_i^\eta/m_i^s)*100$ was evaluated. The results of the experiments are presented in Table 3. From the data in Table 3 it can be seen that such elements as Mn, Zn, Sr are almost completely leached in a 0.1M solution of sulfuric acid. While the degree of Cu leaching is 14-50%. Cd leaching degree is ~20%. In general, it can be concluded that with the right choice of fluid composition and holding time, it is possible to achieve sufficiently high, close to 100%, leaching degrees.

On the basis of the presented data of an experimental study of the hydrolytic leaching of shungite substance, it can be concluded that this method can be used in principle for the neutralization of shungite dumps and the associated extraction of a number of valuable elements.

## Zharikov A.V., Malkovsky V.I., Yudintsev S.V. Rock sample permeability study to assess the colloidal migration of radionuclides. UDC: 621.039.7

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The solid HLW accumulated in Russia are mainly represented by alumophosphate glass. Aging under heating and in water presence leads to its transformation into a set of crystalline phases. It was experimentally found that the largest part of the actinide imitators were included in colloidal-sized crystalline particles resistant to interaction with water. The transport of radionuclides by groundwater depends on the rock permeability. The modified method developed by the authors allows to determine the permeability of the rock sample to water and the Klinkenberg parameter characterizing the rock permeability to gas, as well. Based on these characteristics, the estimation of the mathematical expectation and the standard deviation of the rock pore channels diameters was carried out. Such measurements were carried out on the samples from the Nizhnekanskii massif, which is currently considered as a potential area for the construction of a federal underground HLW storage. It is shown that the proportion of actinide-containing colloidal particles mechanically retained by enclosing rocks exceeds 99%. Taking into account that a significant part of the actinides from the aged Al-P glass matrix enters the groundwater in colloid form, this result is of a great practical importance for assessing the safety of the HLW storage.

High level radioactive wastes from the nuclear power industry and previous defense activities (HLW) are proposed to be placed in underground repositories (URs). Before disposal, liquid wastes are solidified into glass matrices of Na-Al-P composition. Under heating produced by radioactive decay, the glasses crystallize, that reduces the stability of the matrix to groundwater interaction. At the same time colloidal particles, which can transport radionuclides over long distances, penetrate into the solution. As it is known, the most dangerous scenario for the environment ecology is HLW escape from depository and their transport into the biosphere by groundwater. We have estimated the retention of primary colloids formed upon contact of water and a crystallized glass matrix in Nizhnekansky granite gneisses and gneisses. This is the most unfavorable scenario that does not take into account other barriers such as the container and the bentonite buffer.

The composition of primary glass, wt %: 17.3 $Na_2O$, 14.0 $Al_2O_3$, 5.5 $Fe_2O_3$, 51.1 $P_2O_5$, 1.1 NiO, 2.1 SrO, 2.5 $Cs_2O$, 2.1 $Ce_2O_3$, 2.0 $Nd_2O_3$, and 2.3 $UO_2$, where Na, Al, Fe, and P are matrix elements, while the rest ones are waste component simulators: Ni and a part of Fe are corrosion products, Cs and Sr are fission products, Ln (Ce and Nd) are transuranium actinide simulators (Pu, Am, and Cm), and U is introduced instead of Np and Pu in their higher oxidation states (V and VI). To accelerate the crystallization of glass matrix and to reduce its temperature closer to the in situ conditions in the repository, experiments were carried out in water vapor with a humidity of about 70 rel. % for 1-2 days at 200, 250, and 300°C. After these experiments, the solid phases were studied under scanning and transmission electron microscopes. The first very slight changes in the glass were observed at 200°C; the crystallization rate increased to 0.05 mm per hour at 250°C; and at 300°C, it increased by more than one order of magnitude. A cube-shaped glass sample with an edge size of 10 mm was replaced by an aggregate of two Na-Al-Fe phosphates, Ln-U-phosphate with a monazite structure, and hydrous Cs-U-phosphate, probably with an autenite structure (Fig. 1). Their ratio was as follows, wt %: 75% Na-Al-Fe-phosphate-1; 19% Na-Al- Fe-phosphate-2; 5% Sr-Ln-U-phosphate; and 1% hydrous Cs-U-phosphate. The first three phases (or 99% of the sample weight) are anhydrous, and probably they will be crystallized at a given glass composition under the "dry" conditions. Heating of the sample in the absence of water at 300° C did not lead to any changes. This result indicates a significant catalytic role of water vapor during the crystallization process.

