



A Study of Interaction of Mine Drainage Waters with Impregnated Copper-Nickel Ores

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<http://doi.org/10.29227/IM-2018-01-27>

Abstract

The work deals with processes occurring on interaction of mine drainage waters with fine-grain dusty particles, and filtration of the water through sulphide rock mass. The studies have shown that the environmental hazard likely to be caused by the drainage waters of the Severny mining plant of the Kola MMC Ltd is lower than it might be expected owing to precipitating of the heavy metals by iron hydroxides and magnesium hydrosilicates. An assessment of the feasibility of hydrometallurgical processing of impregnated copper-nickel ores has been prepared.

Keywords: copper-nickel ore, mine water, leaching

Introduction

The mining industry has always been confronted with the problem of having to discharge large volumes of under-treated wastewater. The main pollutants are heavy metals, high acidity or alkalinity of mine drainage, salts, oxides, suspended substances, etc. (Masloboev et al., 2014). The cause of quarry, underspoil and mine water pollution is oxidation of the minerals that are unstable under hypergenic conditions, primarily of iron and nonferrous metal sulphides. The hypergenic processes are accelerated when the minerals surface becomes activated as a result of crushing and grinding operations preceding the ore concentration (Amos et al., 2015; Masloboev et al., 2014; Nordstrom, 2011). Another source of pollution is operated and abandoned mining openings, tailings, dumps, including coal spoil banks, natural exposures of sulphide rocks, etc. A crucial factor affecting the rate and consequences of the oxidation processes in sulphide-containing rocks is the type of mineral associations (Chanturiya et al., 2014; Masloboev et al., 2014).

We have conducted experiments on leaching of three specimens of the copper-nickel ores from the Severny mining plant of the Kola MMC Ltd, under conditions simulating the ore contact with mine drainage waters. Apart from assessing the potential environmental hazard, these experiments explored the possibility of employing physicochemical technologies (heap and underground leaching) at the mine.

Objects and methods of research

Samples of the copper-nickel ore were selected in May 2016, in the Severny mining plant by the Kola MMC Ltd geological survey.

Microscopic examination was performed at polished sections of the copper-nickel samples using the Axioplan 2 imaging microscope.

The XRD analysis was performed at a DRON-2.0 diffractometer with CuK α radiation. The diffraction patterns were decoded using the reference material from the JCPDS and ASTM X-ray data catalogue.

Both the total silicate analysis of the copper-nickel ores and the mine drainage analysis were performed at the KGILC Ltd.

The leaching experiments were carried out both in batch and dynamic modes.

In the static regime, interacting between the mine drainage waters and fine-grain dusty particles, forming as a result of drilling and blasting operations, was simulated. Before the experiments, the ore samples were ground to the size of ~ 100 μm . One sample of mine drainage water from the Severny mining plant was used containing, mg/dm^3 : SO_4^{2-} 596.6; Ni 0.012; Cu 0.0041. The experiments lasted for 1, 3, 5 and 10 days at a solid to liquid ratio of $S : L = 1 : 10$ and under periodic stirring. When the experiments were completed, the solutions were analyzed for nickel, copper and sulphate ion, and the pH was determined. The metal concentrations were determined using atomic absorption with direct electrothermal atomization of the samples. The sulphate concentration was determined by the gravimetric method.

Experiments in the dynamic regime simulated the interaction of mine water filtering through the rock mass. The experiments were performed in percolators 300 mm in height and 25 cm in diameter with ore sam-

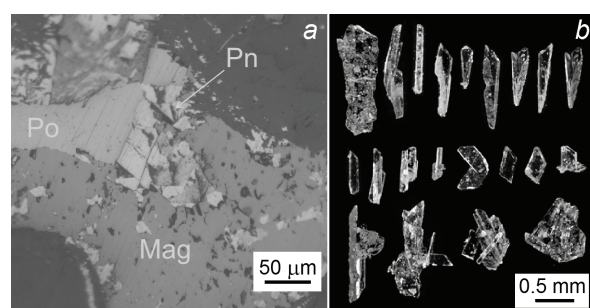


Fig. 1. Microphotographs of Sample 1: the ore (a), individual, pure colorless crystals and twin intergrowths of gypsum (b)

