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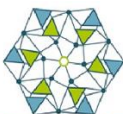
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GEOCHEMICAL BARRIERS FOR WASTEWATER PURIFICATION AND RECOVERY OF NONFERROUS METALS

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Geochemical barriers have been thoroughly examined as a means of combating the underground and surface water pollution. The materials can be either natural (soil, rock, peat, etc.) or artificial (mining and mineral processing waste). Compared to conventional methods relying on chemicals in wastewater treatment, geochemical barriers have the advantage of being less expensive, lacking negative side effects on natural water bodies, and having higher stability while working in continuous regime.

INTRODUCTION

Currently, a view of the earth's crust as a source of minerals is supplemented by the idea of the feasibility of both integrated development and conservation of mineral resources. Mineral resource conservation implies continuously maintaining the economic utility and environmental function thereof. [1]. This can be achieved by managing the entire range of natural and anthropogenic mineral resources, as well as controlling the scale and intensity of management by applying resource-reproducing management methods [2].

Mineral resource conservation requires management of waste as secondary incompletely recovered or prematurely retired resources, so that these remain accessible for extraction at the subsequent stages of mineral resource development [3].

The existing environmental and conservation policy for mining and mineral processing waste (MMPW) requires overburden dumps, concentration tailings, and slag dumps as anthropogenic deposits. For this purpose, by applying the natural mineral concentration patterns that manifest themselves in the formation of placer deposits, MMPW storage should be organized in such a way that commercial minerals become concentrated around the periphery of the storage facility. From there, these can be recovered by using, for example, combined physicochemical geotechnology [2, 3]. The processes of migration and deposition of elements inside the storage facility can be controlled through the use of geochemical barriers.

This brochure describes the applications of engineered geochemical barriers, including those made of MMPW and by-products of the processing industry of Murmansk Region in Russia.

1. GEOCHEMICAL BARRIERS

The concept of geochemical barriers was proposed by Professor A.I. Perelman [4]. Geochemical barriers are sections of the earth's crust, in which, over a short distance, there is a sharp decrease in the migration intensity of chemical elements and, as a result, in the concentration thereof. The phenomenon, presently referred to as a geochemical barrier, has attracted the attention of researchers for a long time, for example, when studying the genesis of minerals and ores and when interpreting the precipitation of elements in aqueous media [4-8]. However, it was considered in isolation, in the context of individual disciplines, such as mineralogy, lithology, soil science, ore deposits, etc. But similar processes of element concentration occur in soils, sea and ocean silts, weathering crusts, artesian aquifers, groundwater in fault zones, and other systems of the earth's crust. This allowed to identify common types of such processes, formulate the concept of a geochemical barrier, which is a fundamental geochemical concept [4].

The main characteristic of a barrier is an abrupt change in the geochemical environment and concentration of elements. There is a deep connection between the concepts of geochemical barrier and geochemical environment: a decrease in the space occupied by the environment leads to a qualitative change, transforming the environment into a barrier (and vice versa) [4].

Geochemical barriers host the ore bodies of most deposits; the concept of geochemical barrier is one of the methodological foundations for the study of geochemical anomalies and, therefore, is important for the development of geochemical prospecting methods. The study of barriers is also important in the prevention of environmental pollution, design of underground ore leaching systems, soil stabilization in civil engineering, and in other practical applications [5-8].

In the earth's crust, various geochemical processes become combined and interconnected. In this connection, complex barriers resulting from the combination of two or more interconnected geochemical processes are known to arise. Bilateral barriers also exist that are formed when different elements approach the barrier from two sides. At a bilateral barrier, the dissimilar association of chemical elements is precipitated. Barriers are classified into lateral, forming when water moves in a subhorizontal direction, for example, on a facies interface, and radial (vertical) barriers, forming as a result of vertical (upward or downward) migration of solutions in fault zones, weathering crusts, etc. [4-8]. Depending on the method of mass transfer, diffusion and infiltration barriers are distinguished.

Geochemical barriers are classified into mechanical, physicochemical, and biogeochemical. The simplest ones are mechanical barriers — areas of a sharp decrease in the intensity of mechanical migration [9]. Various mechanical differentiation products of the precipitates accumulate here. Where there is a sharp

decrease in the intensity of physicochemical migration, physical and chemical barriers form. These develop where temperature, pressure, redox, pH and other conditions change. Biogeochemical barriers arise as a result of a reduction in the intensity of biogenic migration (coal deposits, peat, concentration of elements in living organisms, etc.).

The most important properties of geochemical barriers include gradient and contrast [4, 8].

Barrier gradient G is the change in the geochemical indicators m (t, P, Eh, pH, etc.) in the migration direction of chemical elements.

$$G = \frac{dm}{dl} \text{ or } G = \frac{m_1 - m_2}{l},$$

where m_1 is the value of the given geochemical indicator before the barrier, m_2 is its value after the barrier, l is the width of the barrier.

The contrast of the barrier S is characterized by the ratio of the geochemical indicators in the migration direction before and after the barrier:

$$S = \frac{Cx_1}{Cx_2} = \frac{m_1}{m_2},$$

where Cx_1 and Cx_2 are concentrations of chemical elements before and after the barrier.

The accumulation rate of an element (for example, mineralization) increases with increasing contrast and gradient of the barrier.

As noted by Kraynov and Shvets, water migration of most chemical elements is essentially their passage through a series of homogeneous and heterogeneous barriers [9]. In this regard, two important points should be kept in mind:

- geochemical barriers form not only at the phase boundary (for example, solid-liquid interface), but also in a homogeneous medium with a change in: Eh-pH of the groundwater and shift of carbonate, sulfide and other equilibria (a); concentrations of the individual chemical components (b). Depending on the geochemical features of a given geochemical barrier, the concentrations of certain groups of chemical elements change and, importantly, the groundwater purifies itself from these elements and becomes involved in mineralization processes,

- geochemical barriers may form not only spontaneously in natural (or disturbed) environments controlling the chemical composition of groundwater, but also as a result of engineering activities during the operation of groundwater sources. This makes it possible to control the quality of groundwater [8, 9].

The main types of geochemical barriers, according to the classification proposed by Perelman, are summarized in Table 1.

Table 1. Types of concentration of elements on the biosphere's geochemical barriers from oxygen water [4]

Geochemical barrier	Strongly acidic, pH < 3.0	Acidic or slightly acidic, pH = 3-6.5	Neutral and slightly alkaline, pH = 6.5-8.5	Strongly alkaline, pH > 8.5
Oxygen **A**	**A1** Fe	**A2** Fe, Mn, Co	**A3** Fe, Mn, Co	**A4** Mn
Sulfide, hydrogen sulfide, etc. **B**	**B1** Tl, Pb, Cd, Bi, Sn	**B2** Tl, Fe, Co, Ni, Pb, Cu, Zn, Cd, Hg, U	**B3** T1,Cr, Mo, U, Se, Re, V	**B4** Cu, Ag, Zn, Cr, Mo, U, V, As
Gley **C**	**C1** Cu, U, Mo	**C2** Cu, U, Mo	**C3** Cu, Cr, U, Mo, Re, Se, V	**C4** Cu, Ag, Cr, Mo, U, Re, Se, V, As
Alkaline **D**	**D1** Mg, Ca, Sr, Ba, Ra, Mn, Fe, Co, Ni, Zn, Pb, Cd, Hg, Be, Al, Ga, Y, TR, Cr, P, As, U	**D2** Mg, Ca, Sr, Ba, Ra, Co, Ni, Cu, Zn, Pb, Cd, Hg, Be, U	**D3** -	**D4** -
Acidic **E**	**E1** -	**E2** -	**E3** Si, Mo	**E4** Cu, Zn
Evaporative **F**	**Fl** Na, K, Rb, Tl, Cl, Mg, S, Ca, Sr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Cd, Al, Mo, U	**F2**	**F3** Li, Na, K, Rb, Tl, N, B, F, Cl, Br, I, Mg, Ca, S, Zn, Mo, U, V, Se	**F4** Li, Na, K, Rb, Tl, N, B, F, Cl, Br, I, Cu, Zn, Mo, U, Se
Sorption **G**	**G1** Al, Sc, Ga, Si, Ge, P, V, As	**G2** Si, Ba, Zn, F, Cd, S, Ni, Co, Pb, Cu, U, P, Cl, Br, P, V, Mo, As	**G3** Li, Na, K, Rb, Cs, Tl, Zn, Cl, Br, I, B, F, S, P, V, Mo, As	**G4** Al, Sc, Ga, Si, Ge, P, V, As
Thermodynamic **H**	**H1** _	**H2** Mg, Ca, Ba, Mn, Zn, Pb, Co, Ni	**H3** Li, Mg, Ca, Sr, Ba, Zn, Pb	**H4** Zn, Cu, U
Electromagnetic **N**	Anions and cations of metals			
Radiation chemical **R**	Anions and cations of chemical elements			

2. CLASSIFICATION OF GEOCHEMICAL BARRIERS ACCORDING TO ORIGIN, FORMATION PROCESS, METHOD AND AREA OF APPLICATION

Based on the results of many years of research and existing literature, we have developed a classification of geochemical barriers according to origin, formation process, method and area of application (Fig. 1). Unaltered minerals and rocks, as well as artificial mixtures of chemically active minerals and rocks, by-products of chemical and metallurgical processing of ores and concentrates were examined as geochemical barrier materials [10].
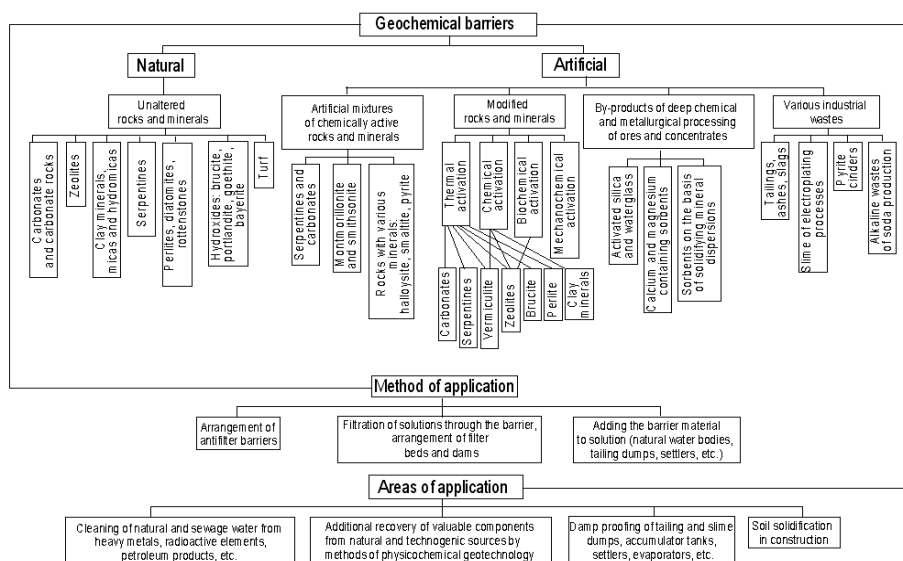

Figure 1. Classification of geochemical barriers [10].

As studies by both Russian and international researchers demonstrate, the following materials can be used in engineered geochemical barriers [2, 10-16, etc.]:

- mining industry waste (overburden, tailings) containing chemically active minerals,

- mixtures of reactive or modified minerals,

- by-products and waste of deep chemical and metallurgical processing of ores and concentrates.

Some studies [10-22 etc..] examine the application methods of geochemical barriers:

- anti-filtration screens,

- filtration of solutions through a barrier with the deposition of pollutants,
- adding the barrier material to a solution (natural water bodies, tailings storage facilities, sedimentation tanks, etc.).

Applications of artificial geochemical barriers, in addition to the purification of natural and waste water from heavy metals, radioactive elements, and oil products, include [2, 10-22 etc.]:
- further recovery of valuable components from natural and anthropogenic mineral feeds using methods of physical and chemical geotechnology,
- waterproofing of tailings and sludge storage facilities, storage tanks, sedimentation tanks, etc.,
- stabilization of soil in civil engineering.

The establishment of engineered geochemical barriers in polluted tundra and north-taiga landscapes (e.g. oil and gas fields, mines, concentrator plants and smelters, etc.) is of particularly high environmental relevance, since Arctic ecosystems are easily destabilized and then recover very slowly [23].

Using MMPW has the potential to reduce environmental cleanup costs.

3. USING GEOCHEMICAL BARRIERS FOR WATERPROOFING OF TAILINGS AND SLUDGE STORAGE FACILITIES, STORAGE TANKS, AND SEDIMENTATION TANKS

To prevent the penetration of toxic and radioactive waste into natural water sources and to protect the environment on and around surface waste storage sites, various types of barriers with anti-filtering and anti-migration properties are applied [24-26]. One of the alternatives is to install an impervious barrier of a polymer gel that forms directly in the pore space of the rock by pumping a liquid polymer, which then turns into a gel [17]. The injected compound is close in its viscosity and density to water, which contributes to its spreading in the rock mass [27].

In practical large-scale applications as a protective curtain compound, aluminosilicate gels are considered promising and can be produced from acid decomposition products of non-feldspar nepheline rocks belonging to the iolytes-urtites group. This rock group is common in the deposits of Russia's Kola Peninsula and Kemerovo Region, where the rocks are mined as a source of alumina. Mining and chemical industry produces waste containing nepheline, which can be processed into barrier compounds. The sand filtration coefficients in the aeration zone and unconfined aquifer reduced by a factor of 200 as a result of installing curtains using silica-alumina gel at the tailings storage facility on the Siberian Chemical Plant industrial site [17].

An integral part of the ore mining process is the formation of mine, quarry, and underspoil water containing heavy metal ions that pollute surface and groundwater. At the Kul-Yurt-Tau deposit in Bashkiria, to contain the underspoil wastewater, a liquid glass-based barrier was applied. As a result of the interaction of the liquid glass with the underspoil water containing free sulfuric acid, a silicic acid gel formed [28].

