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Investigation of the Interaction of the Artificial Geochemical Barrier with Copper Sulphate Solution

D. V. MAKAROV¹, S. I. MAZUKHINA¹, D. P. NESTEROV², YU. P. MENSHIKOV³, I. V. BOCHAROVA²,
A. A. NESTEROVA² and V. A. MASLOBOEV¹

¹*Institute of North Industrial Ecology, Kola Science Centre of the Russian Academy of Sciences,
Ul. Fersmana 14a, Apatity, Murmansk Region 184209 (Russia)*

E-mail: makarov@inep.ksc.ru

²*Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,
Kola Science Centre of the Russian Academy of Sciences,
Ul. Fersmana 26A, Apatity, Murmansk Region 184209 (Russia)*

³*Institute of Geology, Kola Scientific Centre of the Russian Academy of Sciences,
Ul. Fersmana 14, Apatity, Murmansk Region 184209 (Russia)*

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Abstract

Interaction of the artificial geochemical barrier (a combination of serpentine and carbonatite) with the solution of copper sulphate was studied. Chemical, X-ray, derivatographic analyses and thermodynamic modelling were used. It was demonstrated that the products of the interaction of the barrier with copper sulphate solution are basic copper sulphates – brochantite and poznyakite, as well as chlorite-like phases.

Key words: artificial geochemical barriers, copper precipitation, physicochemical geotechnologies, purification of natural and waste water

INTRODUCTION

The concept of “geochemical barriers” was proposed by Prof. A. I. Perelman [1]. The main feature of the barriers consists in abrupt changing the conditions of migration and concentration of elements. Just the geochemical barriers are the sites where orebodies of many fields are formed, so it is important to study the barriers for developing geochemical exploration techniques. In addition, their study is important for developing methods for reducing environmental pollution, for physical and chemical geotechnologies, for organizing underground leaching of ores, for grouting in construction [2–4]. In these technologies one could use existing natural and artificial geochemical barriers. As materials for the barriers one could use both natural features (soil, rocks, peat), and man-caused wastes (pyrite cinder, waste soda products) [2].

It was demonstrated earlier that the combination of the serpentine and carbonatite represents a promising material for the deposition of nickel [5]. The aim of this work consisted in studying the interaction between this barrier and CuSO_4 solution.

EXPERIMENTAL

Products used for artificial geochemical barriers were described in detail in [5]. Carbonate (the overburden of the Kovdor deposit of complex ores, Kola Peninsula) consists of calcite CaCO_3 (80 %) and dolomite $\text{CaMg}(\text{CO}_3)_2$. Total carbonate content amounted up to 92 %. We used serpentine (serpophite) from the Pilguyarvi range (Pechenga ore field, the Kola Peninsula). A simplified formula of the mineral is described as $\text{Mg}_5\text{Fe}(\text{OH})_8[\text{Si}_4\text{O}_{10}]$. A mixture (150 g) of serpophite and carbonatite grinded to a size of

-0.1 ... + 0.05 mm, with the mass ratio of 1 : 1 was placed into a separating funnel of 0.2 m in height wetting with solution CuSO_4 containing 0.1 g/L of copper. The experiment lasted for 500 days. The solution flow rate was equal to 35 mL/day. The feed frequency of the stock solution was 7 mL every two hours during 8 h. The solution after the filtration through the barrier material was accumulated to perform the chemical analysis once every 3–5 days. We determined pH (using I-130.2M.1 ionometer) and residual copper content. We used flame atomic absorption spectrometry technique employing a Kvant-2 AFA spectrometer (with the error less than 10 %). For sampling the solid from the columns we used a thin-walled glass tube. We obtained a core of geochemical barrier substance equal to the funnel height; it was then divided into parts. The composition of each sample was averaged for chemical and XRD phase analysis using DRON-2 diffractometer (CuK_α radiation). The thermogravimetric studies were performed by means of Q-1500D derivatograph.

