Application of Geochemical Barriers for Purification of Industrial Waters from Non-Ferrous Metals

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Summary

The article shows the possibility of using as artificial geochemical barriers various reactive minerals and waste tailings copper-nickel ores of the Pechenga ore field of the Murmansk region. We investigated the sorption of ions nickel by natural magnesium-containing hydrosilicates such as: serpophite $Mg_5Fe(OH)_8[Si_4O_{10}]$, talc $Mg_{2\cdot 5}Fe_{0.5}(OH)_2[Si_4O_{10}]$ and biotite $KMgFe_2(OH)_2[AlSi_3O_{10}]$. The greatest pH growth was observed when serpophite was used. Extraction of nickel increases with increasing ratio of mineral/solution. The diffraction patterns of minerals significantly change in the crystal lattice, manifested in the broadening and strengthening of asymmetry of basal reflections. Interaction of nickel sulfate solutions at pH 1-3 with serpentine minerals leads to the formation of pimelites ($Ni_3Si_4O_{10}(OH)_2.4H_2O$) and when the acidity of the solutions is less minerals of garnierity type $Ni_6Si_4O_{10}(OH)_8$ are formed. The interaction of nickel sulphate solution with talc leads to the formation of villemseites ($Ni_3Si_4O_{10}(OH)_2$). During the interaction of the nickel sulphate solution with biotite the formation of minerals of pimelite type ($Ni_3Si_4O_{10}(OH)_2.4H_2O$) is observed. Also, experiments were conducted on the sorption of iron, copper, nickel by granulated tailings copper-nickel ores thermally activated at 650°C (barrier №1) and 700°C (barrier № 2). The compressive strength of the obtained granules 2.19 (650°C) and 1.92 (700°C) MPa. For the experiments under dynamic conditions granules was wetted with a sulphate solution containing 0.1 g/L of Ni^{2+}, 0.05 g/L Cu^{2+} and 0.1 g/L Fe^{2+}. After 30 days the residual concentration to the ions of non-ferrous metals for the barrier №1 and barrier №2 after filtration through barriers for iron ions was 85.2% and 93.2%, 74.4% of the copper ions and 65.2%, 53.7% of nickel ions and 63.3%, respectively. Interaction sulfate solutions, containing with ions non-ferrous metals, with minerals leads to their deposition as a result of isomorphic substitution of isovalent. Experiments in dynamic conditions, shown perceptivity of using thermally activated tailings copper-nickel ores as material for creating geochemical barriers.

Keywords: geochemical barriers, physicochemical geotechnologies, management of natural and waste water, non-ferrous metal reduction, serpophite, talc, biotite, copper-nickel tailings

Introduction

Mining and processing plants are one of the most powerful sources of anthropogenic pollution. During ore production and dressing huge rock masses are extracted and processed, no more than 2% of the rocks are used in the production process the rest is stored in slag and tailing dumps. According to the reports of the enterprises operating in the Murmansk region the wastes of the mining industry (tailings, waste rock, etc.) comprise more than 99% of all production and consumption wastes in the area.

The areas of storage of mining wastes suffer from environmental pollution which can be prevented by using geochemical barriers on the pollutants migration path. Geochemical barriers represent certain areas of the Earth's crust with a slower drift of chemical elements and, consequently, their higher concentrations (Perelman, 1989). In recent decades the geochemical barriers have been actively used for both technological and environmental purposes.

Apart from the use of artificial geochemical barriers for natural and industrial water purification from heavy metals, radioactive elements and oil products they can be used for:

- re-extraction of valuable components from natural and technological materials using physicochemical geotechnologies;
- damp proofing of tailings and slime dumps, settlers, accumulation tanks, etc.;
- soil solidification in construction.

Geochemical barriers can be used to solve various problems:

- arrangement of antifiltration barriers;
- filtering of solutions through the barrier followed by depositioning of pollutants;
- adding a barrier material to solution (in natural water bodies, tailings dumps, settlers, etc.).

Materials for artificial geochemical barriers can be:

- various industrial wastes (overburden rock, tailings) containing chemically active minerals;
- mixtures of reactive or modified minerals;
- products and wastes of complex chemical and metallurgical processing of ores and concentrates.

Chemically activated minerals such as serpophite $Mg_5Fe(OH)_8[Si_4O_{10}]$, talc $Mg_{2.5}Fe_{0.5}(OH)_2[Si_4O_{10}]$ and biotite $KMgFe_2(OH)_2[AlSi_3O_{10}]$ can be used as a material for creation of geochemical barriers. These minerals can be found in the structure of copper-nickel tailings from the Pechenga ore field. The application of local mining and processing wastes will reduce the cost of pollution abatement.

