

Modelling the Interaction of Artificial Geochemical Barriers with Nickel Sulphate Solution

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Abstract

An interaction of artificial geochemical barriers with nickel sulphate solution was studied using chemical analysis, XRD phase analysis, scanning electron microscopy and thermodynamic modelling. It has been demonstrated that combinations of active silica with carbonatite, as well as of serpophite with carbonatite are promising materials for making artificial geochemical barriers.

Key words: artificial geochemical barriers, active silica, carbonatite, serpophyte, nickel sulphate solution, deposition, sedimentation

INTRODUCTION

According to the classification offered by A. I. Perelman, geochemical barriers represent such sites of the Earth's crust whereon an abrupt decrease at a short distance occurs in the intensity of the migration of chemical elements resulted in concentrating them. These processes can be realized both under naturally occurring geological conditions, and under storage of various man-caused (technogenous) waste products, where the transformations of the technogenous products frequently proceed with high rates [1].

Numerous works are devoted to the development of methods for protecting underground and surface waters from pollution with the use of physicochemical methods such as geochemical barriers [2–6]. The essence of the methods consists in the transformation of polluting components into inactive forms. In this case one could use naturally occurring barriers as well as create artificial geochemical barriers. Both

natural formations (soils, rocks, peat, etc.), and man-caused waste products (pyrite cinders, soda manufacture wastes, etc.) can be employed as materials to create such barriers. One more area of using geochemical barriers is presented by methods of intra-wastepile enrichment. These methods include a selective stacking of a different quality rock mass containing useful components and its further processing under storage when dissolution, migration and sedimentation of useful components occurs within the operative range of barriers, which provides the formation of man-caused ores [7].

In this connection an urgent problem is presented by the search and development of non-traditional reagents representing geochemical barriers obtained from waste products of mining complex or by-products of chemical-and-metallurgical processing of ores and concentrates with whose help it would be possible to carry out efficiently purifying water reservoirs and wastewaters, as well as after extracting

any useful components. In this case the necessary conditions for their application consist in the environmental safety, low cost and availability of such barriers.

Earlier in paper [8] we have demonstrated the efficiency of using a mixture of active silica and carbonatite for water treatment in open water reservoirs including natural, contaminated with dissolved heavy metals (nickel, copper, zinc, iron), as well as wastewaters of mining enterprises. It was interesting to study on the possibility of employing this artificial geochemical barrier in the methods of intra-waste pile enrichment.

As a material for the second geochemical barrier we used a mixture of serpentine (antigorite of ophite-like structure such as serpophite) and carbonatite. The authors of [9] have described a method for water purification in open water reservoirs where they used as a reagent a serpentine product underwent preliminary thermal activation, with the content of serpentine minerals ranging within 80–95 %. The application of the thermally activated serpentine product as a neutralizing reagent is caused by the fact that it exhibits a high activity of interaction with inorganic acids; however, it demonstrates low water solubility, being transformed during the hydration under hypergene conditions into a stable and environmentally safe compound such as serpentine. Non-ferrous metals and iron entering into reaction with the reagent, form silicates stable under hypergene conditions, which prevents the system from secondary contamination [9].

The purpose of the studies was to demonstrate the possibility and efficiency of employing the barriers for sedimentation of nickel ions, which is of currently central importance for the regions of mining and processing of copper-nickel sulphide ores, in particular, for the

Kola Peninsula. So, the annual increase in the stocks of reject materials resulting from enrichment at the Pechenganickel Mining&Metallurgical Combine of the Kola MMC amounts to 7.1 million ton with the content of nickel them equal to ~0.17 % [10]. Except for economic aspect (valuable metal loss), an urgent problem consists in water contamination. So, the content of nickel in water reservoirs located within the activity zone of the Kola MMC, in 2002–2005 ranged from 3.4 to 140 MPC (for fish industry) [11]. Similar situation is inherent also in other nickel-mining regions of both Russia and the world.

EXPERIMENTAL

Active silica was obtained by processing of forsterite concentrate (Table 1) with 25 % sulphuric acid in the presence of a primer at 60 °C. As a primer we used fine-grinded vermiculite those was introduced in the amount of 5 % with respect to the amount of the forsterite concentrate. The presence of the primer provides obtaining silica of lamellar form with improved filtration parameters, which silica exhibits high reactivity due to a highly developed surface.

The composition of carbonatite (the overburden rock of the Kovdor complex ore deposit) is presented in Table 1. As seen, the rock is 80 % composed of calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). The total content of carbonates amounts to 92 %.