Rys. 1. Mikrofotografie próbki 1: rudy (a), pojedyncze, czyste bezbarwne kryształy i bliźniacze przerosty gipsu (b)

Tab. 1. Chemical composition of copper-nickel ore samples

Tab. 1. Skład chemiczny rudy miedziowo-niklowej

Sample	Contents (%)															
	SiO ₂	MgO	FeO	Fe ₂ O ₃	Al ₂ O ₃	CaO	TiO ₂	MnO	K ₂ O	Na ₂ O	NiO	CuO	CoO	SO ₃	H ₂ O*	LOI
1	35.83	29.90	12.51	6.14	2.69	2.22	0.68	0.21	0.13	0.08	0.65	0.19	0.028	3.47	0.20	8.21
2	35.41	27.86	13.67	6.43	2.78	2.16	0.80	0.20	0.14	0.10	0.91	0.41	0.03	5.67	0.18	8.10
3	35.81	26.54	12.23	8.59	3.30	2.69	0.96	0.21	0.24	0.22	0.52	0.24	0.024	3.60	0.23	8.22

ples ground to -3+2 mm for 36 days at 18±2°C using a model solution containing 160 mg/L SO₄²⁻ with pH = 5.59. The ore sample mass was 200 g. Prior to leaching, the ore was saturated in 400 ml of distilled water for 8 days. The leaching solution was added once a day in amounts of 50 ml. The solutions were analyzed on exit from the columns for nickel, copper and sulphate ion, and the pH was determined.

Analysis of material composition of the copper-nickel ore

The results of microscopic studies of the polished sections are presented in Fig.1. In Sample 1, the ore share is composed by magnetite Fe₃O₄, pentlandite (Fe, Ni)₉S₈ and pyrrhotite Fe_{1-x}S. Pentlandite and pyrrhotite usually form intergrowths in large magnetite grains (Fig. 1a). Sample 1 is characterized by the presence of numerous emulsion impregnations of ore minerals in silicates. Sample 2 is similar to Sample 1 in the contents of the base ore minerals, i.e. magnetite, pyrrhotite and pentlandite, but it is different in containing violarite (Fe, Ni)₃S₄, substituting pentlandite. Sample 3 contains large grains of chalcopyrite CuFeS₂. Both pentlandite and pyrrhotite are observed as impregnations in these grains or intergrowths with them.

Mineralogical analysis of the copper-nickel ores has revealed that the non-ore minerals are mostly represented by serpentines (over 60% in all the three samples). Next is olivine, but its content is much lower in Sample 3 where the second abundant mineral is amphiboles. In all the samples, pyrrhotite prevails in sulphide minerals (3.45 to 5.75%). There are also pentlandite, chalcopyrite and pyrite.

The results of silicate analyses of the samples can be seen in the Table. The major components, in de-

creasing order, are silica and magnesium and iron oxides (FeO and Fe₂O₃). The nickel and copper contents are maximal in Sample 2 and minimal – in Sample 3.

The XRD studies were performed on the ore samples preliminarily ground down to -0.05 mm.

The predominant reflexes belonged to the following silicates: lizardite Mg₃Si₂O₅(OH)₄, antigorite (Mg, Fe²⁺)₃Si₂O₅(OH)₄, enstatite Mg₂Si₂O₆, and olivine (Mg,Fe)₂SiO₄. The following ore minerals were diagnosed: magnetite Fe₃O₄, pentlandite (Fe, Ni)₉S₈, chalcopyrite CuFeS₂, and millerite NiS (Fig. 2).

Thus, according to the results of material composition analyses of the copper-nickel ore sampled from different mining floors of the Severny mining plant, the samples represent run-of-the-mine impregnated ores typical of the ore base of the Kola MMC Ltd (Masloboev et al., 2014).