The leaching of crystallized glass matrices in water was studied in a quasi-dynamic mode at 90°C. The sample (Fig. 1) was placed in a Ti autoclave, filled with distilled water, and placed in a thermostat. After 1, 3, 10, and 30 days, the solution was drained, distilled water was again poured into the autoclave, and placed in a thermostat again. Then, the composition of the solution was analyzed by ICP-MS, both in its initial form as well as after filtration through membranes with decreasing pore diameters: 450, 200, 100, and 25 nm (Fig. 2a).

In the case of a dissolved form, the element content should not change after filtration. The content of actinide imitators (Ln and U) decreases (Figs. 2b); therefore, it can be concluded that they are mostly in the form of colloids (Fig. 3).
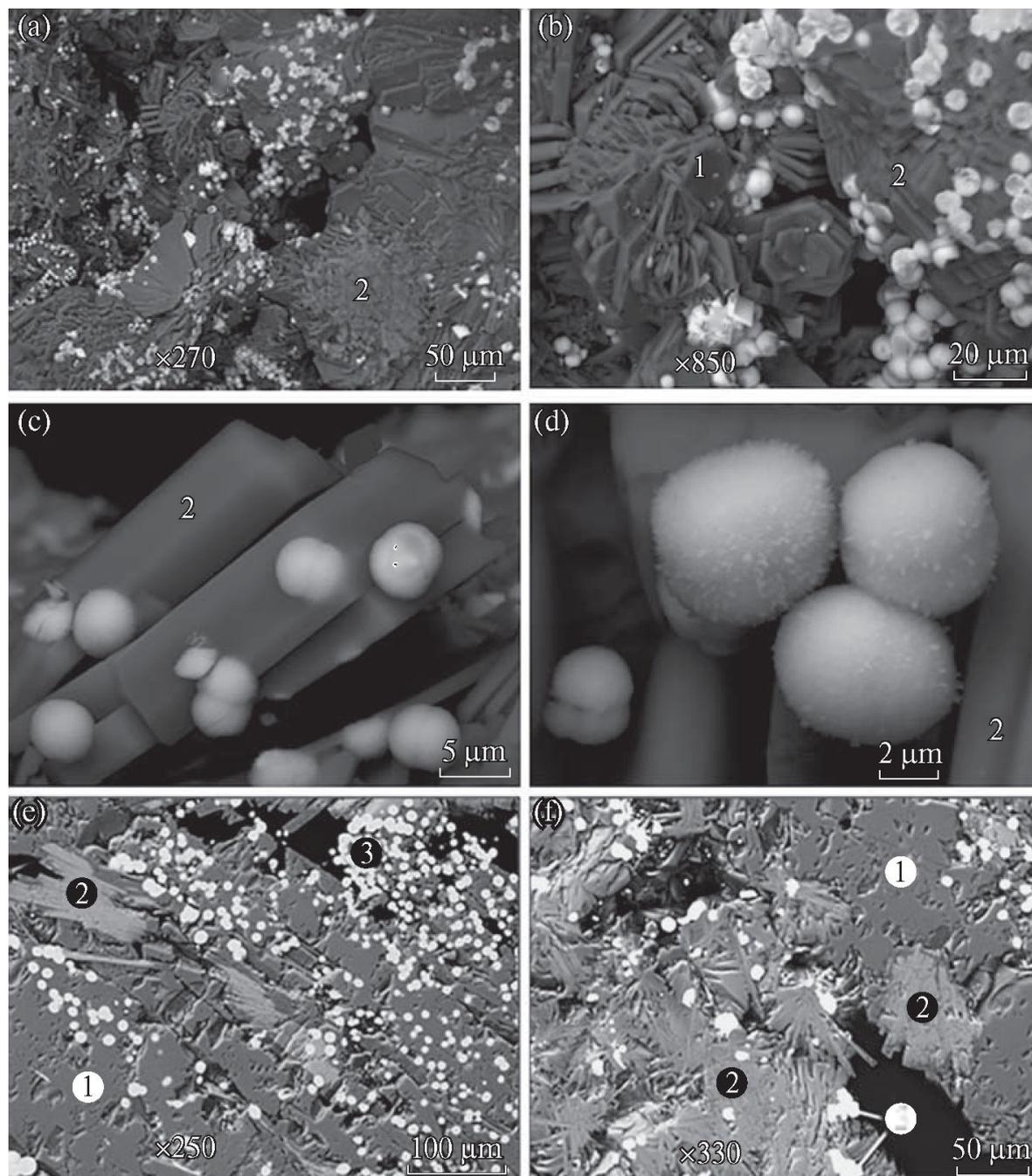