Materials and methods

We carried out experiments on sorption of nickel by natural magnesium-containing hydrosilicates: serpophite $Mg_5Fe(OH)_8[Si_4O_{10}]$, talc $Mg_{2.5}Fe_{0.5}(OH)_2[Si_4O_{10}]$ and biotite $KMgFe_2(OH)_2[AlSi_3O_{10}]$. Monomineral fractions of serpophite and talc from Pilgujarvi massif of the Pechenga deposit were used in the experiments, together with biotite fractions from a ceramic pegmatite vein of the Kuruvaara deposit, the Kola Peninsula. Monomineral fractions were ground down to size 0.1 mm. In static experiments a mineral was added to a nickel -containing solution in proportion of 1, 5, 10, 20, 40 g/L. The reaction of the solution and the mineral was studied with continuous stirring for 3h. The solution pH was checked each 5–10 min. Concentrations of nickel sulfate solution corresponded to 0.1 N in experiments. Then the liquid phase was analyzed using atomic absorption spectrometry (Kvant-2 AFA), solid phases were studied using X-ray diffraction (XRD).

Also the experiments on the sorption of heavy metals by granulated copper-nickel tailings from the Pechenganikel combine were performed. The 60% of the tailings consist of serpentine, chlorite and talc. The tailings were ground down to size -0.063 mm. Granulation was carried out using as a binder lignosulfonate, granule diameter was 0.5 cm. The granules were thermally activated for 2 hours at temperatures of 650^{o}C and 700^{o}C. The compressive strength of the obtained granules was 2.19 (650^{o}C) and 1.92 (700^{o}C) MPa. The sorption of ions of nickel, copper and iron was investigated in dynamic conditions.

For the dynamic experiments 150 g of granules were placed into a column of 0.2 m height, and moistured by a sulphate solution containing 0.1 g/L Ni^{2+}, 0.05 g/L Cu^{2+} and 0.1 g/L Fe^{2+}. Eh and pH values of the solution were 3.84 and 199 mV. The experiments lasted for 30 days. The solution consumption was 75 ml/day. The feed solution was supplied in the amount of 15 ml each 2 hours during 8 hours.

Results and discussion

Interaction of minerals with the nickel sulfate solution

The solid phase acquires a brighter green color after the reaction with the solution. There is large amount of finely dispersed material in it. The graphs of the Fig. 1 show a decrease in pH, which is probably due to the formation of solids on the surface of the mineral which stops the reaction, and its rate is controlled by diffusion of the solution through the film of growths. If the diffusion rate is lower than the rate of hydrolysis of the dissolved salt the pH of the solution decreases. During the interaction of nickel sulphate solution with serpentinite minerals there is the ion exchange between the solid and liquid phases and the equilibrium is established between them. The distribution coefficient of nickel and magnesium in the solid phase and the solution is based on the solution pH.

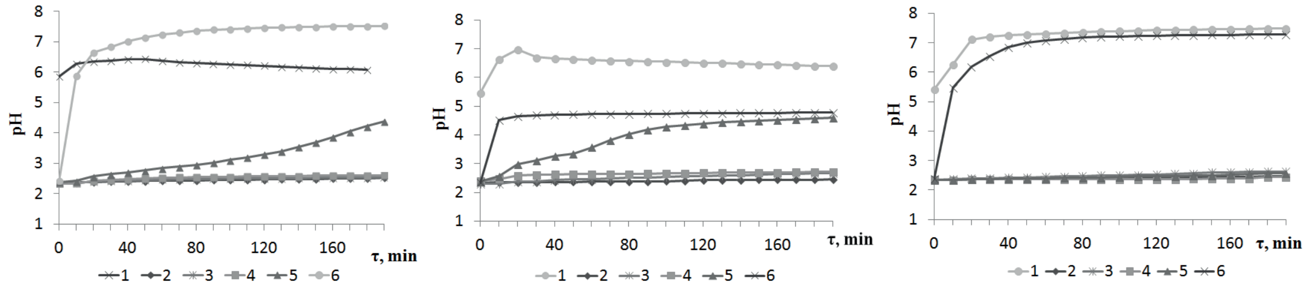
In highly acidic initial solutions (pH=1-3) the Mg-Ni exchange reactions concur with reactions Mg-2H or Mg-2H3O. The resulting montmorillonite-like (saponite) layers in serpentine promote the formation of nickel-bearing saponites (pimelites $Ni_3Si_4O_{10}(OH)_2.4H_2O$).