We used also serpophite from the Pilguyarvi massif (the Pechenga ore field, the Kola Peninsula). A simplified formula the mineral is $\text{Mg}_5\text{Fe}(\text{OH})_8[\text{Si}_4\text{O}_{10}]$ (see Table 1).

The components of barriers were grinded to obtain the coarseness of $-0.1 + 0.05$ mm.

TABLE 1

Composition of initial components for artificial barriers, mass %

Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	NiO	MnO	FeO	Fe_2O_3	TiO_2	ZrO_2	SiO_2	P_2O_5	CO_2	H_2O
<i>Forsterite concentrate</i>															
0.14	0.14	50.50	144	0.05	0.08	–	0.42	5.45	0.25	0.04	0.3	40.54	0.26	0.87	–
<i>Carbonatite</i>															
0.07	0.04	4.05	49.05	–	0.46	–	–	–	–	–	–	1.24	3.80	41.33	–
<i>Serpophite</i>															
0.06	0.05	35.98	0.29	–	2.17	0.04	0.16	5.73	2.21	0.04	–	40.69	–	0.07	11.80

In order to carry out model experiments a mixture of active silica and carbonatite at a ratio 1 : 1 with the mass of 100 g (geochemical barrier No. 1) and a mixture of serpophite and carbonatite (geochemical barrier No. 2) at the same ratio with the mass of 150 g was placed into columns of 0.2 m high and was then humidified by NiSO_4 solution with the nickel concentration amounting to 0.2 g/L, pH 5.8. The experiments were proceeded during 500 days. The flow rate of the solution amounted to 50 mL/day for the first barrier and 35 mL/day for the second barrier. The periodicity of feeding the initial solution was 10 and 7 mL, respectively, every 2 h during 10 h.

The solutions after filtration through the barriers was collected and chemically analyzed three-daily by the method of flame atomic absorption spectrometry with the use of Kvant-2 AFA spectrometer (with the error of 10 %). We determined the pH value with the help of I-130.2M.1 ionometer, as well as the content of nickel and, in some experiments, the content of magnesium was determined.

For sampling a solid substance from the columns we used a thin-walled glass tube of 1 cm in diameter. We obtained a core of the geochemical barrier substance equal in height to that of the column, which core was then divided into parts. The composition of each sample was averaged and was then investigated using an XRD phase analysis technique as well as chemical analysis. The XRD phase analysis of reaction products was performed using a DRON-2 diffractometer (CuK_α radiation). The analysis nonferrous metal cations was carried out after opening the samples according to a technique described in [12] using the method of flame atomic absorption spectrometry with the use of Kvant-2 AFA spectrometer.

Physicochemical investigation of the interaction between NiSO_4 solution and the geochemical barriers was carried out with the help of a Selector software package in the environment of operational system Windows [13]. For this purpose we used a dynamic model Al-B-Ar-Ne-C-Ca-Cl-F-K-Mg-Fe-Mn-N-Na-P-S-Si-Sr-Cu-Ni-Ti-H-O- \bar{e} (\bar{e} denotes electron) containing 103 components in the aqueous phase, 12 components in the gas phase as well as 152 solid phases, which model represents flowing reservoirs under interaction.

Geochemical barrier No. 1. The solid phase contained 60.084 g of amorphous silica, 48.067 g of calcite and 12.017 g of dolomite. The entire megasystem was open with respect to 1 kg of atmospheric air. The external controlling factor was presented by NiSO_4 solution (600 g of this solution with the content of nickel amounting to 0.2 g per 1 kg of the solution).

Geochemical barrier No. 2. The solid phase contained 55.422 g of serpophite, 44.3376 g of calcite and 11.0844 g of dolomite. The megasystem was open with respect to 1 kg of atmospheric air. The external controlling factor was presented by NiSO_4 solution (600 g of this solution with the content of nickel amounting to 0.2 g per 1 kg of the solution).

The repeatability of events allowed us to investigate the process against the scale of relative time units. The calculations were carried out for the temperature of 20 °C.

RESULTS AND DISCUSSION

Interaction between active silica-carbonatite mixture and nickel sulphate solution

The acidity of NiSO_4 solution after the filtration through the artificial geochemical barrier No. 1 in 3 days is characterized by the value of pH ~ 8; this parameter almost does not change in the entire course of the experiment (Fig. 1, a).