The physicochemical study on the interaction of the solution with CuSO_4 geochemical barrier was performed using Selector software package (Windows) as described in [6]. Calculations were carried out at 20 °C. In developing the model we tried make the system close with respect to that observed in the laboratory experiments. The solid phase contained 55.42 g of serpophite, 44.34 g of calcite and 8.11 g of dolomite. The system was opened with respect to to 1 kg of atmospheric air. The barrier thickness was divided into three layers. The external controlling factor was presented by a copper sulphate solution (60 g of solution for a rel-

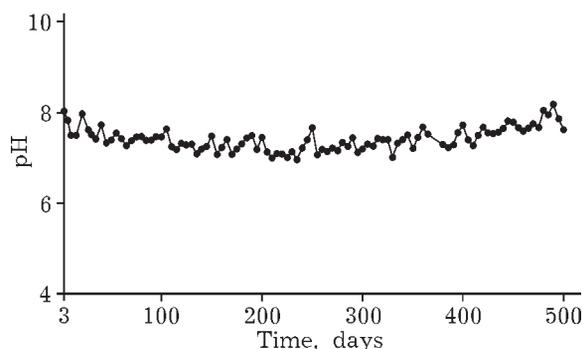


Fig. 1. Changing the pH value of the solution after filtration through CuSO_4 geochemical barrier.

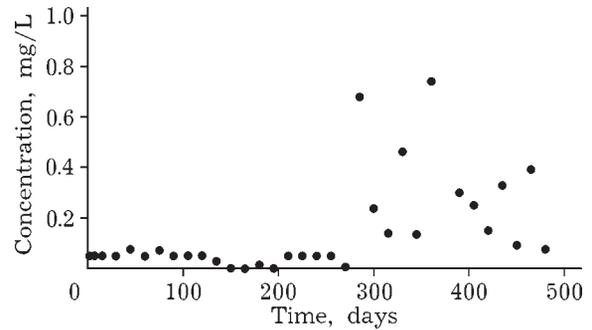


Fig. 2. Residual concentration of copper in the solution after filtration through the geochemical barrier.

ative temporal cycle, the copper concentration being equal to 0.1 g/kg of solution). It was assumed that in each layer the reaction involved 10 % of the substance. The repeatability of events allowed us to study the process in relative time units. The total number of time cycles was equal to 500.

RESULTS AND DISCUSSION

Figure 1 demonstrates changing the pH value for the solution after the filtration through CuSO_4 artificial geochemical barrier. It can be seen that pH changes over time insignificantly, whereas the average of pH is about 7.8.

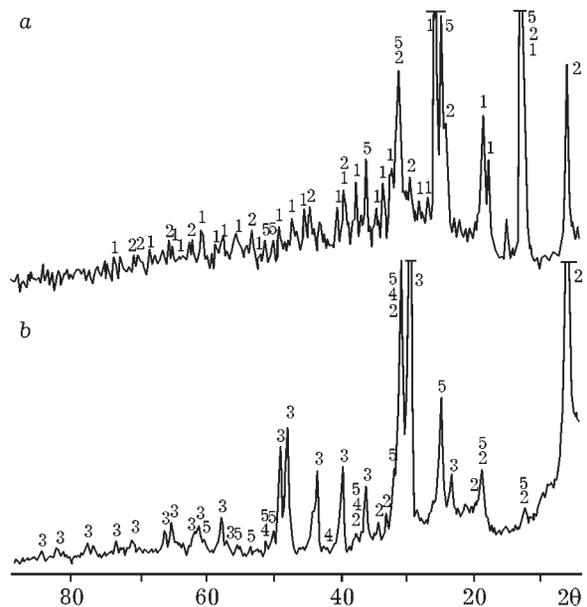


Fig. 3. XRD patterns for the mineral phases of the upper (a) and bottom (b) layers of the geochemical barrier after interacting with CuSO_4 solution: 1 – poznyakite, 2 – chlorite, 3 – calcite, 4 – dolomite, 5 – serpophite.