Kola nepheline concentrate, recovered from the apatite-nepheline ore concentration tailings on the "Apatit" JSC industrial site, is used for the production of alumina, soda, potash, and cement. Small quantities (~200-300 thousand tons) of nepheline concentrate are consumed by the glass and ceramic industries [18].

Using nepheline concentrate for waterproofing of engineered structures and neutralizing acidic effluents is a promising application area. This application is based on the special properties of nepheline — its ability to readily decompose in weak acids, followed by the formation of sols and gels, and then of crystalline hydrates [19].

The possibility of converting nepheline into an ash-like state with subsequent transition to a gel-like substance can be used for obtaining waterproofing compounds with desired properties. The main feature of such waterproofing compounds is that they can within a controllable period of time (3-48 hours) remain in a state close to a mineralized solution and demonstrate high fluidity in porous and fractured soils and rocks. After a predetermined period, such compounds turn into a gel completely sealing all pores and cracks in the soil or rock. These properties of nepheline open up the prospect of designing a process for the production of gel-like waterproofing compounds, which can be successfully used in the waterproofing of oil and gas wells and storage facilities, tailings storage facilities, open-pit mines in the permafrost zone, hydroelectric dams, etc. In addition, the ability of dissolved nepheline to transform into crystalline hydrates can be useful in the disposal of the chemical industry's acidic effluents with the production of coagulants [29].

In the development of a gel-based process for the decomposition of nepheline-containing materials, various mineral acids are used, which is explained by the features and needs of a given industry. For example, in the oil industry, hydrochloric acid is most often used in drilling operations. For the solidification of hazardous brines accumulated in underground tanks, it is preferable to use sulfuric acid, or phosphoric acid where particularly reliable waterproofing is required. Processing of acidic effluents often either does not require additional acidification or is carried out by adding small amounts of sulfuric acid. It should be noted that the main distinguishing feature of nepheline is its ability to easily interact even with weak acids. The high reactivity of nepheline with respect to acids is due to the features of its crystalline structure, mineral and chemical composition [30].

A wide range of acids can be used to decompose nepheline concentrate. Hydrochloric acid is widely used in gas and oil production; therefore, it can be used in these industries to obtain sealing gel formulations based on nepheline concentrate.

However, in multiple situations, for environmental reasons, its scope of application is severely limited due to the fact that hydrochloric acid, as well as nitric acid, in reaction with nepheline releases large amounts of volatile and toxic substances [30].

Sulfuric acid does not form volatile products when interacting with nepheline. Concentrations of 5-15% allows to keep in the liquid phase in the form of a stable sol the silicic acid formed during decomposition. Using a stronger acid leads to a rapid precipitation of silica gel and gelation of the system. At a H_2SO_4 concentration of more than 50%, silica immediately coagulates and precipitates [30].

Therefore, depending on the required range of nepheline-based products, it is possible by varying the concentration of H_2SO_4 to design several sulfuric processing options for nepheline [30].

In some cases, it may be appropriate to use phosphoric or oxalic acid. These do not produce volatile toxic products. Moreover, phosphoric acid-based gels are much stronger and can be used for the most critical applications [30].

4. USING GEOCHEMICAL BARRIERS FOR WASTEWATER AND NATURAL WATER TREATMENT

A highly important and urgent environmental problem in the mining industry is wastewater treatment [31]. Due to the wide range of ionic compositions, high concentration of suspended solids and organic compounds, including petroleum products, as well as large quantities of wastewater, the implementation of treatment processes — typically, a combination of these — involves significant capital and operating costs [31-37].

Among the physicochemical bulk treatment methods for wastewater, the use of geochemical barriers is of particular importance. Geochemical barriers may form not only spontaneously in natural (or disturbed) environments, but also as a result of engineering activities. Numerous studies are focused on the development of methods for protecting groundwater and surface water from pollution using geochemical barriers [10-12, 14-16, 20, 21].

Both engineered and natural materials can be used in geochemical barriers. Among the variety of commercially available engineered sorbents, only few are suitable for water treatment (ionite resins, artificial zeolites, and activated carbons). The advantages of engineered materials include high sorption capacity, constant structure, stable chemistry and, therefore, stable process properties. Widespread adoption of such materials for the treatment of drainage and groundwater is hindered by limited availability and high cost. The treatment cost of 1 m^3 of water when using engineered sorbents is significantly higher than when using natural sorbents or industrial waste [21].

Natural sorbents, whose cost is by an order of magnitude less than that of their engineered counterparts, include zeolite, chert (an amorphous variety of silica), diatomite, tripolite, gaize, active clay, peat, asbestos, expanded vermiculite and perlite [38, 39]. Despite the disadvantages of these materials — such as structural defects, inconsistent chemistry, lower sorption capacity compared to engineered sorbents — they are often more economically justified given the low cost. A significant drawback of most natural zeolites is the extremely small pore size (up to $4 \cdot 10^{-10}$ m). Therefore, their principal applications are dehydration and purification of gases, purification of small amounts of wastewater, and applications as molecular sieves [21].

Another effective natural sorbent is chert — an amorphous variety of silica. Presently, silicon-carbonate sorbents are the most affordable, as these are widely extracted for the building materials industry [21].

In the late 1990s, high sorption properties with respect to heavy metal ions were discovered in brucite $Mg(OH)_2$ — a hydroxide mineral. Under comparable conditions, the sorption capacity of brucite is tens and hundreds of times greater than that of known natural sorbents — zeolites, bentonite clays, schungite, peat, etc. In the dynamic mode, brucite is capable of purifying aqueous solutions with a complex multicomponent composition to the MPC standards [40].

Due to the selective increase in the sorption capacity of brucite as a result of thermal treatment, it becomes possible to increase the recovery of those metals that are difficult to recover from process solutions with a natural sorbent. Thermal treatment of brucite and sorption in the presence of an ultrasonic field makes it possible to improve by an order of magnitude the sorption capacity and the kinetics of mass transfer reactions. This makes it possible to use natural sorbents in process circuits instead of expensive synthetic ion exchangers for the recovery of metals from aqueous media and process solutions [40].

Clays are widely used in multiple industries, including for the recovery of heavy metal ions [41–45] and radionuclides [46–50], both from process solutions and from wastewater. Clays are characterized by high selectivity with respect to the metal being recovered, which allows the process to be carried out with a short duration of the process cycle, relatively low energy inputs, and feed rates of chemicals.
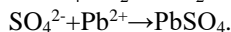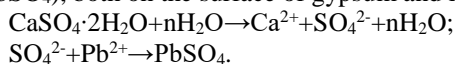
In the Republic of North Ossetia - Alania, Russia, deposits of clay minerals known as irlites are found [51]. Unlike the varieties of clay minerals widely used as sorbents for the recovery of metal ions from aqueous solutions and consisting mainly of minerals of the same group, irlites have a more complex mineralogy, which in most cases improves their sorption properties. The main minerals making up irlites are hydromica, kaolinite, montmorillonite, glauconite, bicarbonates, organic matter, etc. Irlites have not only sorption, but also ion-exchange, coagulation, and flocculation properties [51].

Another promising clay mineral is beidellite, whose adsorption capacity is in the range of 83.3–86.9 mg/g for lead and 42–45.6 mg/g for cadmium [52].

Water can be effectively purified using carbonate-containing tripolites. Carbonate tripolites containing 20-30% or more of calcite are highly effective sorbents of heavy and non-ferrous metal ions, radionuclides of Sr, Cs [53].

In one study, unfired and fired (at a temperature of 900 ºC for 2 hours) oyster shells mainly composed of calcite were used to stabilize arsenic-containing tailings [54]. A sharp decrease in arsenic concentrations was observed only with the use of fired oyster shells (25% wt) after 28 days of residence. This is connected with the high concentration of active calcium, which forms insoluble Ca - As compounds. Moon et al. [55] report that the leachability of arsenic drops with an increase in the Ca/As molar ratio.

In another study, the efficiency of sorption of lead ions by gypsum ($CaSO_4 \cdot 2H_2O$) was investigated [56]. It was shown that the gypsum surface plays an important role in reducing lead concentrations in contaminated water. Sorption mostly occurs as a result of the rapid dissolution of gypsum and the simultaneous formation of anglesite ($PbSO_4$), both on the surface of gypsum and in the solution:

$CaSO_4 \cdot 2H_2O + nH_2O \rightarrow Ca^{2+} + SO_4^{2-} + nH_2O$;

$SO_4^{2-} + Pb^{2+} \rightarrow PbSO_4$.

The sorption capacity of gypsum is limited by its solubility product, and in general, the sorption rate depends on the growth rate of the phase of the newly formed product and the dissolution rate of the gypsum. Gypsum can be a good sorbent for Pb ions in environments where lead reaches toxic concentrations. In addition, there is a natural decrease in Pb concentrations, probably related to the formation of anglesite, especially where, as a result of continuous oxidation of sulfides, acid mine water contains SO_4^{2-} anions [56].

Using industrial waste as a sorbent is a very promising area. Industrial waste includes ash, slag, coke fines, sawdust, rice husks, processed used rubber tires, etc. [57-60]. The cost is low, but applications depend on the presence in the region of the respective processing industries. For example, sorbents exist based on the waste from the pulp and wood-based chemical industry (coniferous bark can be used as an affordable sorbent for purifying water from chromium and nickel ions). Slime-based sorbents are known to purify water from zinc and cobalt [61].

Water treatment waste of thermal power plants can effectively purify water from a number of heavy metal ions. The waste mainly consists of calcium and magnesium carbonates, characterized by homogeneity, fine particle size, relatively consistent chemistry, chemical and radiation safety. In terms of deposition rate, metals can be ordered as follows: $Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. The main — and in the case of iron (III) and chromium (III) ions, practically the only — process that occurs during the precipitation of the studied ions from solutions is the formation of poorly soluble aquahydroxocomplexes due to the mutual intensification of hydrolysis. Mixed hydroxocarbonate phases, solid solutions, etc. can also

form. In addition, metal ions can be adsorbed on the surface of the undissolved reagent and on newly formed particles [62].

To recover heavy metals, affordable activated carbons (AC) obtained by processing rice husks, coconuts, bituminous coal, peat moss, sawdust, or solid industrial waste can be used. Low-temperature carbonization followed by high-temperature co-activation of the waste mixture allows to obtain ACs whose adsorption capacity with respect to Cr (III) and Cr (IV) significantly exceeds that of the commercially available Norit and Merck ACs; such adsorbents can be used to recover copper and other heavy metals from multicomponent aqueous solutions, including process ones. Waste-based active carbons selectively absorb palladium (II) from acidic multicomponent process solutions. Dynamic adsorption reduces the excessive content of associated metals from 20-fold in the solution to 3-fold on the adsorbent [63].

One of the promising areas for the development of sorbents based on natural materials is the use of wood waste, in particular sawdust. However, the poor sorption properties of natural materials hinder the direct use of these as sorbents. It is possible to increase the sorption capacity by applying bentonite clay previously activated with a 5% sodium carbonate solution onto sawdust. As sawdust modifiers, it is preferable to use a 0.5 M HCl solution, since this gives the greatest increase in the mechanical and sorption properties of the material. When sawdust is modified, the sorption capacity with respect to heavy metal ions increases by a factor of 1.5 on average. A sorbent based on soda-activated bentonite clay and sawdust effectively removes copper ions, while adding modified sawdust increases the sorption capacity by a factor of 3.5 on average [64].

A number of studies summarize the research at Perm State University into the applications of both existing natural and engineered geochemical barriers [5-8, 65].

In particular, to neutralize acidic (pH = 2-4) highly mineralized sulfate mine drainage of the Kizelovsky Coal Basin in Perm Region, Russia, characterized by elevated levels of iron, aluminum, and heavy metals, it was proposed to use the alkaline waste of Soda Plant in Berezniki (alkaline barrier D). The pH value of the mine drainage can be increased from 2.5-2.7 to 6.0-6.5. Simultaneously, its total iron content drops from 240 to 0.5 mg/l. Aluminum content after the experiment was below the sensitivity limit of the test (from an initial concentration of 98 mg/l). Sulfate content dropped by 300 mg/l. The reagent can be added directly to the drainage system without the construction of a conventional treatment plant [65].

To reduce groundwater pollution on the mine dumps sites of coal mines, Blinov and Maksimovich proposed the use of barium compounds (hydroxide, chloride), as well as crushed carbonate rock placed in trenches in the dump runoff zone (alkaline barrier D). At the engineered geochemical barrier, sulfates get bound into barium sulfate — barite. Barite formation is practically independent of the pH value of the

environment; barite is stable under exogenous conditions and is not toxic. Field experiments produced encouraging results [65].