**Fig. 1.** SEM image of crystallized glass: （a‑d）surface and （e，f）cross section. (1) Na-Al-Fe-phosphate-1; (2) Na-Al-Fe-phosphate-2; （3）Sr-REE-U-phosphate; （4）hydrous Cs-U-phosphate. Pores are indicated in black. Scale marks: (e) 100, （a，f）50, （b）20, (c) 5, and (d) 2 μm [Malkovsky et al., 2022].
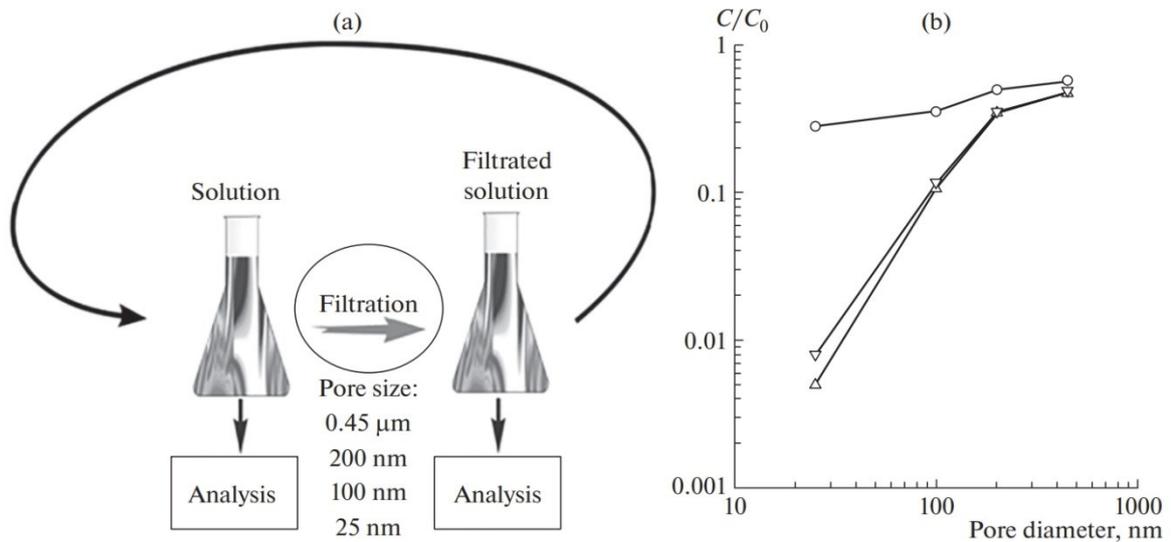
**Fig. 2.** (a) Analysis and (b) dependence of the U concentrations and actinide REE-simulants in the filtrate on the pore diameter. $C_0$ is the initial concentration in the solution before filtration [Malkovsky et al., 2022].
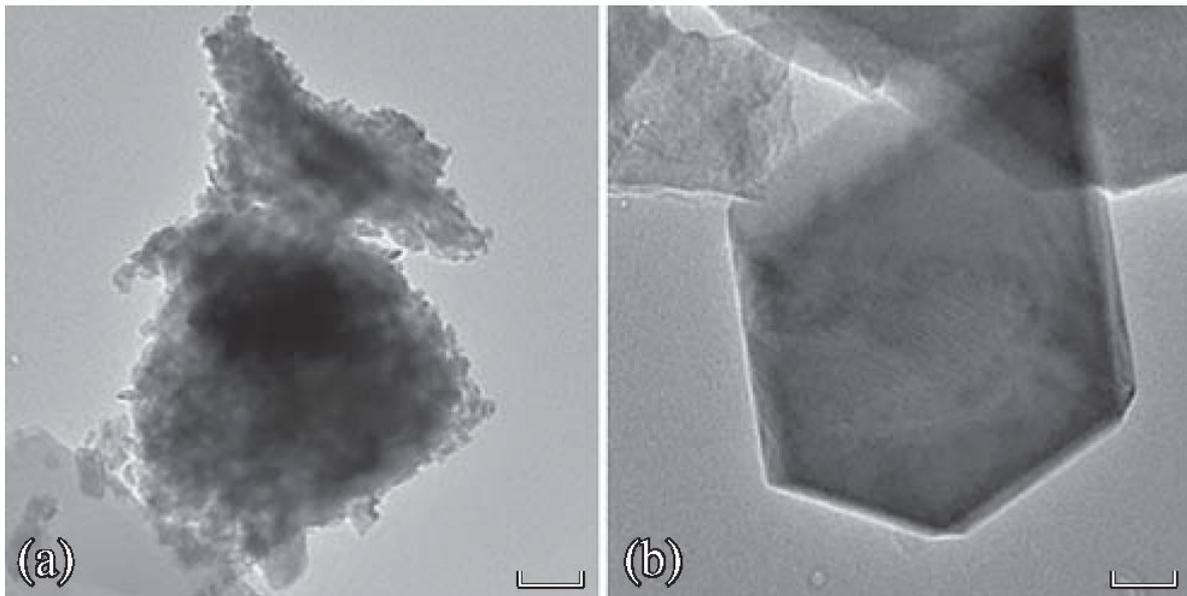