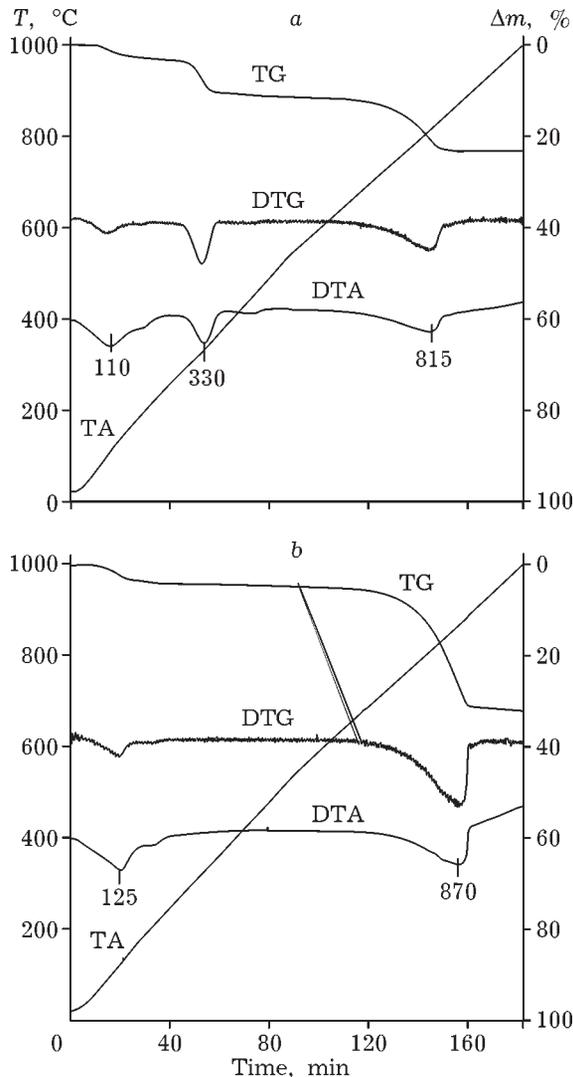


Fig. 4. Derivatographic curves for the samples of the upper (a) and bottom (b) geochemical barrier layers after the reaction with CuSO_4 solution.

The residual concentration of copper ions in the solution after the filtration is mainly less than 0.2 mg/L (Fig. 2). After 300 days of the experiment we observed some “spikes” of the values of the residual concentration up to 0.5–0.8 mg/L, whose cause is not quite clear.

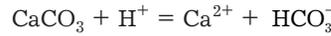
For the solid phase of the barrier, we observed a significant gradient of copper content, from 15.8 % in the thin top layer up to 0.017 % in the bottom layer.

The XRD results for the solid phase inherent in various layers of the barrier are demonstrated in Fig. 3. As the upper layers of the barrier is concerned, basic copper sulphate such as poznyakite $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$ is clearly registered therein. Neither calcite nor dolomite were

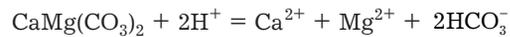
found in the upper layers. Reflexes inherent in chlorite-like phase appeared registered in both upper and lower layers.

In this case, the basic processes to be considered, to all appearance, are they:

– the dissolution of carbonates, mainly in the upper layer:

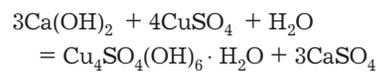


(1)

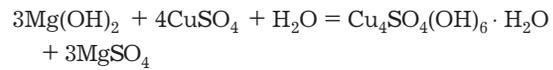


(2)

– the formation of poznyakite according to the reactions

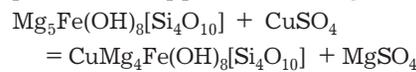


(3)



(4)

– appearing chlorite-like phases, to all appearance, copper-containing ones:



(5)

Figure 4 presents the results of the thermal analysis for the substance of the upper and lower layers of the barrier after the reaction with the solution of copper sulphate. The DTA curve for the material of the top layer of the barrier is characterized by three endothermic effects, corresponding to the three stages of mass loss (see Fig. 4, a). Unfortunately, the process of the thermal decomposition of serpentine, chlorite and poznyakite occur within similar temperature ranges, so the estimation of the proportion of mineral phases basing on the thermogravimetric data is likely not possible. The reduction of the mass within the temperature range of 80–200 °C could be caused by the removal of adsorbed water from serpentine (chlorite) and crystallization water from poznyakite [7]. The endothermic effect accompanied by the mass loss within the temperature range of 275–355 °C, is associated with the removal of water from the poznyakite to form tenorite (CuO), antlerite ($\text{Cu}_3(\text{SO}_4)(\text{OH})_4$) and dolerophanite ($\text{Cu}_2(\text{SO}_4)\text{O}$) [7]. The third area of the mass reduction in the temperature range 672–852 °C could correspond to the removal of OH groups from serpentine (chlo-