General comments on the mine drainage water contamination

The water examined included mine drainage from 12 shaft pumping stations of the minefield and the water at two exits from the Severny mining plant.

Since the water gets mixed at the drainage pumping plants, the pollution level of the water, eventually discharged to the Bystraya and Hauki-Lampi-yoki rivers, is moderate; the MAC requirements for fishing reservoirs are satisfied only in terms of the pH value. The contamination level of the discharge water varies depending on the workload of two pumps located at different horizons with differently polluted water, and also the season of the year. The discharge composition is affected by the processes of water saturation with atmospheric oxygen and bacterial interactions.

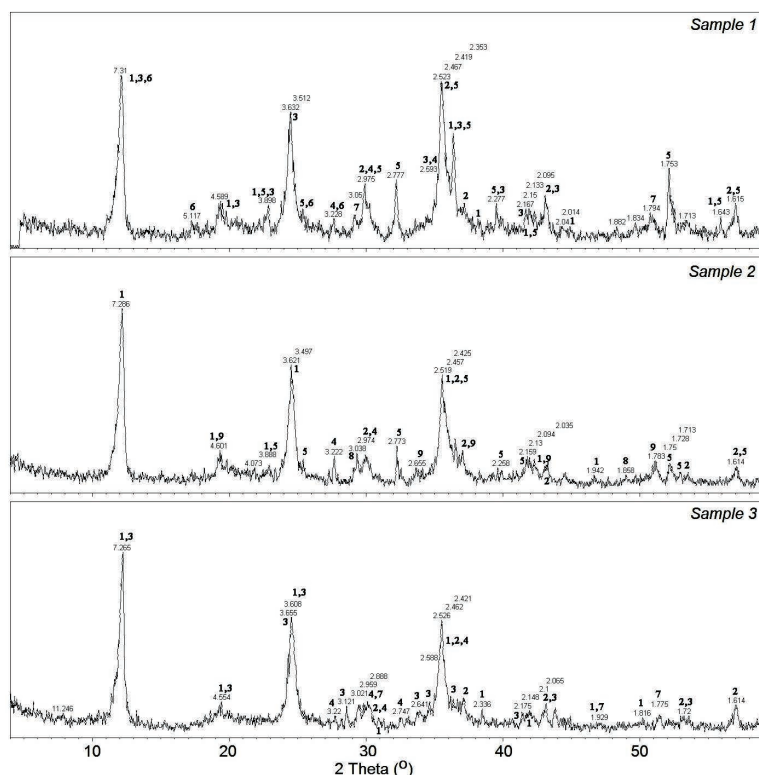


Fig. 2. XRD patterns of the copper-nickel ore samples: 1 – lizardite; 2 – magnetite; 3 – antigorite; 4 – enstatite; 5 – forsterite; 6 – lovozerite; 7 – pentlandite; 8 – chalcopyrite; 9 – millerite

Rys. 2. Analiza XRD próbek rud miedzi i niklu: 1 - lizardyt; 2 - magnetyt; 3 - antygoret; 4 - enstatyt; 5 - forsteryt; 6 - lowozerut; 7 - pentlandyt; 8 - chalkopiryt; 9 - milleryt

The discharged water is invariably contaminated with ammonium (1.9–10.4 mg/ dm³), nitrates (60–75 mg/ dm³), nitrites (12–24 mg/ dm³), sulphate ions (up to 1.5 g/ dm³), and nickel (0.002–0.045 mg/ dm³).