To neutralize acid mine drainage at the Kizelovsky Coal Basin, Maksimovich used as a reagent limestone screenings. To purify the groundwater in the study area, limestone was placed in a trench perpendicular to the flow, which was excavated down to impervious dense clay at a depth of 1–1.2 m. Upstream and downstream of the trench, pits were excavated to monitor the groundwater chemistry (Fig. 2). As a result of the experiments, the filtration properties of the soils were modified. This is due to the intensive precipitation of iron and aluminum hydroxides, as well as some sulfates and hydrosulfates. According to X-ray diffraction analysis, the loam near the contact zone contained goethite (7–32%), jarosite (up to 41%), gypsum (up to 8%), and hematite (up to 4%). The resulting precipitate fills the pore space and makes filtration difficult [5].
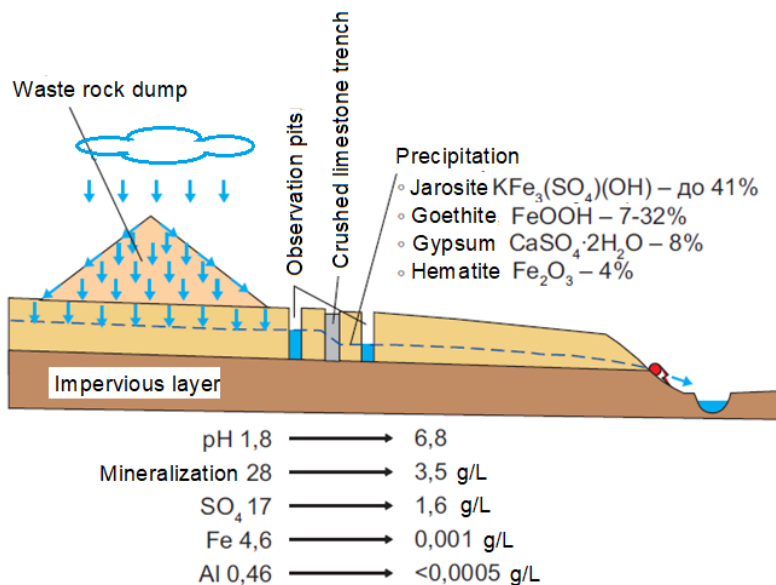

Figure 2. Experimental layout of the waste rock dump site
at the Kizelovsky Coal Basin [5].

The high intensity of groundwater and surface water contamination on the gas treatment waste storage facility site at the Pashi Smelter and Cement Plant, Perm Region, is due to the geology and hydrogeology of the storage area [65]. The waste is a pulp (liquid:solid ratio = 9:1). A study of the pulp composition showed a high mineralization of the liquid phase — 34–42 g/l, and alkaline pH (pH = 8.9–9.4).

Hydrocarbonate (up to 18.2 g/l) and carbonate ions (up to 5.2 g/l), chloride ion (up to 7.8 g/l), as well as sodium and potassium ions (up to 14 g/l) predominate in the macrocomponent composition of the pulp. The microcomponent composition is characterized by high concentrations of Cu, Cd, Pb, Zn, Ni, Mo, As, Ti, Be. Large quantities of organic substances are present: saturated hydrocarbons of higher fractions, aromatic hydrocarbons and their derivatives (polyphenols). Dissolved organic substances form stable complexes with metals that are mobile in an alkaline environment. To protect the groundwater and surface water from pollution on the new waste storage site, an integrated, multi-layer screen barrier at the base of the storage facility was proposed [5, 65]. The screen has three layers. The top layer, 0.1 m thick, is local clay with the addition of gypsum. This leads to a decrease in the alkalinity of the filtered solution, as well as hydrolysis and precipitation of a share of the heavy metals (acid barrier E). The middle layer, 0.1 m thick, is a mixture of peat and pyrite cinder. The main function of this layer is to intercept contaminants by binding metals into sulfides under anaerobic reducing conditions (sulfide reducing barrier B). The bottom layer is composed of local clays and acts as an additional sorption screen (sorption barrier G). The role of the top and bottom layers of clay in the screen structure is also to reduce and disperse the filtration load across the entire storage area and to preserve the middle layer of FeS and peat in order to create anaerobic reducing conditions in it. The lower thickness of the top layer of clay is responsible for a filtration delay of the solutions in the middle layer. An engineered geochemical barrier of this design does not prevent the migration of iron into groundwater. However, given that the solutions filtrate into karst limestones, characterized by flushing and an oxidizing environment, oxidation of dissolved Fe^{2+} and precipitation as amorphous $Fe(OH)_3$ is assumed. Iron hydroxides act as an additional adsorbent of Hg and hydroxyanions As, Se, Ti, V, Mo, as well as anionic hydrocomplexes Be and Zn. This method protects the groundwater from the indicated pollutants over the entire service life of the site [65].

In another paper, an insulating barrier for tailings based on the sediment of municipal sewage treatment plants modified by anaerobic sulfate-reducing bacteria is described [66]. Sewage sediment contains, as a rule, significant amounts of organic compounds that can be consumed by sulfate-reducing bacteria and contribute to their reproduction and growth. When filtering acidic water through the barrier, pollutants such as sulfates and heavy metals precipitate as hydroxides and carbonates. Sulfates are converted into hydrogen sulfide, and then metal sulfides form. Sulfate-reducing bacteria play an important role in reducing heavy metal concentrations. Heavy metal concentration reduction performance was: 97.8% (Zn) and 93.4% (Cd).

Hakkou et al. used alkaline phosphorus waste to neutralize acid mine drainage on the abandoned Kettara mine site in Morocco [67]. Alkaline phosphorus waste is classified into two types — overburden and concentration tailings — and contains

minerals such as calcite (40.7 and 25.5%), dolomite (25.2 and 23%), apatite (25.9 and 48.1%), quartz (8.2 and 3.4%). Both types of waste can be used to neutralize acidic water. Adding alkaline phosphorus waste (15% wt) allows to effectively neutralize acid mine drainage. In addition, the concentration of metals in the filtrate is significantly reduced.

In New Zealand, acidic mine drainage at Stockton opencast coal mine was neutralized by adding limestone. As a result of the interaction between heavy precipitation and pyritic rocks, acidic water is formed with an elevated concentration of Al and Fe [68]. The pH value was adjusted by continuously adding an alkaline suspension using an automatic neutralization system. The suspension was based on ultrafine lime flour (more than 90% of the particles -100 μm). Fe (III) ions dissolved in the feed precipitated as amorphous Fe hydroxide, facilitating the deposition of fine solid particles. The remaining dissolved Fe (II) ions (<5 mg/l) were slowly oxidized to Fe (III) (from several hours to days). Dissolved Al ions gradually precipitated and formed a fine-grained and amorphous Al hydroxide precipitate, which accumulated in the channel. Precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) was observed throughout the limestone mixing zone, and this contributed to a reduction in the concentration of SO_4^{2-} by 30%. Zinc was sorbed on the co-precipitated iron hydroxide, however, the concentration of the dissolved Ni remained unchanged throughout the neutralization process. The measures taken made it possible to reduce pyrite oxidation and to adjust the pH of the acidic water from 2.9 to 6.9 [68].

To reduce the concentration of metals and sulfates and the acidity of the drainage water at the tailings storage facility of a copper-zinc mine (Ore Knob Mine) in the western North Carolina, it was proposed to use glycerin waste, a by-product of biodiesel production [69]. In the aeration zone, pyrrhotite and associated sulfide minerals are oxidized and quickly penetrate the surface water. The annual input of pollutants is estimated at 220 kg of acid, 100 kg Fe, 370 kg of SO_4^{2-}, 0.9 kg of Mn, 2.4 kg of Al, and 0.28 kg of Zn. Dissolved glycerin waste is transported with rainwater seepage deep into the tailings storage facility, neutralizing acidic water. Soluble organic compounds consume oxygen and act as an electron donor to sulfate-reducing bacteria. The application of glycerin waste to the surface effectively reduces the concentration of pollutants — Fe by 83%, Al by 97%, Mn by 84%, Cu by 67% — while the acidity of the wastewater is reduced by an average of 86% [69].

Adsorption on iron-containing minerals is a well-known method of immobilizing heavy and non-ferrous metals in contaminated water and soil. For instance, drainage silt collected from the Hambeak Mine in South Korea was used in a study of sorption of As (III) and As (V) [70]. According to XRD data, the silt was an amorphous material with minor goethite reflexes. The optimum pH for adsorption is 7.0 and the maximum possible adsorption was 58.5 mg/g (As III) and 19.7 mg/g (As V), respectively. Adding drainage silt to arsenic contaminated soil at a mass ratio of 0.5

and 3% allowed to reduce the leaching of As from the soil by 12.7 (As III) and 23.5 (As V) mg/l, respectively.

In addition to natural iron-containing minerals, synthesized samples are also used in wastewater treatment; studies are known where ferrihydrites are synthesized under laboratory conditions [71]. Ferrihydrite $Fe_{10}O_{14}(OH)$ is one of many iron oxides and hydroxides. This mineral is used as a sorbent due to its extremely high surface area, sorption capacity, and high content of reactive groups on the surface. The sorption capacity of ferrihydrite with respect to copper ions, depending on the synthesis conditions, varies in the range from 8.74 to 14.39 mg/g [71].

Modern technology make it possible to achieve almost any desired degree of wastewater purification, and the economic performance of the respective methods comes to the fore [11]. In this regard, geochemical barriers based on affordable materials, natural minerals, and mining waste are considered an economically viable alternative.

5. GEOCHEMICAL BARRIERS IN RESOURCE-REPRODUCING GEOTECHNOLOGY

In this section, we first briefly discuss a number of fundamental problems faced by Russia's mining industry [2, 72]:

- depletion of many high-grade deposits,
- an increase in the processing costs of low-grade feeds and an increase in the amount of MMPW generated,
- weaker interest in integrated mineral processing technologies, etc.

It is obvious that a further increase in the extraction of minerals will lead to an even more significant increase in the amount of MMPW and, as a result, to stronger negative anthropogenic impacts of the mining industry on the surrounding natural environment [72].

The current situation mandates the development and implementation of a fundamentally new concept for the development of mineral resources.

One of the principles of sustainable formation of anthropogenic deposits is taking into account a number of factors related to preserving the site, creating the necessary conditions for its subsequent development, and the rational use of the host rocks. This principle can be achieved through the following [73]:

- purposeful (usually selective) formation of the deposit, taking into account the different nature of changes in the properties of rocks during storage (deterioration of properties, unchanged properties, improvement of properties) and interactions between these,
- designing, if necessary, special containers for storing rocks, shielding coatings and curtains to protect the rock from environmental impacts and interactions,

- placement of rocks of different grade and recording of information about quantities and properties thereof and designing for convenient access in the development phase of the anthropogenic deposit,

- providing priority access to rocks that degrade during storage and rocks with a relatively high grade, etc.

Of particular interest are the possibilities of purposefully improving the properties of some of the stored rocks by creating active interaction systems of the different rock types that make up the anthropogenic deposit.

Compounds that are part of the rocks and are stable in the natural environment of the deposit can be oxidized, reduced, etc., under storage, forming water-soluble compounds migrating within the deposit. Purposeful improvement of the properties of some of the rocks of an anthropogenic deposit is possible by creating during its formation zones of active migration of dissolved compounds of valuable components and corresponding engineered geochemical barriers that cause a sharp change in the geochemical conditions, to form localized concentration zones of valuable components [73].

This principle, in particular, underlies in-situ concentration methods. These include selective stacking of different-grade rock mass containing valuable components with the establishment of engineered geochemical barriers and its further processing during storage. During storage, the dissolution, migration, and deposition of valuable components occurs in the barrier zone of action. This gives an increased concentration of components in a limited (localized) volume and makes its further processing economically viable [74].

As noted by Vorobyov, the most fundamental moment is the establishment of a geochemical barrier in the rock mass of the anthropogenic deposit for the deposition and concentration of valuable components. When implementing resource-reproducing technologies, it is necessary to take into account that the form and type of geochemical compounds play the most important role in the redistribution of valuable components. Anthropogenic deposition of most metals in the rock mass is possible at such barriers as hydrodynamic, sorption, oxidative, reducing, acidic, alkaline, chemical, evaporative [2].

The hydrodynamic barrier is effective in the redistribution of both poorly soluble noble (Au, Pt) and readily soluble (Cu, U, Zn, Pb, etc.) valuable minerals, even in a chemically identical environment. In the latter case, controlled explosions are used to create heterogeneity, providing a permeable medium in the leach zone of metal-bearing rocks. In addition to a sharp change in the intensity of migration of the metal-bearing water, the resulting hydrodynamic barrier is also characterized by a change in the pH and Eh of the solution. In this case, a pronounced correlation arises between the levels of dynamic contraction of flows and the content of the valuable minerals [2, 74].

Some implementation case studies of resource-reproducing technologies are given in [2 73, 74]. Vorobyov considers two fundamental options:

- purposeful creation (or strengthening of existing) in the rock mass of anthropogenic geochemical barriers (for example, by injecting through wells solutions containing specific substances, as well as bacteria and microorganisms),

- artificial mixing of solutions previously passed through the zones of the deposit with dramatically different properties and grades [2].

The second option is preferred for mineral deposits with a complex structure. For example, in the presence of interbedded rocks contrasting in composition (and, consequently, in geochemical properties) — sulfides and carbonates, acidic and basic gneisses and schists, graphite- and pyrite-bearing schists, etc.

When solutions of active agents pass through U-Pb-containing (0.005%) leucocratic carbon-free rocks, they become saturated with uranium and lead. The penetration of these (metal-bearing by this moment) solutions into black carbon-containing shales (or when mixed with solutions passing through them) leads to the deposition of anthropogenic pitchblende (0.08%) and galena (1.2%) ores. Moreover, zonal distribution of the different forms of metals is common: PbS is confined to the central part of anthropogenic ores, then a zone with an isomorphic Pb grade of 1 to 10% wt follows, then with a grade of 10 to 20%, and >20% in the periphery [2].

If acid mine drainage penetrates carbonate rocks or is directly mixed with alkaline water, metals are precipitated locally. For example, the waters of the South vein of the Arkhon Mine (Republic of North Ossetia-Alania, Russia) at a pH of 2 contain, in addition to 3.5-5 mg/l of zinc, some indium and cadmium. Indium represented by sulfide In_2S_3 during oxidation transforms into In_2O_3 or $In(OH)_3$. Germanium, when exposed to hydrochloric acid solutions, transforms into germanic acids GeO_2 and germanium oxychlorides $GeOCl_3$ and $GeOCl_2$. After mixing with the waters of the lower horizons of the deposit, the pH rises to 5.5-6, and indium and cadmium precipitate. A study of the mine workings at the Sadon field showed that such processes are widespread and are in different stages [2].

Carbonates are most widely used in geochemical barriers.