Nickel is present in the mineral due to exchange reactions of 2K-Ni, Mg-Ni and, to a lesser degree, of Fe-Ni reaction. Nickel may be incorporated in the octahedral layers and may act as an interlayer cation. The composition of tetrahedral layers remains practically unchanged. In case of biotite there is no dependence of the coefficient of the nickel and magnesium distribution in the solid phase and the solution from the pH value. Presumably, this is due to the presence of other cations - potassium and, to a lesser extent, iron in solution and in solid phase.

The interaction of nickel sulfate solutions with talc can be generally reduced to exchange processes of the Mg-Ni type and results in formation of villemseit $Ni_3Si_4O_{10}(OH)_2$. There is a correlation between the nickel and magnesium distribution coefficient and the pH value. At higher pH values the concentration of nickel ions is decreasing and the concentration of magnesium ions is increasing.

The authors have studied the mechanism of replacement of Mg-Ni by the example of serpophite, talc, and biotite by using X-ray diffraction method. The diffraction patterns were recorded at a scan rate of 0.5 deg/min in the 2Θ angle range from 6° to 60° for talc, from 4° to 40° for serpophite, from 6° to 46° for biotite.

Talc X-ray diffraction patterns demonstrate the change of the crystal lattice, manifesting themselves in strengthen-



a b c

Fig, 1 Dependence of the solution pH from the time of interaction of 0.1N of $NiSO_4$ solution with minerals (fraction -0,1 mm): a - serpophite, b - biotite, c - talc
1 - without acidification (consumption 5 g/L), 2 - consumption 1 g/L, 3 - consumption 5 g/L,
4 - consumption 10 g/L, 5 - consumption 20 g/L, 6 - consumption 40 g/L

Rys. 1 Zależność pH roztworu od czasu oddziaływania 0,1N roztworu NiSO4 z minerałami (frakcja -0,1 mm):
a - serpofit, b - biotyt, c – talk
1 – bez zakwaszania (pobór 5g/L), 2 – pobór 1g/L, 3 – pobór 5g/L,
4 – pobór 10g/L, 5 – pobór 20g/L, 6 – pobór 40g/L

Tab. 1 Parameters of the talc basal reflections before and after the reaction with 0.05 N of nickel sulfate solution: 1 - without acidification, 2 - with acidification

Tab. 1 Parametry odbicia światła talku przed i po reakcji z 0,05 N roztworem siarczanu niklu: 1 - bez zakwaszenia, 2 - z zakwaszaniem

Parameter	Sample		
	Intact	1	2
H/b006	19.38	10.92	12.87
H/b0010	2.58	1.01	1.28
H/b0012	1.00	0.56	0.96
I006/I0010	19.375	16.620	13.353
I0012/I0010	0.625	0.647	0.662
A006	0.818	1.467	1.571
A0010	0.950	1.182	1.250
A0012	1.000	0.867	0.846

Tab. 2 Parameters of the basal reflections of serpophite before and after the reaction with 0.05 N nickel sulfate solutions (consumption of serpophite: 1 – 15 g/L, 2 – 10 g/L, 3 – 6 g/L, 4 – 2 g/L)

Tab. 2 Parametry odbicia światła serpofitu przed i po reakcji z 0,05 N roztworem siarczanu niklu (zawartość serpofitu: 1 – 15 g/L, 2 – 10 g/L, 3 – 6 g/L, 4 – 2 g/L)

Parameter	Sample				
	Intact	1	2	3	4
H/b001	5.95	8.00	7.09	6.02	6.33
H/b002	6.06	7.75	5.92	6.08	5.49
H/b003	0.88	1.69	1.83	1.21	1.40
I001/I002	0.848	0.862	0.902	0.830	0.812
I003/I002	0.051	0.066	0.072	0.066	0.080
A001	0.39	0.52	0.42	0.38	0.33
A002	1.421	1.5	1.31	1.32	1.38

Tab. 3 Parameters of the basal reflections of biotite before and after the reaction with 0.05 N $NiSO_4$ solutions (consumption of serpophite: 1 – 22.46 g/L, 2 – 13.48 g/L, 3 – 4.5 g/L, 4 – 2.25 g/L)