In most cases, the concentrations of suspended rock particles may vary, or increase, sporadically. The samples of suspended particles obtained after filtration were found to contain the following rock-forming minerals of ore-hosting rocks that had got into the water as dusty particles emerging in the process of rock mass blasting. The typical minerals are: calcite CaCO₃, quartz SiO₂, chlorite (Mn, Al)₆(OH)₈((Si,Al)₂, enstatite Mg₂Si₂O₆, antigorite (Mg,Fe)₃Si₂O₅(OH)₄, talc Mg₃Si₄O₁₀(OH)₂, actinolite Ca₂(Mg,Fe)₅Si₈O₂₂(OH)₂, lepidolite K(Li,Al)₃(Si,Al)₄O₁₀(F,OH)₂, labradorite (Na,Ca)Al(Al,Si)Si₂O₈, forsterite Mg₂SiO₄, montmorillonite (Na, Ca)_{0.3}(Al, Mg)₂Si₄O₁₀(OH)₂ × _n H₂O, sepiolite Mg₄Si₆O₁₅(OH)₂ × 6H₂O.

The laboratory analysis has disclosed that the residues of evaporated mine drainage contained the common salt minerals with prevailing and omnipresent hydrated calcium sulphate – gypsum CaSO₄ × 2H₂O. Some of the evaporation residue samples were found to contain halite NaCl; two of the samples contained, tentatively, yavapaiite KFe(SO₄)₂; one sample contained, presumably, kovdorskite Mg₂(PO₄)(OH) × 3H₂O. Mixing and pumping of the mine waters of dis-

similar composition to different floors of the mining plants generates complex processes, which either promote the settling of gypsum or increase its solubility thus enhancing the mineralization index. Residues of the water evaporation represent large aggregates and individual crystals of gypsum. The purest gypsum crystals were evaporated from water obtained at the deepest level of the mining plant (Fig. 1b).

Ore leaching in static and dynamic regimes

Static regime. The experiment results are demonstrated in Fig. 3 and 4. The concentrations of non-ferrous metals and sulphate ions in the water after interaction with Samples 1–3 of the copper-nickel ore during 1–10 days are given in Fig. 3.

It is evident in all the experiments that the nickel, copper and sulphate-ion concentrations in water increased after interaction of the ore samples. Increment in the nickel, copper and sulphate-ion concentrations was the highest in solution interacting with Sample 1 (Fig. 3a, b).

The levels of the metals and sulphur extraction to solution depending on the interaction time for Samples 1–3 are shown in Fig. 4.

The significant prevalence of sulphur extraction (by two-three orders) over those of nickel and copper is accounted for by the fact that the solution pH re-

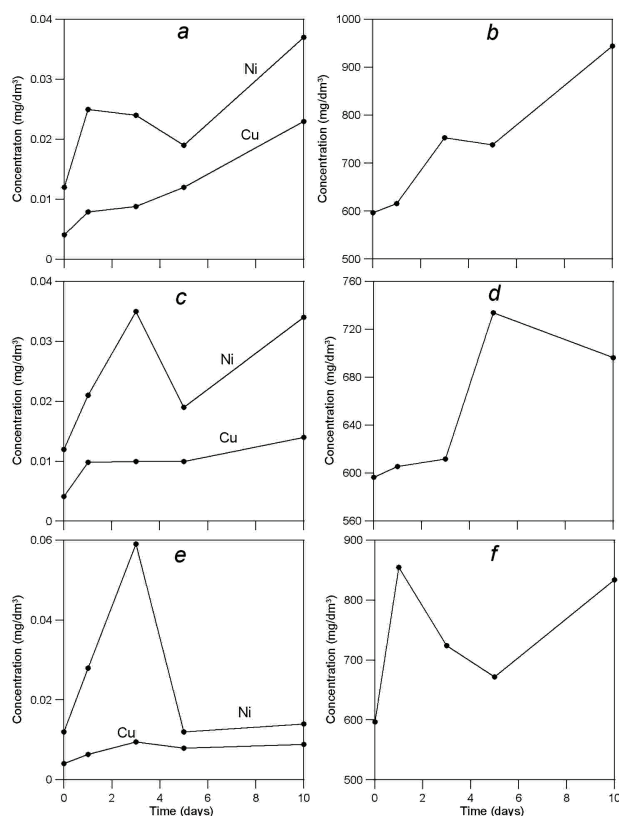


Fig. 3. Concentrations of nickel, copper (a, c, e) and sulphate ion (b, d, f) in solution during the static regime interaction with Samples 1 (a, b), 2 (c, d) and 3 (e, f)