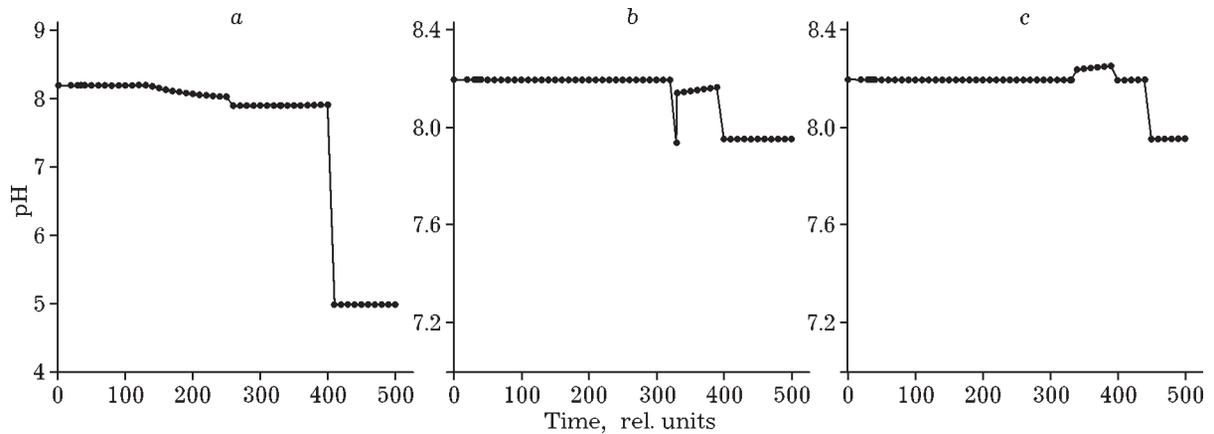


Fig. 5. Solution pH depending on time after filtering through the top (a), middle (b) and bottom (c) layers of the geochemical barrier according to physicochemical modeling.

rite) with the destruction of its structure and desulphation of dolerophanite [7]. The DTA curve for the substance from the lower layer of the barrier exhibits two endothermic effects, corresponding to the two stages of mass loss on the TG curve (see Fig. 4, b). The first effect with a minimum at 125 °C is associated with the loss of adsorbed water by serpentine; the second one (at 370 °C) could be connected with the removal of OH groups from serpentine (chlorite) and with the decarbonisation of calcite [7]. Because of a small amount of the carbonate in the sample of dolomite the effect of MgCO_3 decarbonisation is not recorded as a separate minimum.

Data concerning the physicochemical modelling are presented in Figs. 5–7. It is seen that the upper layer is characterized by a monotonic decrease in the pH of two small inflections.

Then, after 400 cycles, there is a sharp decrease of the value down to level of pH 4.98 (see Fig. 5, a). The inflections on the pH–time curve correspond to reducing the content of calcite and dolomite in the solid phase down to their disappearance; whereas a sharp reduction of the pH corresponds to the disappearance of serpentine (see Fig. 6, a). In contrast to the laboratory experiments those resulted in the formation of poznyakite, in the model there is an initially sharp and then gradual increase in the content of another basic copper sulphate such as brochantite $\text{Cu}_4\text{SO}_4(\text{OH})_6$. In the solid phase, there were also chlorite and silica registered. There is also a synchronous behaviour observed of the residual concentration of copper ions in the solution after filtering through the top layer (see Fig. 7, curve 1). The interac-

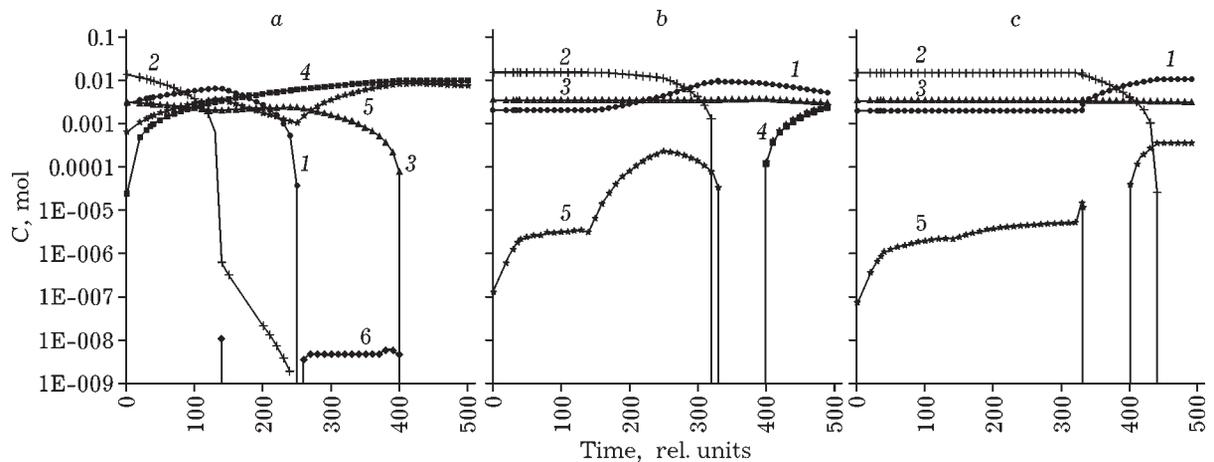


Fig. 6. Content of minerals depending on time in the solid phase of top (a), middle (b) and lower (c) geochemical barrier layers according to physicochemical modelling: 1 – dolomite, 2 – calcite, 3 – serpophite, 4 – brochantite, 5 – silica, 6 – chlorite.