Tab. 3 Parametry odbicia światła biotytu przed i po reakcji z 0,05 N roztworem NiSO4 (zawartość serpofitu: 1 – 22.46 g/L, 2 – 13.48 g/L, 3 – 4.5 g/L, 4 – 2.25 g/L)

Parameter	Sample				
	Intact	1	2	3	4
H/b001	6.19	8.57	7.88	4.76	3.23
H/b002	0.64	2.00	1.50	1.36	0.90
H/b003	8.79	9.49	9.25	8.63	7.23
I002/I001	0.042	0.055	0.058	0.063	0.065
I003/I001	1.53	1.14	1.28	1.57	2.08
I004/I001	0.28	0.30	0.315	0.34	0.302
A001	3.15	1.79	1.75	1.89	1.96
A002	2.44	1.00	1.22	2.67	1.49

ing of 006 and 0010 asymmetric basal reflexes (Table 1).

Serpophite X-ray diffraction patterns record the appearance of montmorillonitic layers, which alternate with serpentinite layers at random. The extra lines characteristic of other layered silicates are not found. The background shows that there is no amorphous phase in the samples. The appearance of montmorillonite layers which alternate with serpentine layers at random, should broaden the reflections, reduce the relative intensity of reflection 001, and strengthen the skewness of reflections 001 and 002 (Table 2). We suppose that some structure ordering is observed in the run at a high reagent consumption. However, at lower reagent/solution ratio the role of the montmorillonite layers increases again (Makarov et al., 2005).

On the X-ray diffraction patterns of biotite after treatment with a solution of nickel sulfate significantly change basal reflections. With high solution consumptions, the basal reflections become narrower and higher, indicating a higher perfection of the mineral structure. At moderate solution consumptions, the reflections become lower and

Tab. 4 Nickel concentrations after interaction with the minerals

Tab. 4 Stężenie niklu po interakcji z minerałami

Consumption, g/L	1	5	10	20	40
Talc					
Concentration Ni, g/L	2.48	2.24	2.35	2.52	2.10
Extraction, %	15.36	23.55	19.80	13.99	28.33
Serpophite					
Concentration Ni, g/L	2.44	2.50	2.25	2.18	1.94
Extraction, %	16.72	14.68	23.21	25.60	33.79
Biotite					
Concentration Ni, g/L	2.52	2.35	2.37	2.21	1.88
Extraction, %	13.99	19.80	19.11	24.57	35.84

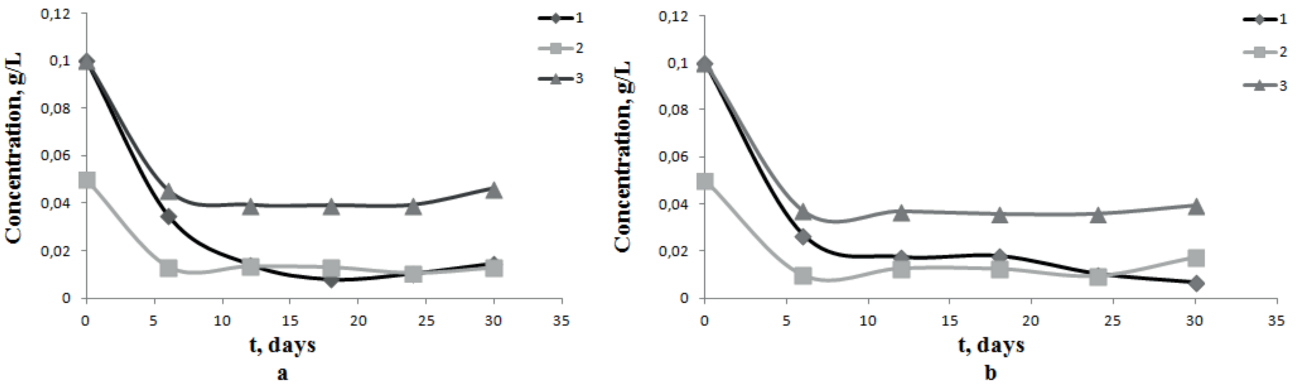


Fig. 2 The residual concentration of ions of the iron (1), copper (2), nickel (3) in solution after filtration through a barrier №1 (a) and the barrier №2 (b)

Rys. 2 Resztkowe stężenie jonów żelaza (1), miedzi (2), nikilu (3) w roztworze po przesączeniu przez barierę №1 (a) i barierę №2 (b)