Rys. 3. Stężenia niklu, miedzi (a, c, e) i siarczanu (b, d, f) w roztworze podczas interakcji statycznej z próbkami 1 (a, b), 2 (c, d) i 3 (e, f)

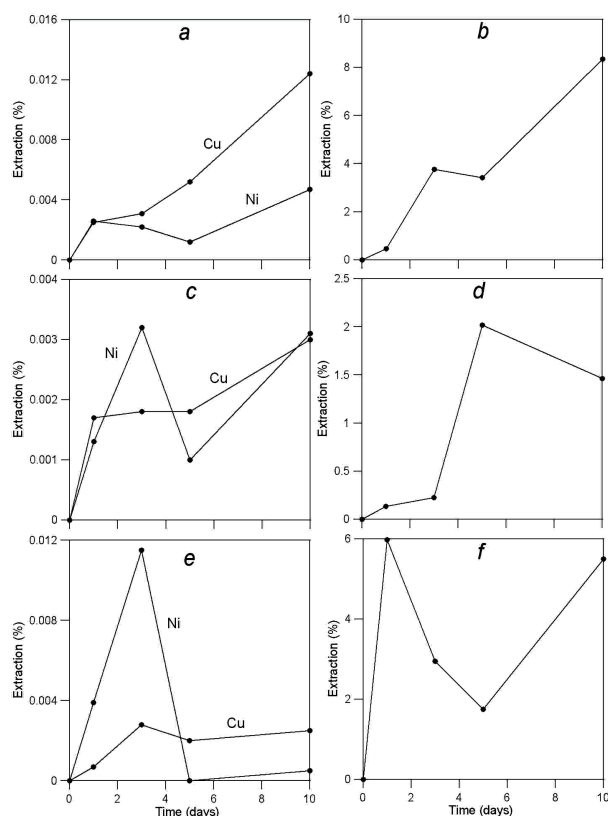


Fig. 4. Extraction of the metals (a, c, e) and sulphur (b, d, f) from the ore Samples 1 (a, b), 2 (c, d) and 3 (e, f). Static regime

Rys. 4. Ekstrakcja metali (a, c, e) i siarki (b, d, f) z próbek rudy 1 (a, b), 2 (c, d) i 3 (e, f). Warunki statyczne

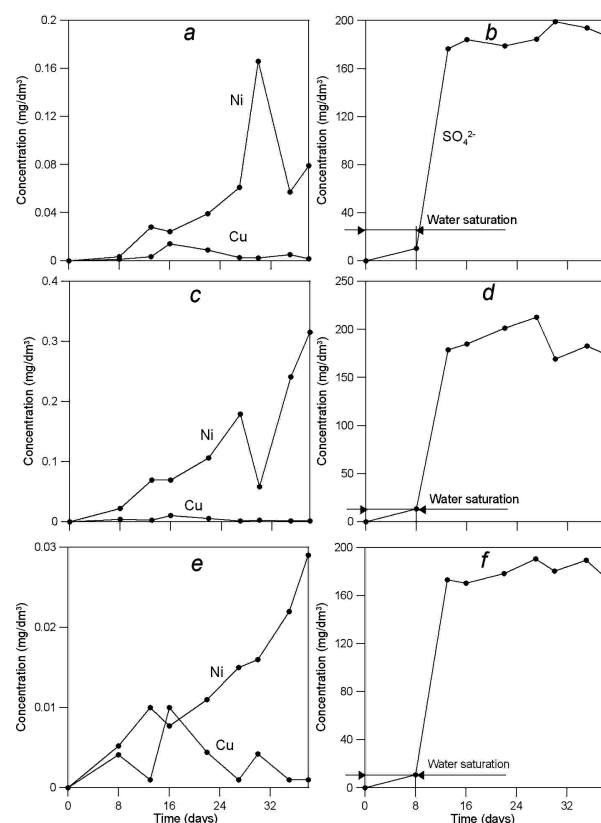
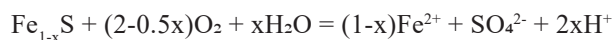