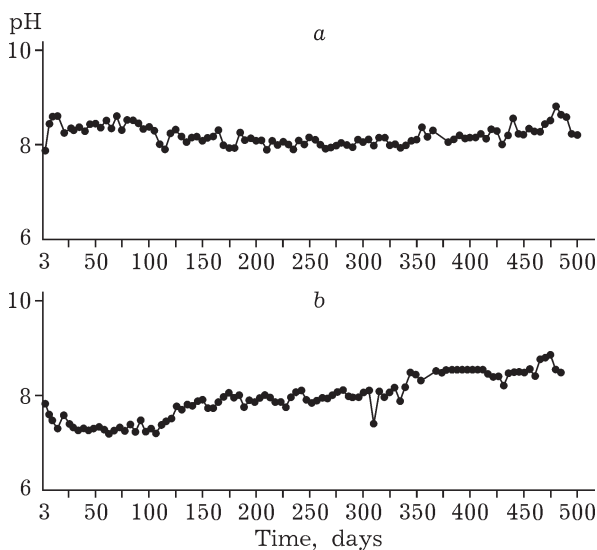


Fig. 1. Variation in the pH of NiSO_4 solution after the filtration through geochemical barriers Nos. 1 (a) and 2 (b).

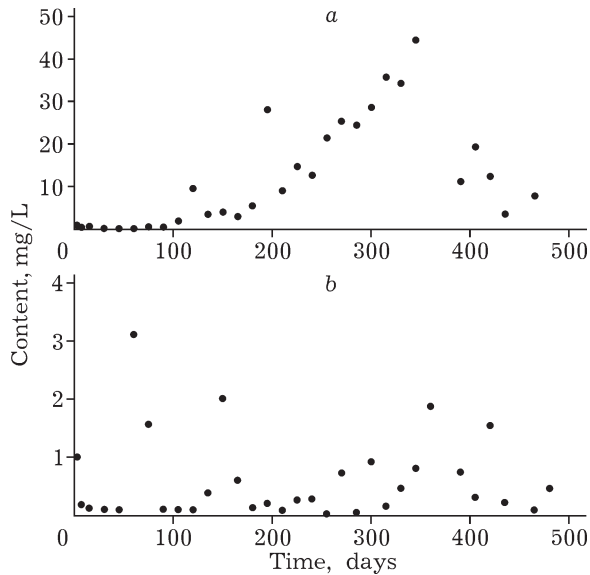


Fig. 2. Residual content of nickel in the solution after the filtration through geochemical barriers Nos. 1 (a) and 2 (b).

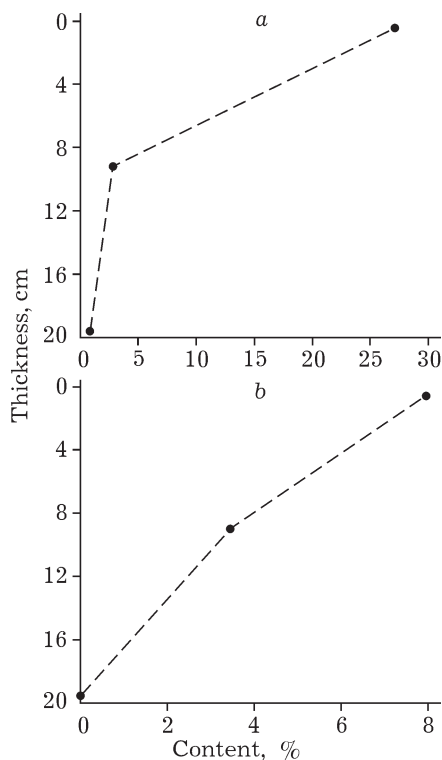
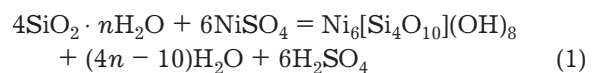


Fig. 3. Nickel content distribution over the layer thickness for geochemical barriers Nos. 1 (a) and 2 (b).

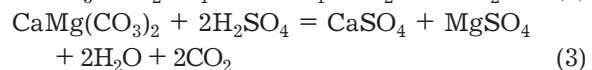
The residual concentration of nickel ions in the solution after the filtration starts to increase slightly after 200 days of the experiments (Fig. 2, a); however after 500 days of the experiment more than 90 % of nickel contained in the solution is observed to precipitate onto barrier No. 1. The cause of somewhat increase in the residual concentration during the second half of the experiment and of the subsequent decrease is not clear yet.

Figure 3, a demonstrates the nickel content distribution over the layer thickness for geochemical barrier No. 1. The observed significant gradient of content is caused by the fact that the purification of solutions occurs in the top layer. It might be assumed that with the increase in the duration of experiments the distribution of nickel content over the thickness of the barrier would be more uniform. After 500 days the average content of nickel in the material of barrier No. 1 has amounted to 2.7 %.