For instance, in a study, it was shown that copper precipitation from sulfate solutions of natural calcium carbonates occurs in the form of basic sulfates [75]. Due to the low solubility of calcite ($6.5 \cdot 10^{-2}$ g/l) CO_3^{2-} concentration in the solution is insufficient to precipitate copper in the form of malachite or its analogues. The solubility of the hydrocarbonate formed as a result of hydrolysis is much higher (up to 1.66 g/l at 20 °C), however, is limited by the low rate of the primary reaction and only leads to an increase in the pH at the grain surface of the initial mineral. This is sufficient for the rapid hydrolysis of copper with the formation of hydroxide and subsequent co-precipitation with copper sulfate in the form of brochantite ($CuSO_4 \cdot 3Cu(OH)_2$) Abundant gypsum is formed and CO_2 is removed since the pH of the copper sulfate solution is approximately 5. Formation during storage of hydrated forms (poznyakite $CuSO_4 \cdot 3Cu (OH)_2 \cdot H_2O$) does not contradict the proposed

mechanism. The lower activity of marbled and especially dolomitic limestone leads to the incorporation of the gypsum molecule in the precipitate structure and the formation of devilline (CaSO$_4$·CuSO$_4$·3Cu (OH)$_2$·H$_2$O). For all the variety of chemistry of copper precipitation, the final stage in most cases is devilline.

Using this mechanism for the precipitation of copper, in addition to the low cost of the precipitator, has several process advantages. Creating an artificial geochemical carbonate barrier around the perimeter of the pollution source or to intercept the main drainage flows on the ground or in the groundwater allows to avoid the construction of a copper recovery plant and significantly reduce capital costs. It becomes possible to mine unprepared ore piles and tailings storage facilities, including low-grade ore stockpiles. The barrier material is periodically removed and sent for processing. The long-term effect of the precipitant eliminates the problem of low metal grade of the pregnant solution. With the right selection of material and its replacement frequency, it is possible to produce a copper concentrate suitable for long-term storage and processing at an existing smelter with no concentration costs. Final solutions contain less than 0.01 mg/l of copper, less than the existing sanitary standards, which allows in some cases to dump the spent solutions on the ground without any environmental risk [75].

The studied copper precipitation mechanism can also be used to form high-grade copper deposits during geotechnological preparation of deposits [75]. In this case, the geochemical barrier is a disintegrated carbonate rick mass, natural or engineered, onto which copper-containing solutions draining from the ore body are dumped. Depending on the conditions of occurrence of the geochemical barrier and the gas regime, deposits can form with secondary copper minerals of sulfate or carbonate composition.

The processing technology of the resulting material, which is anthropogenic oxidized copper ore, varies depending on the metal grade and its mineral form. At a sufficiently high copper grade, the ore after drying and roasting can be added to the copper concentrate during smelting. Otherwise, pre-concentration is advisable, consisting in classification to move the bulk of the residual calcium carbonate to the undersize and obtain a copper-rich slime product. Blister copper concentrate can then be concentrated by well-known methods — flotation, segregation roasting, cementation leaching, etc. The undersize is reused as a precipitant.

Anthropogenic ore processing methods based on the binding properties of gypsum, if it is present in significant quantities, are of interest. To partially dehydrate gypsum and give it binding properties, the ore is treated with hot steam at a temperature of 150-160 °C, and then pelletized. The resulting pellets are more convenient for transportation than run-of-mine ore. At a high content of residual calcium carbonates, pelletized ore is used as a precipitant in the geochemical barrier [75].

To create a sorption geochemical barrier using natural and engineered materials, serpentine of the Pechenga ore field and carbonatite from the overburden of the

Kovdor multimetal ore deposit can be blended. Carbonatite consists mainly of calcite and dolomite. Under dynamic conditions, when filtering sulfate solutions of nickel and copper through a mineral layer, it is possible to obtain high-grade nickel and copper concentrates (10% or higher) [11].

A promising material for use in geochemical barriers is the calcined concentration tailings of the copper-nickel ores of the Pechenga ore field, in whose mineral composition the share of serpentines is 60% [10].

In geochemical barriers, products of chemical and metallurgical processing of ores and concentrates can also be used, which include amorphous silica — a bulk by-product of acid processing of many ores and concentrates (for example, nepheline) [11].

The use of active silica as a barrier ensures the precipitation of mainly basic non-ferrous hydrosilicates, for example, nickel and cobalt. Carbonatite in the barrier plays the role of a pH regulator, neutralizing the sulfuric acid formed during the synthesis of hydrosilicates and ensuring that the solutions are consistently alkaline. By using this barrier, concentrates containing more than 25% nickel and copper can be obtained. This barrier is also effective in natural and wastewater treatment [76].

Douglas investigated the possibility of establishing an engineered alkaline barrier on the Baal Gammon minesite in Australia, which was mined for tin and non-ferrous metals between 1967 and 1983 [77]. Sediment includes ore minerals, such as pyrrhotite, chalcopyrite, arsenopyrite and, to a lesser extent, pyrite. In order to purify and neutralize the acidic ore drainage, 58 tons of $MgCl_2 \cdot 6H_2O$ was initially added in batches of 5 t. Mine drainage circulated for three days after the addition of $MgCl_2 \cdot 6H_2O$, then 132 tons of NaOH solution (50% wt) was added. Additionally, to the bottom water layer, 57 tons of a 50% NaOH solution diluted to 1% wt was added to the drain. The surface and bottom water was continuously recycled for five days [77].

The duration of the experiment was 22 days. The pH value of the surface and bottom water remained the same (pH = 2.9), even during and after the addition of $MgCl_2 \cdot 6H_2O$. When the addition of NaOH started, a significant increase was observed in the pH value of the surface and bottom layers (up to 9.0), then the pH value slightly decreased and stabilized at 8.5 [77].

As a result of the addition of $MgCl_2 \cdot 6H_2O$, a precipitate formed, mainly consisting of hydrotalcite. It is important to note the ability of hydrotalcite to adsorb a wide range of elements, including Al, Cd, Cr, Cu, Fe, Mn, Ni, and Zn. The hydrotalcite obtained in this study contained significant concentrations of Cu (8.00%) and Zn (3.87%) [77].

Based on iron-containing minerals, both physical and chemical barriers can be established. Secondary minerals precipitated during the weathering of the tailings absorb metals, thereby limiting their release into the environment. In the hardpan, which forms as a result of the precipitation and cementation of secondary minerals in the mining waste, arsenic is concentrated. At Montague Gold Mines in Nova Scoti, tailings are sandstone, partially cemented by seeping iron-containing solutions [78].

As a result, the arsenate is immobilized in the form of scorodite ($FeAsO_4 \cdot 2H_2O$). The formation of scorodite makes it possible to effectively limit the migration of arsenic in aqueous solutions given its poor solubility (<1 mg/l, pH = 3-4) and high content in scorodite (43-52% wt As_2O_5) [78].

Hardpans formed as a result of repeated periods of wetting and drying. The progressive weathering of the tailings over time led to the oxidation of arsenopyrite and the formation of scorodite precipitates under suitable conditions [78]:

$$FeAsS+14Fe^{3+}+10H_2O \rightarrow FeAsO_4 \cdot 2H_2O+14Fe^{2+}+SO_4^{2-}+16H^+$$

Concentrations of As and Fe in the hardpan are 8.92% wt and 9.35% wt, respectively [78].

The physical and chemical weathering of minerals over time has an impact on the migration of pollutants in surface and groundwater. The use of geochemical barriers will help to reclaim contaminated sites and avoid environmental disasters in the future. The results of these studies can be used to design a recycling strategy and reduce the environmental risks associated with the high hazard of the mining industry's waste worldwide.

6. ENGINEERED GEOCHEMICAL BARRIERS FOR WATER PURIFICATION AND RECOVERY OF NON-FERROUS METALS BASED ON MMPW AND MIDDLINGS OF THE MINING AND METALS INDUSTRY OF MURMANSK REGION

As shown above, a relevant problem is finding and examining the feasibility of engineered geochemical barriers based on the mining industry's waste or by-products of chemical and metallurgical processing of ores and concentrates for the cost-efficient purification of water bodies and effluents, as well as for the further recovery of valuable minerals. Such barriers must be environmentally safe, have a low cost and high availability.

The goal of the studies presented in this section is to demonstrate the feasibility and effectiveness of using engineered geochemical barriers for the further recovery of nickel and copper, which is highly relevant in areas where copper and nickel ores are mined and processed, in particular, in Russia's Murmansk Region.

The following materials were studied as engineered geochemical barriers:
- concentration tailings of copper-nickel ores thermally activated at 650 ˚C (barrier No1),
- a 1:1 blend of active silica and carbonatite (barrier No2),
- a 1:1 blend of serpentine and carbonatite (barrier No3),
- magnesium-containing sorbent based on concentration tailings of vermiculite ores (barrier No4).

Serpentines predominate in the composition of the concentration tailings (up to 60%), appreciable amounts of talc, amphiboles, and magnetite are also present. The total sulfide content (pyrrhotite, pentlandite, chalcopyrite) is 2-3%.

Active silica was obtained by treating forsterite concentrate (composition, % wt: MgO 50.50; SiO_2 40.54; FeO 5.45; CaO 1.44; CO_2 0.87; MnO 0.42; P_2O_5 0.26; Fe_2O_3 0.25; K_2O 0.14; Na_2O 0.14; Zro_2 0.3; SrO 0.05; TiO_2 0.04; Al_2O_3 0.08) with a 25% solution of sulfuric acid in the presence of inoculum at 60 ˚C. For the preparation of inoculum, finely ground vermiculite was used, which was added in an amount of 5% of the forsterite concentrate quantity. The inoculum produced plate-shaped silica with improved filtration properties and high reactivity because of its large surface area.

Carbonatite (overburden of the Kovdor complex ore deposit) is composed of 80% of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) The total carbonate content is 92%.

Serpentine (serpophite) from the Pilgujarvi rock mass of the Pechenga ore field on the Kola Peninsula was also used. Simplified mineral formula is $Mg_5Fe(OH)_8[Si_4O_{10}]$. Chemical composition, % wt: MgO – 35.98; SiO_2 – 40.69; H_2O – 11.80; FeO – 5.73; Fe_2O_3 – 2.21; Al_2O_3 – 2.17; CaO – 0.29; MnO – 0.16; CO_2 – 0.07; Na_2O – 0.06; K_2O – 0.05; NiO – 0.04; TiO_2 – 0.04.

Magnesium sorbent was obtained by acid processing of the concentration tailings of vermiculite ores from "Kovdorslyuda" LLC [79]. It was composed of brucite mixed with calcite $CaCO_3$.

Studies of the interaction of barriers with nickel- and copper-containing solutions were carried out in dynamic and static modes.

For dynamic experiments, the barrier material was ground to a particle size of -0.1+0.05 mm. Barrier material samples of 200 g (barrier No1), 100 g (barrier No2), and 150 g (barrier No3) were placed in 0.2 m high separation funnels and moistened with $NiSO_4$ and $CuSO_4$ solutions containing 0.2 and 0.1 g/l of the metals, respectively. The daily consumption of the solutions was 100 ml (barrier No1), 50 ml (barrier No2), and 35 ml (barrier No3). The feed frequency of the initial solution was 20, 10, and 7 ml, respectively, every 2 hours for 10 hours. After filtration through the barrier, the solutions were collected and analyzed every 3-5 days. pH (ion meter I-130.2M.1) and residual metal content were measured. Flame atomic absorption spectrometry (Quant-2 AFA instrument with a measurement error of up to 10%) was used. A solid thin-walled glass tube with a diameter of 1 cm was used for sampling solids from the columns. A core sample of the geochemical barrier material equal to the height of the funnel was collected and then divided. The composition of each of the samples was averaged and studied by X-ray diffraction (XRD) and thermogravimetric (TGA) analysis and chemically. For XRD of the reaction products, a DRON-2 diffractometer with $Cu_{k\square}$ radiation was used. For TGA, a Q-1500D derivatograph was used.

Interactions of barrier No3 with solutions of nickel and copper sulfates were studied by physicochemical modeling using the software suite Selector running on OS Windows [80].

The solid phase of barrier No3 contained 55.42 g of serpentine, 44.34 g of calcite, and 11.08 g of dolomite. The barriers were divided by thickness into three layers (reservoirs). The external controlling factors were a solution of copper sulfate (60 g of solution in a single time cycle, Ni and Cu concentrations 0.1 g/kg of solution) and 1 kg of atmosphere. It was assumed that in each layer, 10% of the barrier material reacted. The recurrence of events allowed to study the process in relative units of time. The total number of time cycles was 500. The calculations were carried out at a temperature of 20 ˚C.

When modeling the interaction of metal-containing solutions with barrier No4, chemical equilibrium was calculated of solutions containing $CuSO_4$, $NiSO_4$, and $FeSO_4$, depending on the degree of interaction of minerals (ξ) at initial metal concentrations of 1000 mg/kg H_2O in a system open to the atmosphere. The mass of the solution was 1.001 kg. The value of ξ ranged from 5 to 0 (from 10^{-4} to 10 g of the mineral blend took part in the interaction). The mass of Mg $(OH)_2$ and $CaCO_3$ was 0.13718 and 0.01998 mole, respectively. Modeling was carried out at P = 1 bar and T = 298 K. Calculations were made for both individual solutions and for a solution containing ions of all three metals.

In static experiments, a certain amount of the barrier material No2 and No3 (2-20 g/l) was added to continuously stirred sulfate solutions. The particle size was -0.16+0.10 mm. The pH of the solution was measured periodically. The time of the experiments was 0.5-2 hours. Then the solutions were filtered.

Experiments on the interaction of barrier 4 with multicomponent sulfate solutions containing 0.25 g/l of copper, 0.5 g/l of iron, and 0.5 g/l of nickel were carried out for 5-60 minutes with continuous stirring. Sorbent was added to the solution at 1, 3, 5, 7 and 10 g/l.