Fig. 5. Concentrations of nickel, copper (a, c, e) and sulphate ion (b, d, f) in solution during the dynamic regime interaction with Samples 1 (a, b), 2 (c, d) and 3 (e, f)

Rys. 5. Stężenia niklu, miedzi (a, c, e) i jonu siarczanowego (b, d, f) w roztworze podczas dynamicznego oddziaływania z próbkami 1 (a, b), 2 (c, d) i 3 (e, f)

mained in the alkaline region throughout the experiment attaining a maximum after 1 day. It should be noted that before the experiment, the pH value of the drainage water had also been alkaline (pH=9).

It is obvious that these conditions favor the precipitation of amorphous iron hydroxides adsorbing heavy metals (Filip et al., 2007). Besides, the concentrations of heavy metals (nickel and copper) decrease abruptly owing to concurrent ion-exchange reactions with serpentines (antigorite and lizardite), generating the nickel- and copper-containing hydrosilicates (Makarov V. et al., 2005). Due to low sulphide concentration in the ore, the mineral oxidation, occurring, among others, by the reaction



and yielding sulphuric acid, is not sufficient to transfer the pH to the acidic region (Masloboev et al., 2014). On the other hand, this reaction decreases the water pH value, which was observed for all the ore samples after 3, 5 and 10 days of interaction.

So, the heavy metal concentrations and, hence, their potential environmental hazard for the drainage water of the Severny mining plant are dependent on the composition of non-ore minerals. The hazard level is much lower than that from the copper-zinc ores mined in the

Urals, where the copper and zinc concentrations in the drainage water of the Uchalinsky MPP are 67 and 189 mg/dm³, respectively (Orechova et al., 2008). At the same time, the sulphate-ion concentrations remain high.

Dynamic regime. Experiments in the dynamic regime simulated interacting between the mine drainage waters filtering through the rock mass. The model solution contained 160 mg/dm³ SO₄²⁻. The experiment results are presented in Fig. 5, 6.

The concentrations of non-ferrous metals and sulphate ion in the water after the copper-nickel ore Samples 1–3 were saturated in distilled water for 8 days and interacted with model solution for 30 days are presented in Fig.5. It shows a growth in concentrations of all components with the exception of copper. At the same time, similar to the static regime experiments, the sulphate-ion concentrations by far exceed those of nickel and copper, the latter in particular. This behavior of the ions is attributable to precipitation of the metals on iron hydroxides and the exchange reactions with chemically active serpentines (Chanturiya et al., 2004; Masloboev et al., 2014), which is facilitated by the high pH value of the solutions.

The levels of the metals and sulphur extraction from the copper-nickel ore Samples 1–3 to solution as a result of interaction in the dynamic regime are presented in Fig. 6.

