

## **Nonoxidative Leaching of Non-ferrous Metals from Wastes of Kola Mining by Sulphuric Acid**

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**Abstract:** *Dressing tailings and metallurgical slags, while being a major source of non-ferrous metals, pose a serious environmental hazard if unprocessed. In this study, the leaching kinetics of copper and nickel from low-grade wastes of Kola Mining was investigated. Leaching experiments were conducted in sulfuric acid electrolyte at a room temperature. The output solutions were analyzed using the atom-absorption spectrometry and the solid phase was analyzed using X-ray diffraction. The dynamics of metal leaching in the experiment show that heap leaching is quite advantageous when re-extracting metals from pelletized copper-nickel ore dressing tailings of current production, or of lean additional concentrate of tailings flotation. Taking into account the availability of excess sulphuric acid turned out by the "Kola MMC" JSC enterprises, sulphatization of pellets, where  $H_2SO_4$  acts as a binder in tailing pelletizing, is recommended.*

**Keywords:** *Cu-Ni ore dressing tailings, granulated slag, heap leaching*

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### **1. INTRODUCTION**

From the accumulated on the territory of Russia wastes three quarters fall to the mining industries. For producing of a ton of metal it is formed from 30 up to 100 tons of tails of beneficiation. For their removal and storage it is spent from five to eight percents of the costs of produced metals.

Modern view on the decision of the problem consists in the considering wastes of mining as new resources. It assumes, mainly:

- Perfection of the technologies of mining and mineral processing concentrating, development of the new methods of extraction of minerals from entrails and deep treatment of mineral raw materials, increasing of its comprehensive exploitation, that allows to reduce volumes of wastes;
- It seems to us important a development of the technologies of recycling of mining wastes, their processing with producing of the new kinds of products or diversification of mining manufacture;
- The important point is the development of the technologies of handling of dangerous wastes with the purpose of their isolation and their output from biosphere processes.

It is known that cut-off grade sulphide ores from both abandoned and currently developed deposits, overburden rock and dressing tailings, while being a major source of non-ferrous metals, pose a serious environmental hazard if unprocessed. So, any reasonable utilization of rock waste dumps, tailings and low-grade ore is beneficial both from environmental and economical viewpoints [1].

Such natural and man-made resources can be processed using heap leaching whereby a sulphuric acid solution, an oxidizer (oxygen, iron (III) ions etc.) and microorganisms (*Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* etc.) are fed both onto a heap surface and interior. Uniform spreading of the solution is achieved via a system of pools, drain gutters, networks of half-socket pipes, or spraying. The enriched solution leaking from under the heap is collected in gutters or pipes and sent to further processing [2].

As shown by the hydrometallurgical practice worldwide, heap leaching of non-ferrous metals is quite advantageous when applied to lean ores and mining and processing wastes [2, 3]. Together with dump leaching of mine waste, heap leaching contributes about 20% of annual world copper production [3]. Pilot test works of the heap leaching of low-grade copper-nickel sulphide ores (Radio Hill, Western Australia; Talvivaara, Sotkamo, Finland; Jinchuan, China) were initiated in the last decade [4-13].

In Russia, however, heap leaching is not widely used being, which is partly due to severe climatic conditions at most of the mined ore deposits. Similar enterprises elsewhere are located in warmer climates favouring the use of hydrometallurgical processes including bacterial ones [2]. At the same time, sulphide oxidation is known to proceed by the exothermal mechanism, therefore high sulphide contents (including iron sulphides) in the ore can promote heating of the heap's substance and facilitate leaching.

Decomposing of sulphide minerals can be enhanced by employing new, environmentally friendly and power-saving methods involving physical, physical-chemical and mechanical-chemical effects [1, 14, 15]. In recent years, there have been developed geochemical foundations for a geotechnology permitting to recover non-ferrous metals at negative temperatures and in permafrost [16, 17].

Heap leaching enables to use ore with content that may be significantly lower than for conventional metallurgical techniques. For example the company "Talvivaara Mining Company Plc", which located in the subarctic zone in the north-east Finland, applies the heap leaching at a nickel mine deposit of complex ore the average content of the ore is 0.27 % Ni, 0.14 % Cu, and 0.56 % Zn [4].

The conditioning metals content of man-made ore can be even lower due to the fact that the cost of production has been largely incurred and transportation costs made under source of reclamation.

Sulphide containing tailings and non-ferrous slags are not only an additional source of non-ferrous metals, but they are also environmentally dangerous deposits [18-20].

## 2. METHODS

Percolation leaching was performed with sulphuric acid in columns. The pellets were preliminarily moistured with water to saturation. The output solutions were analyzed using the atom-absorption spectrometry (AAC), AAnalyst™ 400 spectrometer. The solid phase was analyzed using X-ray diffraction (XRD), DRON-2 diffractometer, Cu K $\alpha$  radiation.

## 3. OBJECTS OF RESEARCH

The objects of the above research were copper-nickel ore dressing tailings and copper-nickel smelting granulated slags of Pechenganickel Processor of Kola Mining Company.

Pechenganickel Processor operates since 1965 and now its tailings deposit is one of the largest sources of the non-ferrous metallurgy of Russia. The amount of accumulated wastes now exceed 200 Mt. In copper-nickel ore dressing tailings, the grain size and mineral compositions can vary over a certain range depending on process characteristics. But the bulk of the grains are of the fraction -0.1 mm; and in many cases 50% of the grains have the size of -0.044 mm. The tailings mostly consist of serpentines (~60%) with noticeable amounts of pyroxene, amphiboles, talc, chlorites, quartz and feldspar [21]. The principal ore minerals are magnetite, pyrrhotite, pentlandite and chalcopyrite. The total content of sulphide minerals is 1-3%.