The pH value and residual concentrations of cations in the solutions were measured by flame atomic absorption spectrometry.

Interaction of barrier No1 with solutions of nickel and copper sulfates
in a dynamic mode

Earlier, we determined the ratio of the silicate and sulfide forms of nickel in fresh and mature (more than 30 years) concentration tailings of copper-nickel ores [81]. It was shown that during storage, not only the oxidation of sulfides occurs with the transition of nickel into soluble sulfates, but also the interaction of sulfate solutions with layered silicates acting as geochemical barriers. To intensify the interaction, the activation of minerals is most likely to be advisable. As is known, when serpentines are heated, there is a temperature interval in which the structure of the original mineral due to the loss of constitution water has already been destroyed, while new high-temperature phases have not yet formed [82]. Serpentine minerals that underwent heat treatment in that interval have high chemical activity, which made it possible to use them for the purification of natural water from heavy metals [76].

Based on the aforesaid, concentration tailings of copper-nickel ores thermally activated at 650 ˚C were chosen as the material of the engineered geochemical barrier No1. Concentration tailings contain 60% of serpentines (simplified formula $Mg_6[Si_4O_{10}](OH)_8$) and 1% of carbonates (calcite $CaCO_3$ and dolomite $CaMg(CO_3)_2$). These minerals are chemically active.

Figure 3a shows the change in the pH value of the $NiSO_4$ solution after filtering through barrier No1. A monotonic decrease in pH is observed; after 500 days, the pH value was 6.8. The change in the pH value of $CuSO_4$ solution (Fig.ure 3b) is qualitatively similar, however, the decrease rate is higher. After 500 days, the pH was 6.2.

The residual concentration of nickel ions in the solution after filtration through barrier No1 begins to increase noticeably after 100 days of experiment. After 500 days, on average 40% of the nickel contained in the solution precipitates (Figure 4a). For copper, the change in the residual concentration in the solution is different (Figure 4b). Noticeable growth in copper is observed after 300 days of experiments. After 500 days, about 80% of the copper contained in the solution precipitates on barrier No1.

Figure 5a shows the distribution of nickel content over the thickness of the geochemical barrier No1. A gradient can be seen, however, it is not as expressed as in copper (Figure 5b). This is probably due to differences in the concentration of solutions and, possibly, in the precipitation mechanism of nickel and copper ions. The observed gradient of contents is due to the fact that the solutions are purified in the top layer. With an increase in the duration of the experiments, the distribution of metal contents over the thickness of the barrier is expected to become more uniform. At the end of the experiments, the average nickel and copper content was 2.15 and 1.89%, respectively.

The mechanisms of nickel and copper ion precipitation from sulfate solutions by layered silicates have been earlier studied by Makarov et al. [82, 83, etc.]. It was shown that in thermally activated serpentines, a nickel-containing mineral is formed as a result of ion exchange with magnesium and nickel hydroxide. When using inactive minerals, nickel sorption on active sites (surface and structural OH^- groups) is also observed. The following reaction is likely to be the main process:

$$Mg_5Fe[Si_4O_{10}](OH)_8 + 5NiSO_4 = Ni_5Fe[Si_4O_{10}](OH)_8 + 5MgSO_4. \qquad (1)$$

In addition, it should be taken into consideration that serpentine minerals form magnesium oxide and silica under thermal activation. Therefore, when SiO_2 interacts with a solution of nickel sulfate, the following reaction may occur:

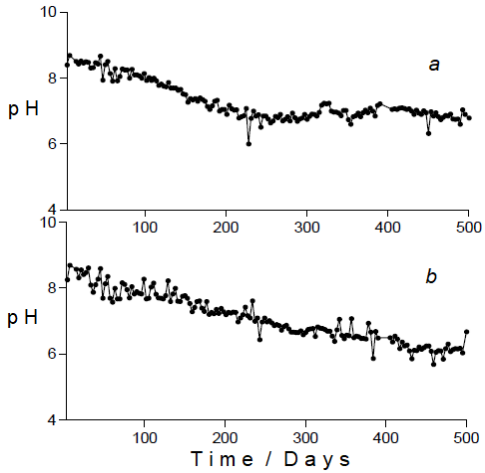$$4SiO_2 \cdot nH_2O + 6NiSO_4 = Ni_6[Si_4O_{10}](OH)_8 + (4n-10)H_2O + 6H_2SO_4. \qquad (2)$$

Figure 3. Change in the pH of the solutions of nickel (a) and copper (b) sulfates after filtration through barrier No1.
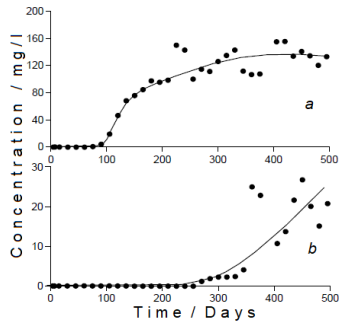

Figure 4. Residual concentration of nickel (a) and copper (b) in the solutions after filtration through barrier No1.
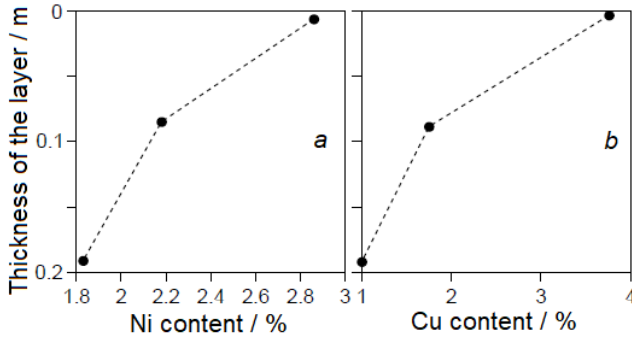
Figure 5. Distribution of nickel (a) and copper (b) grade over the thickness of barrier No1.

Where serpentines interact with $CuSO_4$ solutions, the formation of the basic sulfate brochantite $Cu_4SO_4(OH)_6$ predominates, which is a product of the following reaction:

$$3Mg(OH)_2 + 4CuSO_4 = Cu_4SO_4(OH)_6 + 3MgSO_4. \qquad (3)$$

Magnesium hydroxide is formed when MgO is dissolved in water.

It was previously shown that when $CuSO_4$ solutions react with carbonates (calcite and dolomite), basic copper sulfates — poznyakite $Cu_4SO_4(OH)_6 \cdot H_2O$ and brochantite — also form [84]. It was found that carbonates are not effective enough in the purification of nickel-containing sulfate solutions [85]. At the same time, taking into account the low carbonate content in the tailings, processes involving these are clearly secondary.

To confirm the specified interactions, the solid phase after the experiments was analyzed by XRD. The results are shown in Figures 6, 7.
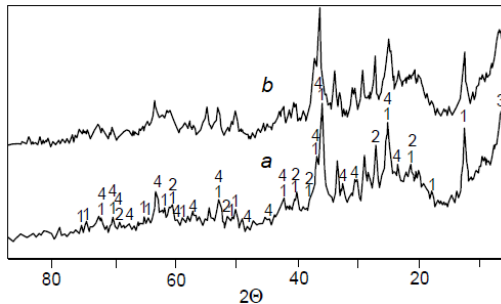

Figure 6. Mineral phases after the interaction of the top (a) and bottom (b) layers of the geochemical barrier No1 with a $NiSO_4$ solution. Numbers indicate reflexes:
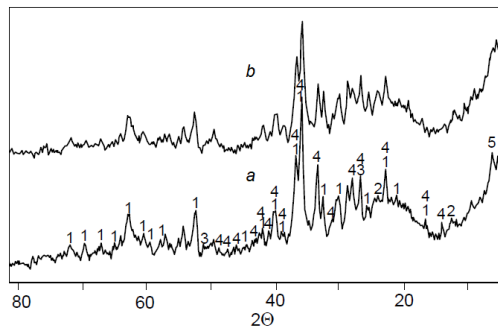1 - antigorite, 2 - quartz, 3 - chlorite, 4 – forsterite.

Figure 7. Mineral phases after the interaction of the top (a) and bottom (b) layers of the geochemical barrier No1 with a CuSO$_4$ solution. Numbers indicate reflexes: 1 - forsterite; 2 - antigorite, 3 - quartz, 4 - brochantite, 5 – chlorite.

As it can be seen, after the interaction of barrier No1 with a NiSO$_4$ solution, layered silicates form, such as nickel-containing antigorite and chlorite-like phases, and the relative intensity of reflexes in the top layer of the barrier, where a stronger interaction was observed, is higher (Figure 5). The appearance of a halo in the areas of angles $2\Theta = 20\text{-}40^\circ$ may indicate the formation of amorphous silica during thermal activation of the tailings.
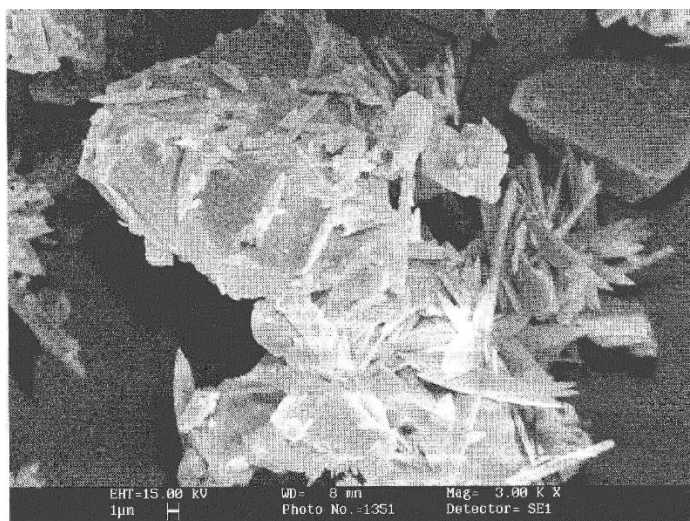

Figure 8. Brochantite crystals on the surface of mineral grains.

In contrast to the above, after the interaction of barrier 1 with a $CuSO_4$ solution, the reflex intensities of layered silicates are much lower (Figure 7). At the same time, the diffractograms clearly show reflexes of brochantite, which are also more intense in the top layer of the barrier. The formation of brocanthite is also confirmed by SEM. Prismatic crystals characteristic of brochantite are clearly visible (Figure 8).

Thus, the conducted studies allow to conclude that thermally activated concentration tailings of copper-nickel ores are promising materials for use in engineered geochemical barriers.

To treat wastewater to the MPC standards, barrier thickness needs to be adjusted.

As a result of model experiments, the average grade of nickel deposited on barrier No1 (in the resulting anthropogenic ore) increased in comparison with the initial tailings grade by a factor of 12, that of copper by a factor of 28. Probably, these results can be improved. At the same time, the achieved grades are sufficient for subsequent processing of the anthropogenic product by known methods.
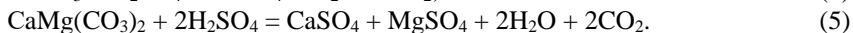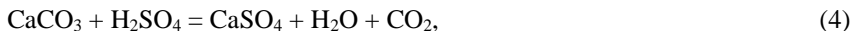
Interaction of barrier No2 with nickel and copper sulfate solutions under dynamic conditions

The pH value of the $NiSO_4$ solution after filtering through barrier No2 3 days later made about 8 and practically did not change during the entire experiment (Figure 9a).

The residual concentration of nickel ions in the solution after filtration begins to somewhat increase after 200 days of experiments (Figure 9a), however, after 500 days over 90% of nickel, contained in the solution are deposited on the barrier. The reasons of a certain increase of the residual concentration in the second half of the experiment and then, its decrease, are not clear so far.

The distribution of nickel content over the thickness of the layer of geochemical barrier No2 proved non uniform after experiments. In the top layer the content of metal reached 27.1 %, in the bottom one – 0.87 %. The observed significant gradient of contents is stipulated by that the deposition of nickel took place basically in the top layer. Upon the completion of 500 days of experiment the average nickel content in the barrier material made 2.7 %.

The application of activated silica in the material of barrier No2 results in the formation of deposit of basically main hydrosilicates of heavy metals, in our case nickel, stable in supergene conditions. At the interaction of SiO2 with solution of nickel sulfate the reaction (2) is possible. Carbonatite performs a part of an pH regulator in the barrier. At that a stable alkaline reaction of solutions is created. Sulfuric acid, generated as a result of reaction (2) is neutralized according to the patterns:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2, \qquad (4)$$
$$CaMg(CO_3)_2 + 2H_2SO_4 = CaSO_4 + MgSO_4 + 2H_2O + 2CO_2. \qquad (5)$$

The XRD (Figure 10a, b) results are evidence of similar interactions. The generation of sheet silicates of chlorite type (apparently, nickel-bearing one) in reaction (2) was registered, while the relative intensity of reflections in the top layer of the barrier, where a stronger interaction was observed, is higher. For the upper layer the absence is characteristic of reflections of calcite, consumed in reaction (4). Dolomite is not observed either in the top or in the bottom layers. A halo around the degrees of $2\Theta = 20$-$30°$ may be an evidence that there is activated silica available.

The thermal analysis results of the material of the top and bottom layer of barrier No2 are presented in Figure 11a, b. One can observe on the DTA curve of the material of the top layer the endothermic effect with a minimum at 130 °C and exothermic effect with a maximum at 325 °C, then a weak endothermic peak at 440 °C (Figure 11a). A sudden loss of the mass corresponds to the first effect, then over the entire distance of the survey a monotonous mass loss can be observed, with a slight discontinuity, which corresponds to the endothermic peak at 440 °C. Probably, the first effect on the DTA curve corresponds to the exudation of interlayer water, which has been registered for many supergene chlorite samples. The nature of the exothermic effect is not quite clear. The endothermic effect at 440 °C is connected with the exudation of the structure water by the chlorite-like phase. On the DTA curve of the material from the bottom layer of the barrier two clearly manifested endothermic effects are observed, which correspond to two stages of the mass loss on the TG curve (Figure 11b). The low temperature area of the mass loss is connected with the exudation of interlayer water by the chlorite-like phase, the second one at 870 °C – with the removal of OH group from chlorite and decarbonisation of calcite.