**Fig. 3.** The high-resolution transmission electron microscope image of colloid particles from the experimental solution with a crystallized sample of the Na-Al-P-glass matrix: (a) Sr-REE-U phosphate, (b) Na-Al-Fe phosphate. Scale marks are 100 nm [Malkovsky et al., 2022].

To assess the long-term safety of the underground vitrified HLW repository, it is necessary to study the UR-hosting rock potential for radionuclide retention. The colloid mobility in the underground medium depends on the water flow rate, and the mechanical colloid retention governed by the cross section of the filtration channel. Flow dynamics of the natural and technogenic fluids in the geological environment is controlled by the rock permeability. To estimate the possibility of mechanical retention for primary colloids using the special method developed by the authors [Malkovsky et al., 2022], the values of water permeability ($k_w$) and the Klinkenberg parameter ($b$) were determined on core samples from the wells drilled in the Itatsky and Kamenny sites of the Nizhnekansky massif. The

samples are collected from the depthes of 450-500 m corresponding to the probable locations of the HLW repository [Zharikov et al., 2014]. It was found that the rocks of the Nizhnekansky massif are mainly represented by gneisses and granite gneisses with very low values of water permeability ($10^{-18} - 10^{-20}$ m²) and porosity (0.14 – 0.95 %) (Fig. 4).
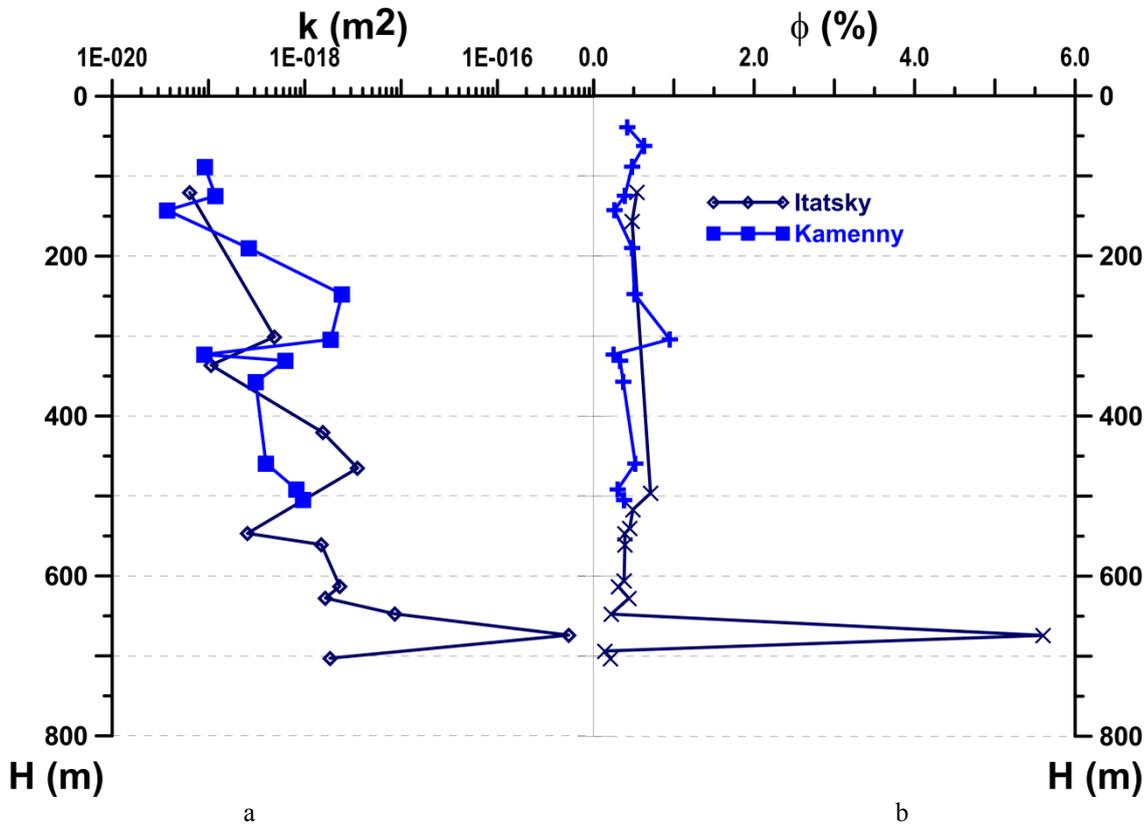