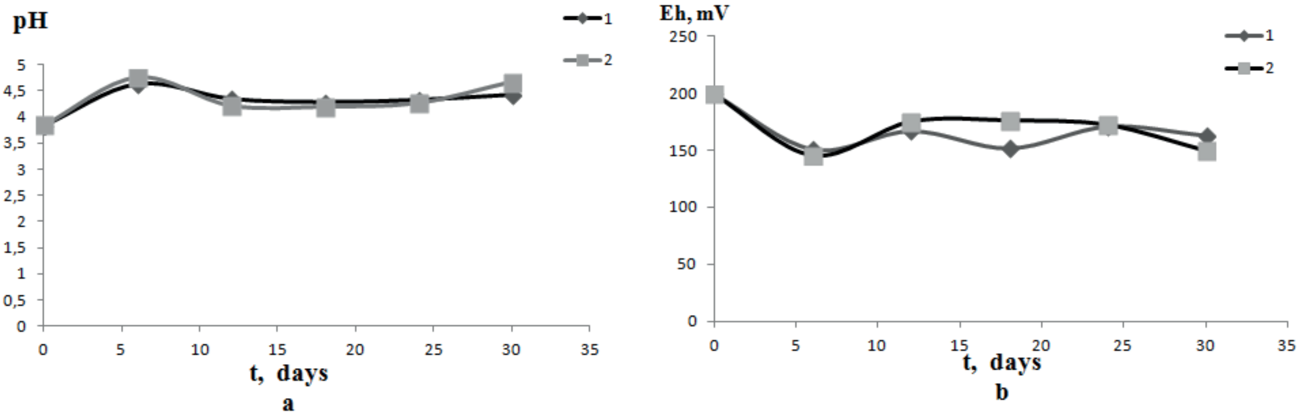


Fig. 3 Changing of value pH (a) and Eh (b) a solution of sulphate nickel, copper and iron after filtration through a thermally activated tailings copper-nickel ores (1- barrier №1 by thermal activation at 650°C; 2- barrier №2 by thermal activation at 700°C.)

Rys. 3 Zmiana wartości pH (a) i Eh (b) w roztworze siarczanu niklu, miedzi i żelaza po filtracji przez aktywowane termicznie odpady rudy miedziowo-niklowej (1- bariera №1 przez aktywację termiczną w temperaturze 650°C; 2- bariera № 2 przez aktywację termiczną w temperaturze 700°C).

broader. The reflection intensity I003/I001 decreases at high solution consumptions and increases at low consumptions relative to those in the starting mineral. The intensity ratios I002/I001 and I004/I001 in all treated samples are higher (Table 3), whereas the reflection asymmetry is lower than in the starting mineral (Makarov et al., 2008).

The X-ray diffraction studies didn't reveal any new mineral phases. Optical methods failed to reveal them either.

In static conditions the mineral fractions of the size -0.1 mm with various mineral/solution ratio were used for nickel deposition from the solution. The initial Ni^{2+} concentration in the solution was 2.93 g/L, reaction time - 3 hours. The nickel recovery grows with increase of the consumption of the minerals.

Interaction thermoactivation tailings with sulfate solution containing nickel, copper and iron

During the filtration of a multi-component sulfate solution containing 0.1 g/L Ni^{2+}, 0.05 g/L Cu^{2+} and 0.1 g/L Fe^{2+}, through granulated a copper-nickel tails, the extraction of iron ions for the barrier №1 (copper-nickel tails thermally activated at 650° C) and barrier № 2 (copper-nickel tails thermally activated at 700° C) after 30 days was 85.2% and 93.2%, ions copper 74.4% and 65.2, ions nickel 53.7% and 63.3% respectively (Figure 2). The value pH increased in at the beginning of the experiment, then there was a decrease and value stabilized at 4.43-4.67 (Figure 3).

Conclusions

When minerals interact with the nickel sulfate solution the pH value grows with the increase of consumption of a mineral, more significantly when adding serpophite. The diffraction patterns of the minerals show a significant change of the crystal lattice which manifested itself in broadening and strengthening of the asymmetry of basal reflections. Interaction of nickel sulfate solutions at pH 1-3 with serpentine minerals leads to the formation of pimelites ($Ni_3Si_4O_{10}(OH)_2.4H_2O$) and when the acidity of the solutions is less minerals of garnierity type $Ni_6Si_4O_{10}(OH)_8$ are formed. The interaction of nickel sulphate solution with talc leads to the formation of villemseites ($Ni_3Si_4O_{10}(OH)_2$). During the interaction of the nickel sulphate solution with biotite the formation of minerals of pimelite type ($Ni_3Si_4O_{10}(OH)_2.4H_2O$) is observed. The interaction of non-ferrous metal sulfate solutions with these minerals leads to their deposition as a result of isomorphic substitution of isovalent. The nickel extraction increases with increased natural mineral/solution ratio.