The pH value of $CuSO_4$ solution after seeping through barrier No2 three days later made about 8.5 and varied very insignificantly over the entire duration of the experiment (Figure 9b).
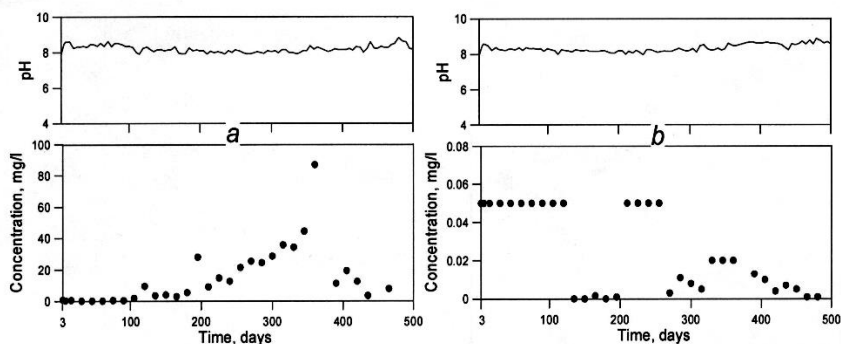

Figure 9. Change of the pH value and residual concentration of metals after filtration through barrier No2 of solutions of $NiSO_4$ (a) and $CuSO_4$ (b).

The residual concentration of copper ions in the solution after the filtration during the entire duration of the experiments did not exceed 0.05 mg/l (Figure 9b).

The analysis of the copper content distribution showed a significant gradient in the barrier layer thickness. In the narrow top layer the metal content reached 33.4 %, while in the bottom one it made only 0.005 %.
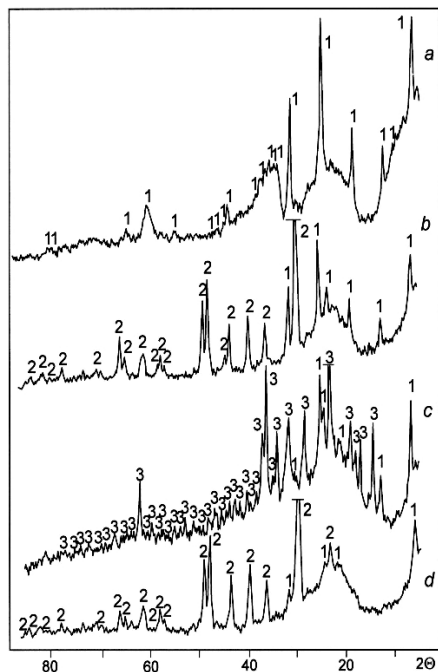

Figure 10. XRD patterns of mineral phases of barrier No2 after interaction with solutions of NiSO$_4$ (a, b) and CuSO$_4$ (c,d). The top layer – a, b; the bottom layer– c, d.
Numbers stay for reflections of: 1 – chlorite; 2 – calcite; 3 – brochantite.

The solid phase of the material of barrier No2 after the interaction with CuSO$_4$ solution was investigated by XRD method (Figure 10c, d). In the material of the top layers, the generation of the basic sulfate – brochantite Cu$_4$SO$_4$(OH)$_6$ was registered. Chlorite-like phases, probably, the copper-bearing ones are diagnosed. It is characteristic for the top layers of the barrier not to have calcite reflections. Dolomite is not observed wither in the top or in the bottom layers. A halo around the degrees of $2\Theta = 20\text{-}30^\circ$ may be an evidence that there is activated silica available.
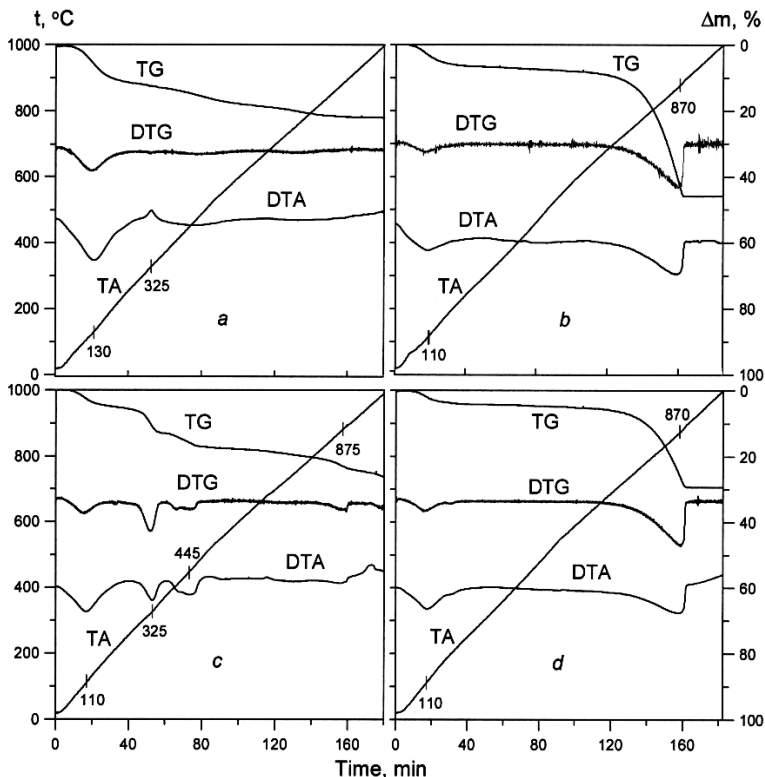
Figure 11. TA, DTA, TG and DTG curves of the material of barrier No2 after
interaction with solutions $NiSO_4$ (a, b) and $CuSO_4$ (c, d).
The top layer – a, b; the bottom layer – c, d.

Figure 11c, d presents the results of TGA of the material of the top and bottom
layer of barrier No2 after the interaction with copper sulfate solution. For the DTA
curve of the material from the top layer of the barrier four endothermic effects are
characteristic, which correspond to the four stages of the mass loss (Figure 11c). The
decrease of the mass within the 80-200 °C temperature interval is stipulated by the
removal of adsorption water from chlorite. Endothermic effect at 325 °C is connected
with the removal of combined water from brochantite resulting in generation of
tenorite, antlerite and dolerophanite. An extensive endothermic peak with a minimum
at 445 °C is connected with the exudation of the first portion of combined water from
chlorite. The fourth area of mass reduction at temperatures above 800 °C may be
identified as belonging to the OH groups removal from chlorite, resulting in its

32

structure destruction and in dolerophanite desulphatization. On the DTA curve of the material from the bottom layer of the barrier two endothermic effects are observed, which correspond to two stages of the mass loss on the TG curve (Figure 11d). The first effect with a minimum at 110 °C is connected with the chlorite's loss of adsorption water, the second at 870 °C – as well as after the interaction with nickel sulfate solution – with removal of OH group from chlorite and calcite decarbonisation.
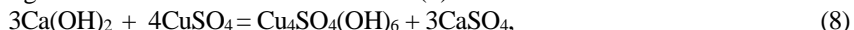
Thus, based on the investigations of barrier No2 material after a long interaction with solution $CuSO_4$ the following processes can be assumed:
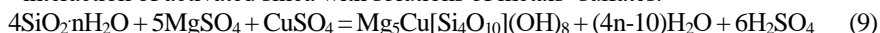- carbonates' dissolving:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-,\tag{6}$$
$$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO^{3-},\tag{7}$$

accompanied by a pH increase;
- generation of brochantite in reaction (3) and:

$$3Ca(OH)_2 + 4CuSO_4 = Cu_4SO_4(OH)_6 + 3CaSO_4,\tag{8}$$

- interaction of activated silica with solutions of metals' sulfates:

$$4SiO_2 \cdot nH_2O + 5MgSO_4 + CuSO_4 = Mg_5Cu[Si_4O_{10}](OH)_8 + (4n-10)H_2O + 6H_2SO_4\tag{9}$$

involving the generation of chlorite-like phases;
- neutralization of sulphuric acid by carbonates in reactions (4, 5).

Interaction of barrier No3 with solutions of nickel and copper sulfates in dynamic conditions

The pH value change of $NiSO_4$ solution after filtration through barrier No3 is shown in Figure 12a. An insignificant increase of the pH value is observed, 500 days later this value made 8.5.

The residual concentration of nickel ions in the solution after filtration during the experiments did not exceed 3 mg/l (Figure 12a), as a result, 500 days later, over 99% of nickel, contained in the solution are deposited on barrier No3. In this case, there is also observed a considerable gradient of contents (from 8% practically to 0%), stipulated by the cleaning of solutions in the top layer of the barrier. Upon the completion of a 500 day term of experiment the average content of nickel in the material of barrier No3 made 2.2 %.

Chlorite, probably nickel containing, is clearly registered in the top layer of barrier No3 (Figure 13a). Calcite reflections in the top layer are less intensive than in the bottom one (Figure 13b). dolomite is diagnosed tentatively due to reflections' overlapping. Apparently, the following can be considered the basic process (1).

Figure 12b shows the change of pH value of $CuSO_4$ solution after filtration through barrier No3. As one can see, an insignificant change of pH value is observed with the course of time, the average pH value reading is about 7.8.
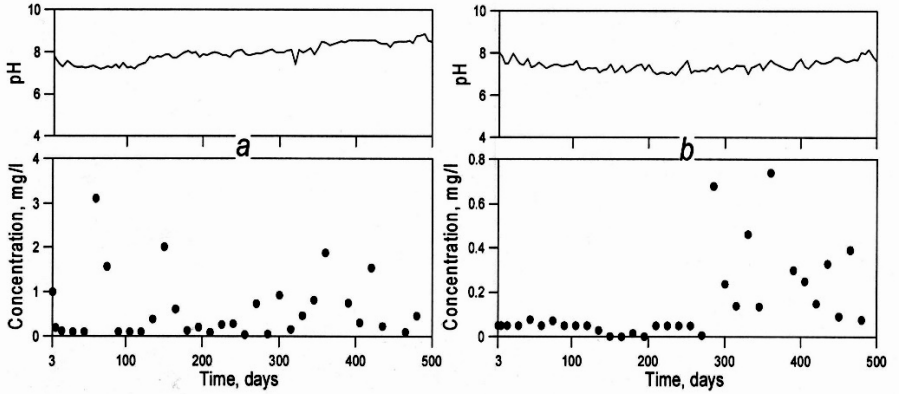
Figure 12. Change of the pH value and the residual concentration of metals after filtration of solutions $NiSO_4$ (a) and $CuSO_4$ (b) through barrier No3.
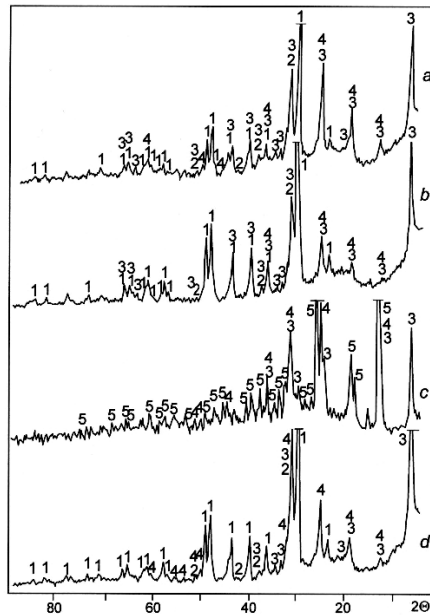

Figure 13. XRD patterns of mineral phases of barrier No3 after interaction with solutions $NiSO_4$ (a, b) and $CuSO_4$ (c, d). The top layer – a, b; the bottom layer – c, d. Numbers stay for reflections of: 1 – calcite; 2 – dolomite; 3 – chlorite; 4 – serpophite; 5 – poznyakite.

The residual concentration of copper ions in the solution after filtration in most tests did not exceed 0.2 mg/l (Figure 12b). After 300 days of experiments separate "bursts" of residual concentration up to 0.5-0.8 mg/l were registered, which reasons are not quite clear.

In the solid phase of barrier No3, a considerable gradient of copper contents was observed from up to 15.8 % in the thin top layer to 0.017 % in the bottom one.

The results of the XRD of the solid phase of various layers of the barrier are presented in Figure 13c, d. In the top layer of barrier No3 the basic copper sulfate is registered – poznyakite $Cu_4SO_4(OH)_6 H_2O$. Calcite and dolomite are not found in the top layers. Reflections of chlorite-like phases appear and they are registered both in the top and bottom layers.

In this case, dissolving of carbonates takes place in reactions (6, 7) basically in the top layer of the barrier, the formation of poznyakite according to patterns

$$3Ca(OH)_2 + 4CuSO_4 + H_2O = Cu_4SO_4(OH)_6 H_2O + 3CaSO_4, \qquad (10)$$
$$3Mg(OH)_2 + 4CuSO_4 + H_2O = Cu_4SO_4(OH)_6 H_2O + 3MgSO_4, \qquad (11)$$

and also, probably, the generation of copper-bearing chlorite-like phases is similar to process (1).