**Fig. 4.** Permeability (a) and porosity (b) of samples collected in the wells drilled at the Itatsky and Kamenny sites in the Nizhnekansky massif.

The Kozeny-Carman model was used for the theoretical analysis of fluid movement through filtration channels. The probability density function for channel cross-sectional diameters $d_c$ was approximated by the log-normal relation

$$f(d_c) = \frac{1}{d_c \sigma \sqrt{2\pi}} \exp\left[-\frac{(\ln d_c - L_c)^2}{2\sigma^2}\right]$$

where $\sigma$ and $L_c$ are the lognormal distribution parameters.

These parameters are related to $k_w$ and $b$ as follows:

$$\begin{cases} 2L_c + 6\sigma^2 = \ln(8k_w/\varphi), \\ L_c + \frac{7}{2}\sigma^2 = \ln\left(\frac{16}{3\pi\sqrt{2}}\frac{k_B T}{bd^2}\right). \end{cases} \quad (1)$$

Here, $\phi$ is the effective rock porosity (0.003), $k_B$ is the Boltzmann's constant, $T$ is the absolute temperature, and $d$ is the kinetic diameter of Ar molecule, 0.36 nm.

Taking into account the colloid size distribution (Figs. 2b, 3), the mass fraction of colloidal particles y retained by rocks is determined by the following relation:

$$\gamma \geq \frac{1}{2}\left\{\frac{C_0 - C_1}{C_0}\left[1 + \text{erf}\left(\frac{\ln D_1 - L_c}{\sigma\sqrt{2}}\right)\right] + \sum_{n=1}^{3}\frac{C_n - C_{n+1}}{C_0}\left[1 + \text{erf}\left(\frac{\ln D_{n+1} - L_c}{\sigma\sqrt{2}}\right)\right]\right\} \quad (2)$$

where $C_n$ is the concentration of Ce or Nd in the solution after the membrane with a pore diameter of $D_n$ ($n = 1, ..., 4$).

The system of equations (1) is linear relative to $L_c$ and c . Its solution was used to calculate value of γ using formula (2). According to the calculation results, more than 99% of the actinide colloidal fraction (which appears in the solution after contact with the crystallized Na-Al-P glass) will be mechanically retained in the samples studied. The cross sections of the fractures are strongly higher than for microcracks in the rock matrix. If such fractures controlling the effective permeability of the rock do not connect between each other, water flows between them along the undisturbed rock matrix. It means that the estimated colloid retention is also valid in this case. If some colloids occur in the fracture network with a high water conductivity, then the decrease in

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radionuclides concentration over time will mainly depend on the flow dilution with pure water and the radionuclide decay rate. The calculated colloid retention is the same for gneisses and granite gneisses, because it does not depend on the rock mineral composition, but it controlled by the structure of pores and microcracks in these rocks.

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