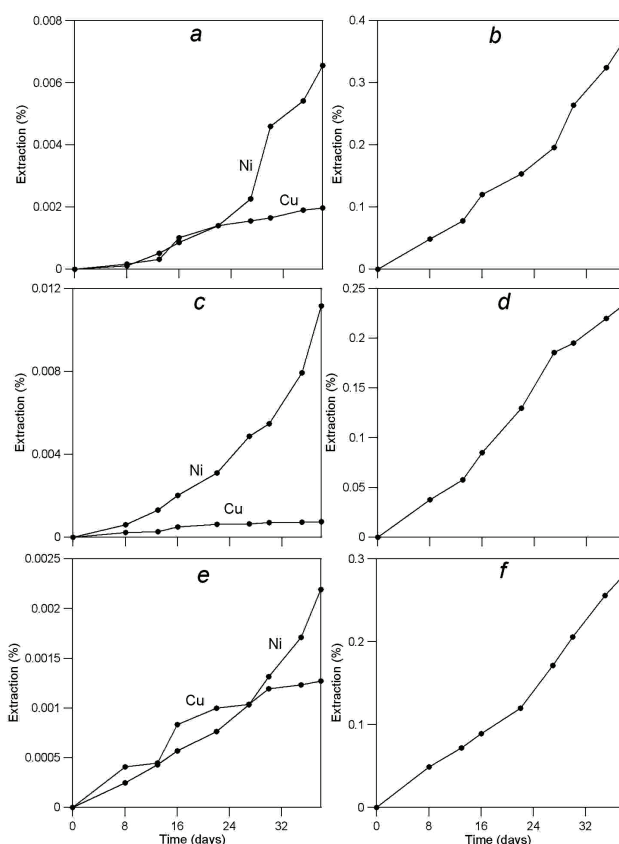


Fig. 6. Extraction of nickel, copper (a, c, e) and sulphur (b, d, f) from the ore Samples 1 (a, b), 2 (c, d) and 3 (e, f). Dynamic regime

Rys. 6. Ekstrakcja niklu, miedzi (a, c, e) i siarki (b, d, f) z próbki rudy 1 (a, b), 2 (c, d) i 3 (e, f). Warunki dynamiczne

It should be noted that the pH value increases by 3.5–4 units as a result of water saturation, passing to the alkaline region. Filtration of the model solution causes the pH value to decrease but slightly; it remains higher than 7.

The dynamic experiments have revealed a similarity with the batch experiments relatively the sulphur extraction, which exceeded the nickel and copper extractions by 2 orders. The figure was lower compared to the batch-mode one, but this can be attributed to the large size of ore lumps and insufficient contact time of model solution with the ore, the filtration factor being tens of meters per day (Fig. 6). Nonetheless, during the filtration experiment the SO_4^{2-} concentrations in solution increased by 10–50 mg/dm³ (Fig. 5). The copper recovery is poor in this case because it is incorporated in the slowly oxidizing chalcopyrite (Masloboev et al., 2014).

Conclusion

As established by experiments carried out in static and dynamic regimes, sulphide minerals oxidize, intensively forming sulphates, even on short-time contact of mine drainage water with the copper-nickel ore. Evidently, these processes can occur both as a result of mine water interaction with fine-grained dusty particles generated during the drilling and blasting op-

erations and when the water filters through the mass of sulphide-containing rocks. Due to the presence of chemically active non-ore minerals and a stable alkali reaction of the solutions, the heavy metals are precipitated by iron hydroxides and magnesium hydrosilicates, which considerably reduces the potential hazard of the mine drainage water of the Severny mining plant for the environment.

Experiments have demonstrated that the examined impregnated copper-nickel ores are not quite suitable for hydrometallurgical processing. In further experiments with sulphuric acid leaching of the copper-nickel ores, a final conclusion will be made about the applicability of physical-chemical technologies to this ore type. This work sequence was previously followed by us when experimenting with dumped copper-nickel process slag (Makarov D. et al., 2013; Svetlov et al., 2015).

Acknowledgements

The study was performed within the RAS Programme No I.4P “Deposits of strategic minerals in Russia: innovative approaches to anticipated reserves, their assessment and development” and a partial support of the RFFR (project No14-05-98804p_sever_a). The authors acknowledge the participation of Elena Zenovich in recording the XRD patterns.

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Abstrakt

Praca dotyczy procesów zachodzących w interakcji wód drenazowych kopalnianych z pyłowymi cząstkami drobnopiękistymi oraz filtracji wody poprzez masy skał siarczkowych. Badania wykazały, że zagrożenie dla środowiska spowodowane przez kwaśny drenaż wody kopalni Severny w Kola MMC Ltd jest niższe niż można się było spodziewać z powodu wytrącenia ciężkich metali za pomocą wodorotlenków żelaza i hydrokrzemianów magnezu. Dokonano oceny wykonalności przeróbki hydrometalurgicznej impregnowanych rud miedzi i niklu.

Słowa kluczowe: ruda miedzowo-niklowa, woda kopalniana, ługowanie