In our research we managed to achieve significant reduction of the ion concentrations of Ni^{2+}, Cu^{2+} and Fe^{2+} when granulated thermally activated copper-nickel tailings were used as a sorbent. The sorption of ions Ni^{2+} and Fe^{2+} was more active in the barrier № 2, which consisted of granulated copper-nickel tailings thermally activated at 700°C. The sorption of Cu^{2+} ions was more active in the barrier № 1, which consisted of granulated copper-nickel tailings thermally activated at 650°C. This can be explained by the fact that the amorphization of serpentine minerals followed by the release of constitutional water was not finished in the copper-nickel tailings at 650°C.

Acknowledgements

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Zastosowanie barier geochemicznych w celu oczyszczania ścieków przemysłowych z metali nieżelaznych

Artykuł przedstawia możliwość zastosowania różnych reaktywnych metali i odpadów końcowych z rud niklowo-miedzianych z rud Penchenga z regionu Murmańsk jako sztucznych barier geochemicznych. Zbadano sorpcję jonów niklu za pomocą naturalnych hydrosilikatów zawierających magnez takich jak: serpofity $Mg_5Fe(OH)_8[Si_4O_{10}]$*, talk* $Mg_{2.5}Fe_{0.5}(OH)_2[Si_4O_{10}]$ *i biotyt* $KMgFe_2(OH)_2[AlSi_3O_{10}]$*. Największy wzrost pH zaobserwowano gdy użyty był serpofit. Ekstrakcja niklu zwiększa się wraz ze wzrastającym stosunkiem minerał/roztwór. Obraz dyfrakcyjny minerałów zmienia się znacznie w sieci krystalicznej, okazując się w poszerzaniu i wzmacnianiu asymetrii odbicia podstawowego. Interakcja roztworu siarczanu niklu z minerałem serpentynowym przy pH 1-3 prowadzi do powstawania pimelitów (*$Ni_3Si_4O_{10}(OH)_2.4H_2O$*), a gdy kwasowość roztworu jest mniejsza tworzą się minerały typu garnierytu* $Ni_6Si_4O_{10}(OH)_8$*. Interakcja roztworu siarczanu niklu z talkiem prowadzi do powstawania villemseitów (*$Ni_3Si_4O_{10}(OH)_2$*). Podczas interakcji roztworu siarczanu niklu z biotytem obserwuje się powstawanie minerałów typu pimelitu (*$Ni_3Si_4O_{10}(OH)_2.4H_2O$*). Przeprowadzono również eksperymenty sorpcji żelaza, miedzi i niklu za pomocą odpadów rud miedziowo-niklowych aktywowanych termicznie w 650°C (bariera nr 1) i 700°C (bariera nr 2). Wytrzymałość na ściskanie uzyskanych granulek wyniosła 2,19 (650°C) i 1,92 (700°C) MPa. W przypadku eksperymentów w warunkach dynamicznych granulki były zwilżone roztworem siarczanu zawierającym 0,1 g/L* Ni^{2+}*, 0,05 g/L* Cu^{2+} *oraz 0,1 g/L* Fe^{2+}*. Po 30 dniach stężenie resztkowe jonów metali nieżelaznych dla bariery nr 1 i bariery nr 2 po filtracji przez bariery dla jonów żelaza wynosiło odpowiednio 85,2% i 93,2%, dla jonów miedzi 74,4% i 65,2% oraz dla jonów niklu 53,7% i 63,3%. Interakcja roztworu siarczanu, zawierającego jony metali nieżelaznych, z minerałami prowadzi do ich depozycji w rezultacie izomorficznej substytucji izowalentu. Eksperymenty w warunkach dynamicznych pomogły dostrzec możliwość użycia aktywowanych termicznie odpadów z rud niklowo-miedzianowych jako materiału do tworzenia barier geochemicznych.*

Słowa kluczowe: bariery geochemiczne, fizykochemiczne geotechnologie, zarządzanie wodą i ściekami, redukcja metali nieżelaznych, serpofit, talk, biotyt, odpady miedzowo-niklowe