Carbonatite in the composition of the reagent plays the role of a medium regulator. In this case there is a steady alkaline reaction of solutions created. Moreover, the application of active silica included into the composition of the barrier provides forming mainly the deposit of basic hydrosilicates of heavy metals (in our case it is those of nickel) stable under hypergene conditions. The interaction of SiO_2 with the solution of nickel sulphate could result in the reaction



The sulphuric acid formed as the result of the reaction is neutralized with carbonatite:



The occurrence of similar interactions is indicated by the results of XRD phase analysis (Fig. 4). We have registered the formation of laminated silicates of peach type (to all appearance, nickel-containing one) according to reaction (1); in this case the relative intensity of reflexes has been revealed to be higher in the top layer of barrier No.1, wherein a stronger interaction was observed. An absence of calcite reflexes is also inherent in the top layer of barrier No.1, which calcite is consumed according to reaction (2). Dolomite was observed neither in the top layer, nor in the bottom layer.

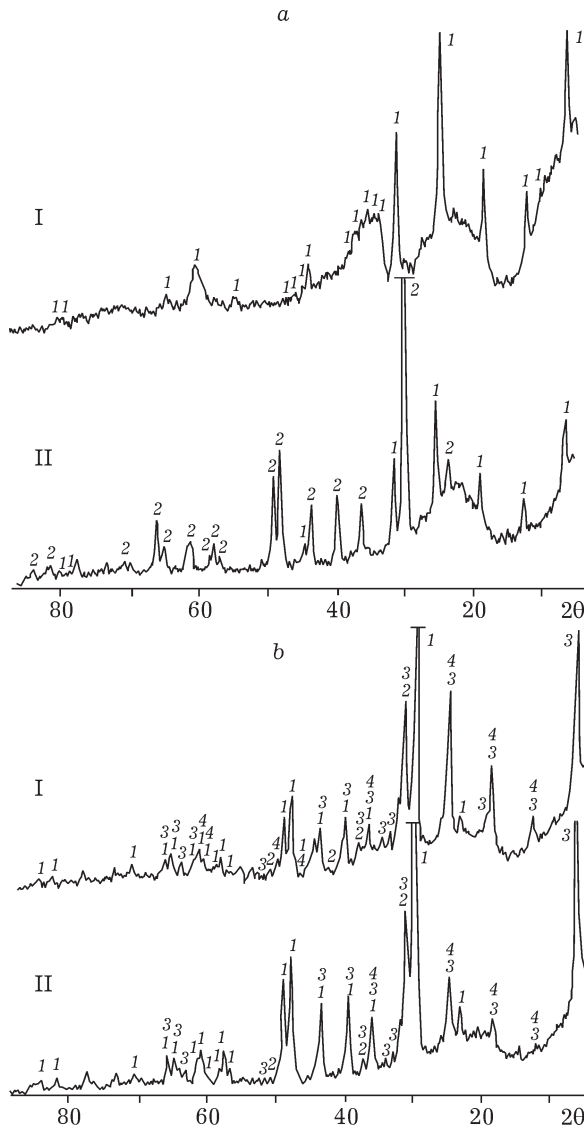


Fig. 4. XRD profiles for mineral phases of geochemical barriers Nos. 1 (a) and 2 (b) after the interaction with NiSO₄ solution. Figures designate the following reflexes: a – peach (1), calcite (2); b – calcite (1), dolomite (2), peach (3), serpophite (4); I, II denote the top and the bottom layer, respectively.

A halo within the range of angles with $2\theta = 20\text{--}30^\circ$ could indicate the presence of active silica.

The results of thermodynamic modelling are presented in Fig. 5, a. The values of pH vary within the range from 8.13 to 8.08, which is in a good agreement with experimental values. With the increase in time we observed an insignificant increase in the concentration of nickel ions. The residual concentration varies within the range from $8.71 \cdot 10^{-6}$ to $1.7 \cdot 10^{-5}$ mg/kg of H₂O. As dolomite is consumed according to reaction (3), there is a considerable increase in the concentration of calcium ions observed to