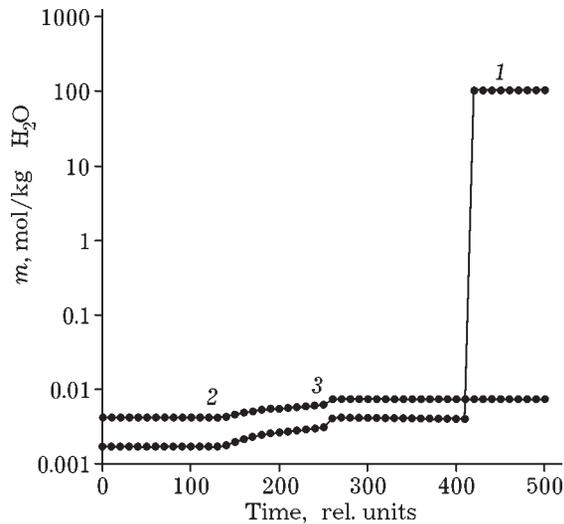


Fig. 7. Residual concentration of copper ions depending on time in the solution after filtering through the top (1), middle (2) and lower (3) geochemical barrier layers according to physicochemical modelling.

tion between CuSO_4 solution and the middle and lower layers is similar. The decrease of the solution pH at the outlet of the middle layer from pH 8.16 to 7.95 correlates with a decrease in pH after filtering through the top layer (see Fig. 5, a, b). After 300 cycles, the content of calcite in the solid phase abruptly decreases (see Fig. 6, b). The content of the serpentine is stable, whereas the dolomite content somewhat increases. After 400 cycles, in the middle layer the formation of brochantite begins (see Fig. 6, b). The residual concentration of copper ions in the solution after the filtration through a middle layer during 500 cycles increases insignificantly (see Fig. 7, curve 2). The pH value after filtering through the lower layer slightly decreases (from pH 8.20 to pH 7.95) after 440 cycles (see Fig. 5, c). This moment of time corresponds to the reduction of the content of calcite in the solid phase of the layer (see Fig. 6, c). The residual concentration of Cu^{2+} ions changes with time like it does for the middle layer (see Fig. 7, curve 3).

Thus, the model reflects the zonation observed in the thickness of the geochemical barrier concerning the distribution of initial and newly formed mineral phases and copper content. It is obvious that with the increase in temporal cycles the patterns observed for the top layer, there should be observed in the middle

and lower layers up to a complete disappearance of the initial minerals and the saturation of the barrier.

CONCLUSIONS

It was demonstrated that the combination of serpentine and carbonatite represents a promising geochemical barrier for copper deposition. Long-term interaction between minerals and copper sulphate solution results in the formation of new phases, basic sulphates such as poznyakite (brochantite) and layered hydro-silicates such as chlorite. The results of physicochemical modelling confirm in general the data of laboratory experiments and allow one to predict the behaviour of the barrier in the course of interaction with the solution.

One of possible scopes of the geochemical barriers is physicochemical geotechnology where they can act as a layer under enriching with the formation of a technological barrier in the material of ores [4, 5]. During the entire time our experiment more than 99.8 % of metal (except for separate "bursts") was deposited on the barrier. The average copper content in the material of the barrier amounted to 1.16 %. In principle, provided an associated deposition of other non-ferrous metals (nickel, cobalt), the resulting product could be characterized as a man-caused ore to be profitably processed using hydro- and pyrometallurgical methods. It should be also noted that this demonstrates the fundamental possibility of the barrier in geotechnology. It is required to search for the best technological solutions in order to provide the intensification of filtering the solutions and metal deposition, reducing the metal content gradients across the thickness of the barrier layer, etc.

The second scope for using the geochemical barriers is presented by natural and waste waters. We performed laboratory tests of the barrier with the use of contaminated water in the area of the enterprise PC «Kola MMC». We used natural water from the Nyudyavr Lake located within the zone of the Severonickel Plant. The water has the following composition, g/L: Ni 389, Cu 53.7, Fe 264, pH 6.8. Our experiments were carried out under static conditions simulating the ability to add reagents to the aqueous phase of a tailing pit as well as to nat-

ural reservoirs. It was found that with the reagent-to-water ratio equal to 10–20 g/L the residual concentrations of metals in the solution does not exceed the maximum permissible concentration for fishery ponds.

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