Physical-chemical modeling of interaction of barrier No3 with solutions of nickel and copper sulfates

The results of physical-chemical modeling of the interaction of barrier No3 with nickel sulfate are shown in Figures 14, 15. A slight decrease of the pH value of the solution is observed as it leaves the top layer, while its increase is observed then, after 370 cycles (Figure 14a, curve 1). The pH values of the solution, after filtration of $NiSO_4$ solution through the medium and the bottom layers of geochemical barrier No3 practically do not change during the entire model experiment (Figure 14a, curves 2, 3). For the solid phase of the top layer a sharp decrease in calcite content and a slower one in serpentine are characteristic (Figure 15a). At the same time an increase in the contents of chlorite and nickel-bearing chlorite is observed, while silica generation is registered. In the medium and the bottom layers the mineral formation is significantly less intense, no nickel-bearing minerals are registered (Figure 15b, c). The residual concentration of nickel ions grows monotonously and insignificantly, while a small sudden change is observed after 370 cycles (Figure 14c), which corresponds to the growth of pH (Figure Figure 14a) and disappearance of silica (Figure 15a). We should note that the change of the residual concentration of metal in the solution is practically the same for all layers.

The data of physical-chemical modeling of the interaction of barrier No3 with solution of copper sulfate are presented in Figures 14, 15. As one can see, characteristic for the top layer are a monotonous decrease of pH value of the solution with two small discontinuities and then, after 400 cycles, a sudden drop to the level of 4.98 (Figure 14b, curve 1). The discontinuities on the curve pH – time correspond to the decrease of calcite and dolomite contents in the solid phase to the point of their disappearance, while a sudden decrease of

pH corresponds to the disappearance of serpentine (Figure 15d). In the model, first a sudden and then a smooth growth of content of the basic copper sulfate – brochantite $Cu_4SO_4(OH)_6$ is observed. In the solid phase chlorite and silica are registered as well. The residual concentration of copper ions in the solution behaves synchronously after the filtration through the top layer (Figure 14d, curve 1). The interaction with solution $CuSO_4$ of the medium and the bottom layers is qualitatively alike. The decrease of pH value of the solution as it leaves the medium layer, from 8.16 to 7.95 corresponds to the drop of pH index after filtration through the top layer (Figure 14b, curve 2). After 300 cycles the content of calcite in the solid phase goes sharply down (Figure 15e). The content of serpentine is stable, while that of dolomite somewhat increases. After 400 cycles, the formation of brochantite begins in the medium layer (Figure 15e). The residual concentration of copper ions in the solution after filtration through the medium layer during 500 cycles grows insignificantly (Figure 14d, curve 2). The pH value after filtration through the bottom layer decreases insignificantly (from 8.20 to 7.95) after 440 cycles (Figure 14b, curve 3). The decrease of calcite content in the solid phase of the layer (Figure 14f) corresponds to that moment. The residual concentration of ions Cu^{2+} changes in time much as the medium layer (Figure 14d, curve 3).
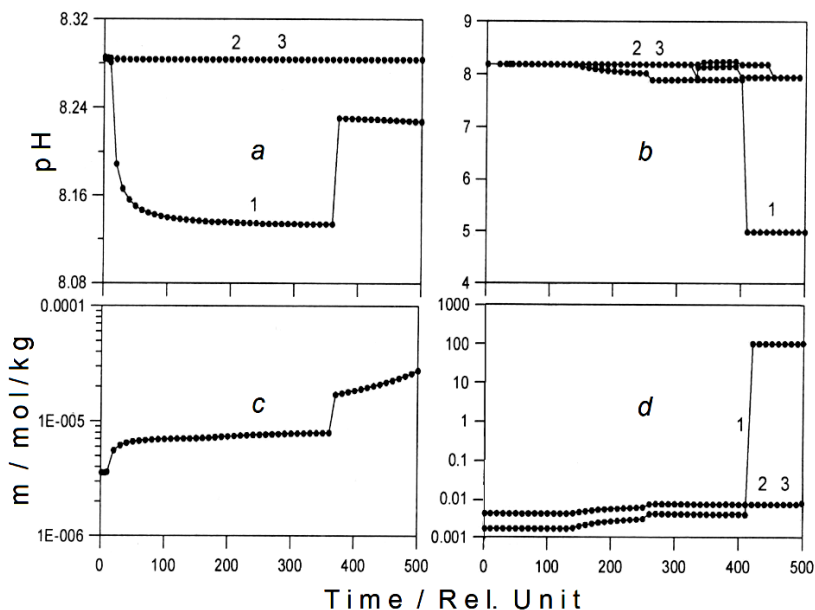

Figure 14. Change of the pH value (a, b) and the residual concentration of nickel (c) and copper (d) ions in solution after filtration through the top (1), medium (2) and the bottom (3) layers of barrier No3 with the course of time.

In spite of the qualitative adequacy of the model, there are some discrepancies with laboratory experiments. In experiments with solutions NiSO$_4$, unlike in modeling, the saturation of the barrier was observed much faster than in the tests with CuSO$_4$ solutions, the residual concentration of nickel was in all cases higher than that of copper. In experiments with copper sulfate solution there was registered generation of poznyakite rather than brochantite. The comparison of data of physical-chemical modeling with laboratory experiments allows to conclude that one has to consider kinetic factors in the model. Discrepancies can be stipulated by the fact that the possibility of generation of copper-bearing chlorite-like phases was not taken into consideration either.
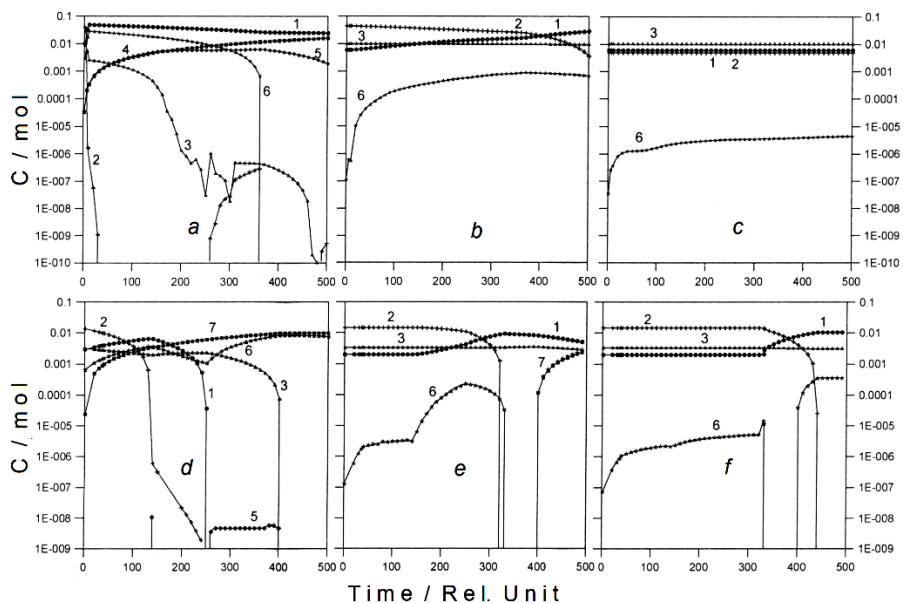

Figure 15. Change of content of minerals at the solid phase of the top (a, d), medium (b, e) and the bottom (c, f) layers of the geochemical barrier after filtration of solutions NiSO$_4$ (a, b, c) and CuSO$_4$ (d, e, f) with the course of time. Numbers stay for minerals: 1 – dolomite; 2 – calcite; 3 – serpophite; 4 – nickel-bearing chlorite; 5 – chlorite; 6 – silica; 7 – brochantite.

Interaction of artificial geochemical barriers No2, 3 with nickel and copper sulfates' solutions in static conditions

Since this series of tests was modeling the possibility of adding reagents in natural water bodies, the number of reagents introduced should have provided acceptable indices of nickel and copper ions' recovery in deposit, while keeping at the same time the pH level within the range of 6.5-8.0, which is determined by the requirements to water quality.

The parameters of the process and the degree of water purification from metals' ions in some of the performed laboratory tests are summarized in the table 2.

Besides, there were carried out laboratory tests of barriers No2 and No3 in static conditions with polluted natural water. Water was taken from lake Nyudyavr, located in the impact area of "Severonickel" smelter of the "Kola MMC" JSC. The water contained, μg/l: of nickel – 389, of copper – 53.7, of iron – 264, the pH level – 6.8. It was found that with Solid to Liquid ratio of 10-20 g/l the residual concentrations of metals in the solution do not exceed the MAC for fishery water bodies.

Table 2. Parameters of the process and the degree of water purification

Metal	Initial concentration, mg/l	Reagent : solution ratio, g/l	pH level of water after interaction	Degree of solution purification, %
Barrier No2				
Ni	29.5	2	7.6	90.2
		10	7.7	98.6
		20	8.0	99.5
Cu	31.8	5	7.5	91.2
		10	7.7	99.1
		20	7.8	99.7
Barrier No3				
Ni	32.1	2	7.7	89.5
		10	7.9	98.1
		20	8.0	99.8
Cu	30.2	5	7.4	92.2
		10	7.6	99.1
		20	7.9	99.8

Interaction of barrier No4 with sulfate solutions of copper, nickel, and iron

Magnesium-containing products from ore concentration waste can be used as a process feed for the production of magnesia binders, sorbents, pigments, building materials, etc. An earlier study [86] showed the possibility of processing concentration

tailings of vermiculite ores into a magnesium ameliorant, where magnesium and iron were leached with sulfuric acid to obtain a poorly water-soluble magnesium salt $Mg_2(OH)_2SO_4$. The ameliorant has a prolonged and mild effect, compensates for nutrient loss, partially immobilizes aluminum and heavy metal compounds. Earlier, we studied the processes of leaching magnesium and iron from the concentration tailings of vermiculite ores with hydrochloric acid to obtain products based on magnesium and iron hydroxides and amorphous silica [87].

The results of studies of the sorption properties of the naturally occurring mineral brucite $Mg(OH)_2$ with respect to heavy metal ions and strontium are presented in [88, 89]. A combined sorption process for the recovery of metals from natural water and process solutions in a wide range of concentrations is proposed.

Therefore, we wanted to study the magnesium-containing product of acid processing of the concentration tailings of vermiculite ores consisting of brucite with a calcite $CaCO_3$ impurity, whose preparation is described in [70], as a sorbent of non-ferrous and iron ions.

Physicochemical modeling was applied to study the interaction of the sorbent with multicomponent sulfate solutions in order to identify the conditions of both selective and collective precipitation of metals, which can be used in the development of hydrometallurgical processes and wastewater treatment methods. Chemical equilibrium modeling results of $CuSO_4$, $NiSO_4$, $FeSO_4$ – $Mg(OH)_2CaCO_3$ in a system open to the atmosphere at a fixed $\xi_1 = 0$, which corresponds to 1 kg of atmosphere, depending on the interaction degree between the minerals are presented in Figures 9-11.

As can be seen in Figure 16a, a noticeable increase in pH begins with an increase in the reagent feed rate ($\xi = 1.0$-0). In the same range of ξ values, the redox potential shifts somewhat to the negative region from 1.04 to 0.67 V (Figure 16a).

The distribution of equilibrium ion concentrations in the solution indicates that iron is deposited to a large extent in the entire range of ξ values (Figure 17a). A sharp decrease in the concentration of iron ions occurs at $\xi = 2.0$-0. Thus, in a system open to the atmosphere, iron can be selectively transferred to the solid phase even at a low mineral feed rate.

The main iron phase in the interval of $\xi = 5.0$-0.8 is hematite Fe_2O_3, at $\xi = 4.0$-0.8, goethite $FeOOH$ is also present (Figure 18a).

The modeling results also indicate the possibility of separating copper and nickel by adjusting the reagent to solution ratio (Figure 17a). In a narrow range of values $\xi = 0.8$-0.6, the concentration of nickel ions exceeds the concentration of copper ions by 5-6 orders of magnitude. The precipitation of copper occurs in brochantite $Cu_4(OH)_6SO_4$ (Figure 18a). With an increase in the interaction degree of the minerals ($\xi = 0.6$-0), the transition to the solid phase of nickel begins — both as the hydroxide $Ni(OH)_2$ and as part of trevorite $NiFe_2O_4$ (Figure 18a).
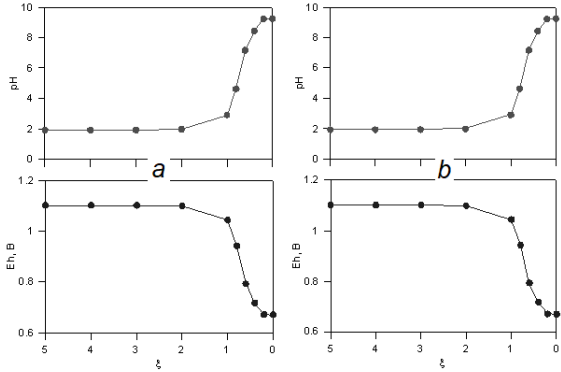
Figure 16. Change in pH and Eh of the solution in equilibrium (a) and metastable (b) system open to the atmosphere CuSO₄, NiSO₄, FeSO₄ - Mg (OH)₂, CaCO₃, as a function of ξ
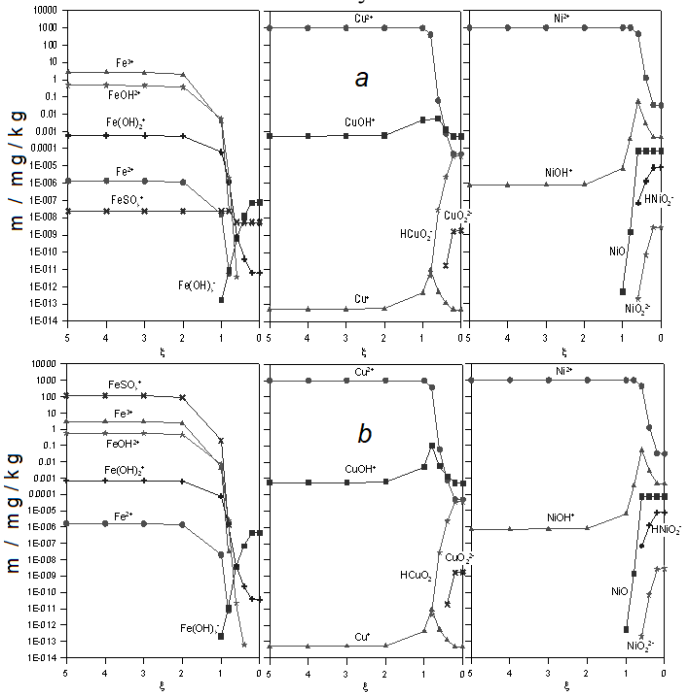

Figure 17. Change in the solution composition in equilibrium (a) and metastable (b) system CuSO₄, NiSO₄, FeSO₄ - Mg (OH)₂, CaCO₃, as a function of ξ

Figures 16–18 present the modeling results of interactions in a system open to the atmosphere, and in order to bring the model closer to actual technological processes, it was assumed that complete equilibrium is not achieved. In particular, a restriction was imposed on the formation of oxides—- hematite Fe_2O_3 and trevorite $NiFe_2O_4$.