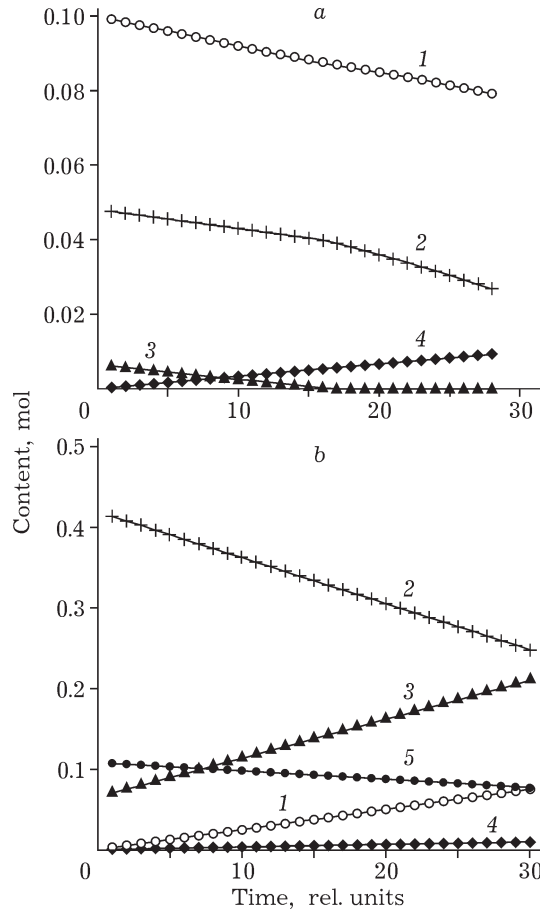


Fig. 5. Variations of the content of minerals in the solid phase of geochemical barriers Nos. 1 (a) and 2 (b) in the course of time: 1 – silica, 2 – calcite, 3 – dolomite, 4 – nickel-containing peach, 5 – serpophite.

occur. As far as the solid phase is concerned, one can observe a quite appropriate decrease in the content of amorphous silica and calcite therein, with disappearing dolomite. The content of nickel-containing peach increases (see Fig. 5, a). The data of modelling are in a good agreement with the processes observed in the laboratory-scale experiments.

Interaction between serpophite-carbonatite mixture and nickel sulphate solution

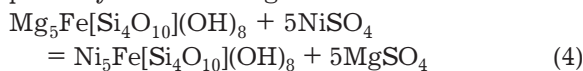
Figure 1, b demonstrates the variation in the pH value for NiSO₄ solution after the filtration through artificial geochemical barrier No. 2. As seen, an insignificant increase in pH value is observed, and after 500 days of such treatment the value has amounted to 8.5.

The residual concentration of nickel ions in the solution after filtration did not exceed 3 mg/L

for all the experiments (see Fig. 2, b), as a result after 500 days of the treatment more than 99 % of nickel contained in the solution is precipitated within barrier No. 2.

Figure 3, b demonstrates the nickel content distribution over the layer thickness for geochemical barrier No. 2. In this case a significant gradient of content (from 8 % almost up to 0) also takes place due to purifying the solutions within the top layers of the barrier. After 500 days of running the experiment, the average content of nickel in the material of barrier No. 2 has amounted to 2.2 %.

The mechanisms of nickel ions precipitation from sulphate solutions with the use of serpentine-like minerals were studied earlier by the authors of [14, 15]. They have demonstrated that there take place both ion exchange, and nickel adsorption onto active centres (surface and structural OH groups). The basic process, to all appearance, could be considered to express by the following reaction:



which results in the formation of nickel-containing peach-like neogenic phases.

The results of XRD phase analysis confirm the fact that similar processes occur (see Fig. 4, b). Within the top layer of the barrier we have distinctly identified peach being, to all appearance, nickel-containing one. The reflexes from calcite in the top layer are less intense than in the bottom layer. Dolomite is detected in an uncertain manner due to a superposition of reflexes. Serpophite is present both in the top, and in the bottom layer.

The results of thermodynamic modelling are presented in Fig. 5. The values of pH are equal to 8.28, which is in a good agreement with the values observed in the experiments. The residual concentration of nickel ions in the solution almost does not change ($\sim 3.6 \cdot 10^{-6}$ mg/kg of H_2O). With the increase in time we observed a decrease of nickel content in the solid phase of calcite, whereas the content of amorphous silica, dolomite and nickel-containing peach exhibits an increase (see Fig. 5, b).

CONCLUSION

It is demonstrated that the combinations of active silica and carbonatite, as well as of ser-

pophite and carbonatite represent promising materials in order to construct artificial geochemical barriers.

As known, the content of nickel in oxidized nickel ores ranges, as a rule, within 0.3–0.4 %. Thus, the average content of nickel precipitated within geochemical barriers obtained as the result of model experiments in formed technogenous ore are quite plausible for organizing its subsequent processing by means of known pyrometallurgical or hydrometallurgical methods [16].

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