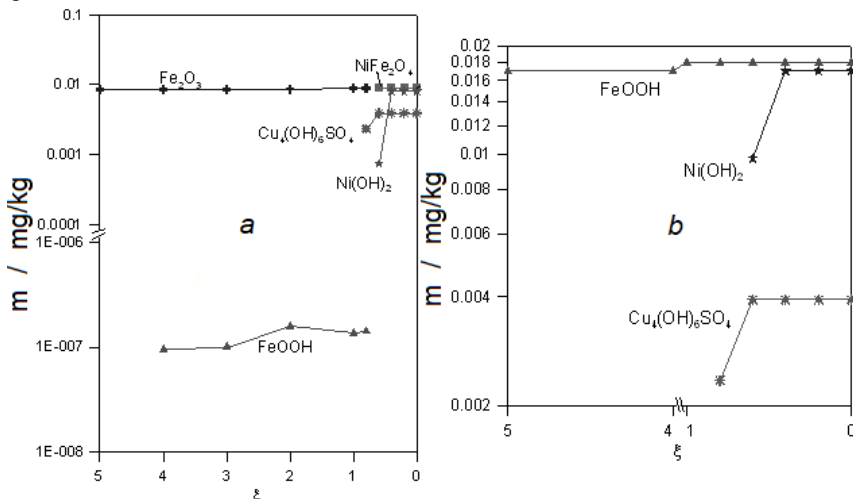No major changes in the nature of pH — ξ and Eh — ξ dependencies were observed (Figure 16b).

Figure 18. Change in the solid phase composition in equilibrium (a) and metastable (b) system $CuSO_4$, $NiSO_4$, $FeSO_4$ - $Mg(OH)_2$, $CaCO_3$, as a function of ξ

The main iron phase in the metastable system is goethite FeOOH, whose content is stable over the entire range ξ (Figure 18b). Copper precipitation also occurs in the form of brochantite $Cu_4(OH)_6SO_4$, and an increase in the mineral content is observed in the range of ξ= 0.8-0.6 (Fig. 11b). Starting from the mineral interaction degree ξ= 0.6, the precipitation of nickel as part of hydroxide $Ni(OH)_2$ begins (Figure 18b).

Analysis of the distribution of ions in the solution shows that the iron concentration rises in comparison with the equilibrium system, and $FeSO_4^+$ becomes the dominant ion in the range ξ= 5.0-1.0 (Fig. 10b). At ξ= 0.4-0, $Fe(OH)_4^-$ prevails(Figure 16b). The residual concentration of iron in the solution at ξ= 0 is four times higher than in the equilibrium system (Figure 18b). The change in the composition of the solution in terms of copper and nickel ions in the metastable system is qualitatively similar (Figure 18b). For copper, the dominant ion is Cu^{2+} and only when ξ= 0.4-0 does $Cu(OH)^+$ become dominant. For nickel, over the entire range of ξ, Ni^{2+} ions have the highest concentration (Figure 18b).

Thus, in the metastable system, iron can be most fully converted to solid phase iron in the range of ξ= 1.5-1.0. At ξ= 0.8, copper concentration decreases more than twice. Under these conditions, nickel remains in solution (Figure 18b). It is advisable to selectively precipitate copper in the range of ξ= 0.8-0.7.

To verify the modeling results and the data on the newly formed mineral phases, a number of laboratory experiments were carried out.

Experiments with individual sulfate solutions of copper, nickel, and iron with a concentration of 1 g/l under static conditions showed significant differences both in the kinetics of metal ion precipitation and in the amount of sorbent necessary for the most complete purification of the solutions [79]. Copper precipitates most quickly and with the least input of sorbent. Nickel ions performed worst. Using X-ray phase analysis and scanning electron microscopy, it was found that copper precipitates in the form of poznyakite $Cu_4(OH)_6SO_4 \times H_2O$, iron forms hydroxides, mainly goethite $\alpha FeOOH$, nickel precipitates as hydroxide $Ni(OH)_2$. The results of a SEM analysis of the morphology of the newly formed phases are presented in Figures 19-21.
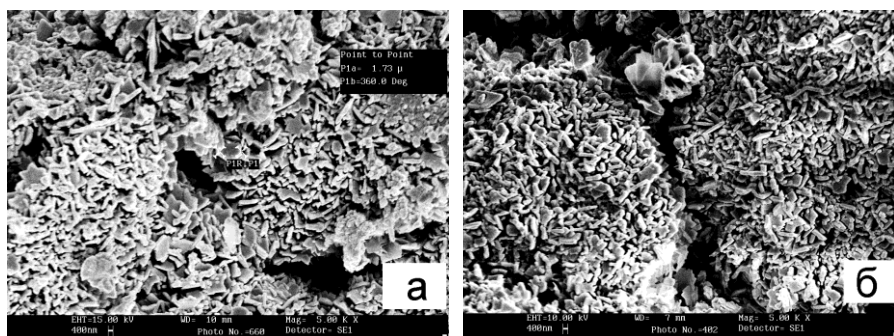

Figure 19. Poznyakite crystals on the surface of untreated (a) and thermally activated (b) barrier 4 after interaction with a $CuSO_4$ solution.

Figure 22 shows the change in the recovery of copper, iron, and nickel depending on the interaction time and the barrier to solution ratio. As one can see, the concentration of copper in the solution decreases almost twice already at a minimum ratio of 1 g/l, and at 5 g/l copper is precipitated almost completely in 60 minutes. Iron was precipitated by 99% at a ratio of 7 g/l. The residual concentration of nickel in the solution, even at a maximum ratio of 10 g/l, decreased by only 65%. The increase in pH is directly proportional to the interaction time of the solution with barrier No4, while at the maximum barrier to solution ratio, the pH value did not exceed 9.
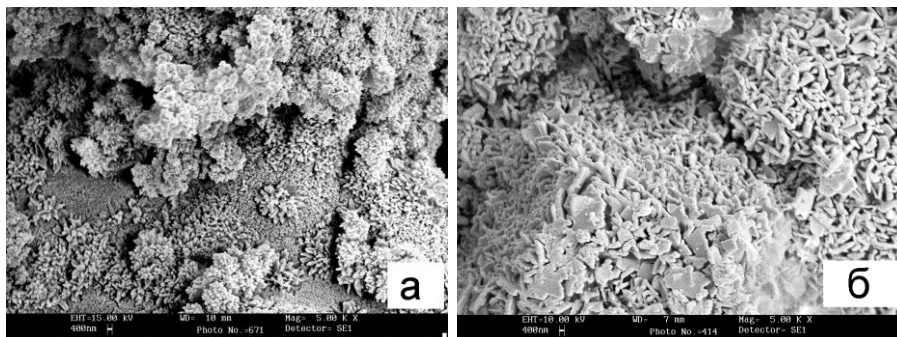
Figure 20. Lamellar morphology of iron hydroxide on the surface of untreated (a) and thermally activated (b) barrier 4 after interaction with FeSO$_4$.
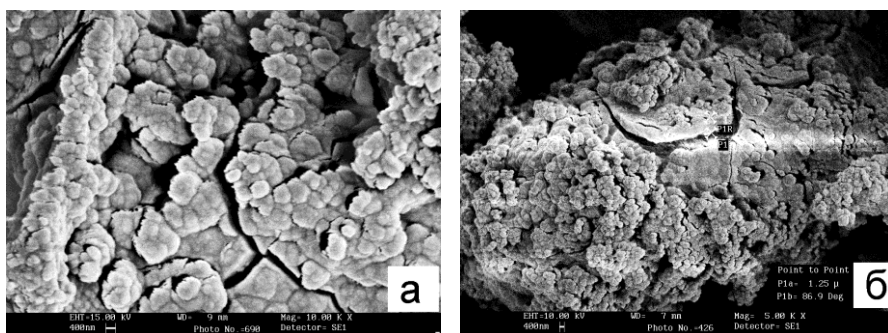

Figure 21. Morphology of nickel hydroxide on the surface of untreated (a) and thermally activated (b) barrier 4 after interaction with NiSO$_4$.

Studies [88, 89] showed that thermal modification of naturally occurring brucite at 400-600 ºC leads to the formation of a new crystalline phase — periclase MgO — and a significant increase in the sorption capacity. Given this finding, we wanted to study the interaction of a thermally activated sorbent with solutions.

Figure 23 shows the recovery of copper, iron, and nickel depending on the interaction time with barrier No4 thermally activated at 500 ºC. As one can see, there are noticeable differences. Already at a barrier to solution ratio of 3 g/l, copper is precipitated by 98% in 60 minutes, the residual concentration of iron in the solution under these conditions is more than halved. At a barrier to solution ratio of 7 g/l, recovery of copper was 99%, of iron 70%, of nickel 35% after 5 minutes, and at the end of the experiment, copper and iron ions were almost completely recovered from the solution, and the nickel concentration was reduced by 80%. At a barrier to solution ratio of 10 g/l, the solution was completely purified from ions of the studied metals.
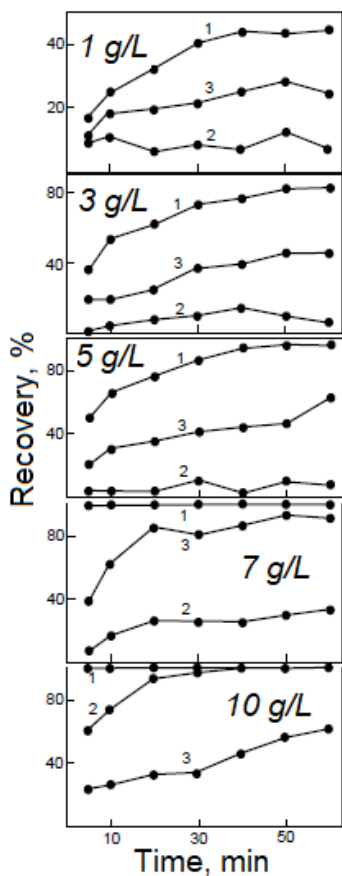
43

Figure 22. Recovery of copper (1), nickel (2), and iron (3) from the solution by barrier No4

Figure 23. Recovery of copper (1), nickel (2), and iron (3) from the solution by thermally activated barrier No4

Studies have shown that a magnesium-containing sorbent is an effective geochemical barrier with respect to metal ions. Physicochemical modeling of the interaction of the barrier with a multicomponent sulfate solution in an open to the atmosphere system made it possible to identify the ranges of the barrier to solution ratio for the separation of metal ions. Thermal activation significantly improves the sorption capacity of the barrier No4. These results can be used in the development of selective and complete treatment processes for wastewater and process water to remove copper, nickel, and iron ions.

CONCLUSION

1) A classification of geochemical barriers by origin (natural and engineered), method of application, and area of application is proposed. Opportunities and prospects are shown for the use of geochemical barriers in anti-filtration screens, treatment of wastewater and natural water, and further recovery of non-ferrous metals. Purposeful establishment of geochemical barriers in the drainage areas of mine and underspoil water on mining and metals waste storage sites will address the needs of environmental protection and resource conservation through the precipitation of valuable minerals in the barriers.

2) It has been found that concentration tailings of copper-nickel ores and blends based on active silica and carbonatite, serpophite and carbonatite are promising materials for use in engineered geochemical barriers. It has been found that using barriers, concentrates can be obtained containing more than 25% of nickel and copper. Average nickel and copper grades achieved in laboratory experiments on geochemical barriers are sufficient for subsequent cost-effective processing by pyro- or hydrometallurgical methods.

3) It has been shown that a magnesium-containing sorbent obtained by processing vermiculite ore concentration tailings is an effective barrier for the precipitation of copper, nickel, and iron. The conditions for the separation of metal ions are described. Thermal activation significantly improves the sorption capacity of the barrier. These results can be used in the development of selective and complete treatment processes for wastewater and process water to remove copper, nickel, and iron ions.

4) The fundamental possibility of using engineered geochemical barriers in physicochemical geotechnology has been identified [90, 91]. Further research in this direction will make it possible to purposefully form anthropogenic non-ferrous ores with a simultaneous decrease in the environmental load. Optimal processes are needed to intensify the filtration of solutions and precipitation of metals, to reduce metal grade gradients over the thickness of the barrier layer, to produce selective non-ferrous metal concentrates, etc.

5) Physicochemical modeling data makes it possible to predict the behavior of barriers under prolonged interaction with solutions. The models reflect the observed zoning over the thickness of the geochemical barrier in terms of distribution of the original and newly formed mineral phases and metal grades. Obviously, as the number of time cycles increases, the patterns observed for the top layer will also be observed in the middle and bottom layers until the initial minerals completely disappear and the barrier becomes saturated.

6) Laboratory tests of geochemical barriers using contaminated water from the industrial sites of Kola MMC JSC were carried out. The possibility of purifying water from heavy metals to the MPC standards for fishery water bodies has been shown.

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