**Fig. 1.** Tailings of Cu-Ni ore (a) and slag dump (b). "Pechenganickel" Combine, "Kola MMC" JSC.

Slag dumps of Pechenganickel metallurgy production (Fig. 1b) were formed in 1945 and this man-made deposit contains more than 45 Mt of raw materials. Impound current and old slag was analyzed for the extent of property alteration and environmental hazard. Old slag (15 years) differed from their current counterparts in increased contents of fraction -0.1 mm. Old slag was more heterogeneous in

grain size, which characterized all grain sizes classes. Apparently, this is due to substance differentiation and, possibly, hypergenic processes occurring in dumps [22]. Higher contents of non-ferrous metals in slag of current production are due to higher richness of initial concentrates and leaching out in dumps. In granulated slag of current production, sulphides impregnations are distributed nonuniformly and not in all grains of the slag matrix consisting of olivine and glass (Fig. 2). The chemical composition of sulphides in both old and current slag can be satisfactorily described by the formula of pentlandite  $(NiFe)_9S_8$ . As revealed by dynamic experiments, leaching of both non-ferrous metals and iron is fairly intensive both from mature and fresh slag.

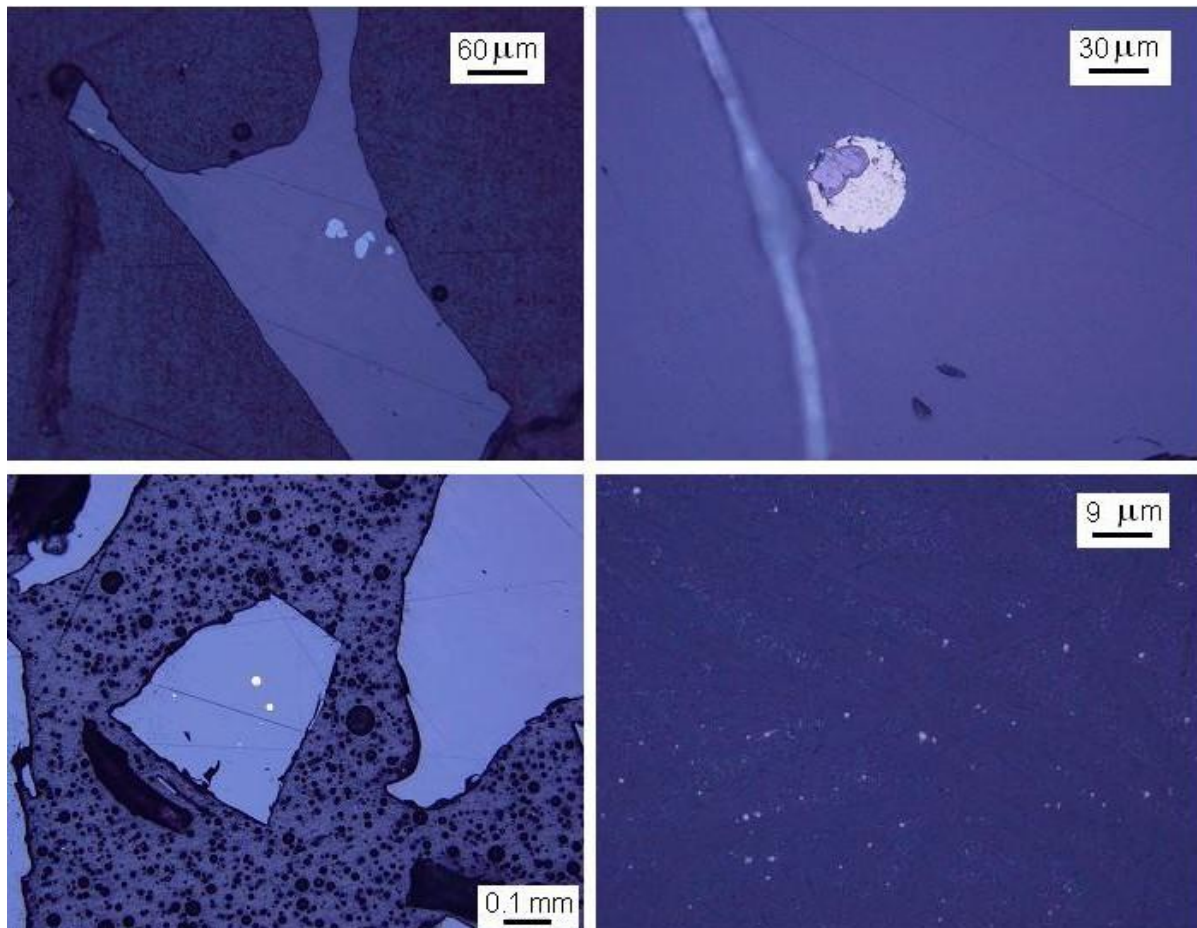


Fig. 2. Sizes and forms of sulfide grains (light with high reflectivity) in silicate matrix of slag [22].

## 4. RESULTS AND DISCUSSION

### 4.1 Copper-Nickel Ore Dressing Tailings

Processing of fine-grained anthropogenic products and natural minerals with high contents of layered hydrosilicates (clay minerals) is hindered by colmatage, which decreases permeability in the heap up to termination of the process. We observed these phenomena in aged copper-nickel ore dressing tailings where filtration, blocked by a claylike artificial soil formed by chlorites and mixed layered formations with alternating chlorite and smectite layers, dwindled 100 fold [23].

This problem can be addressed by granulating the materials with binders such as lime and Portland cement. Thus, in work [24] are reported the results of pilot testing of heap leaching of copper-zinc ore dressing tailings ("Buribaevskiy GOK" JSC) where pellets were prepared using 5% of caustic limestone.

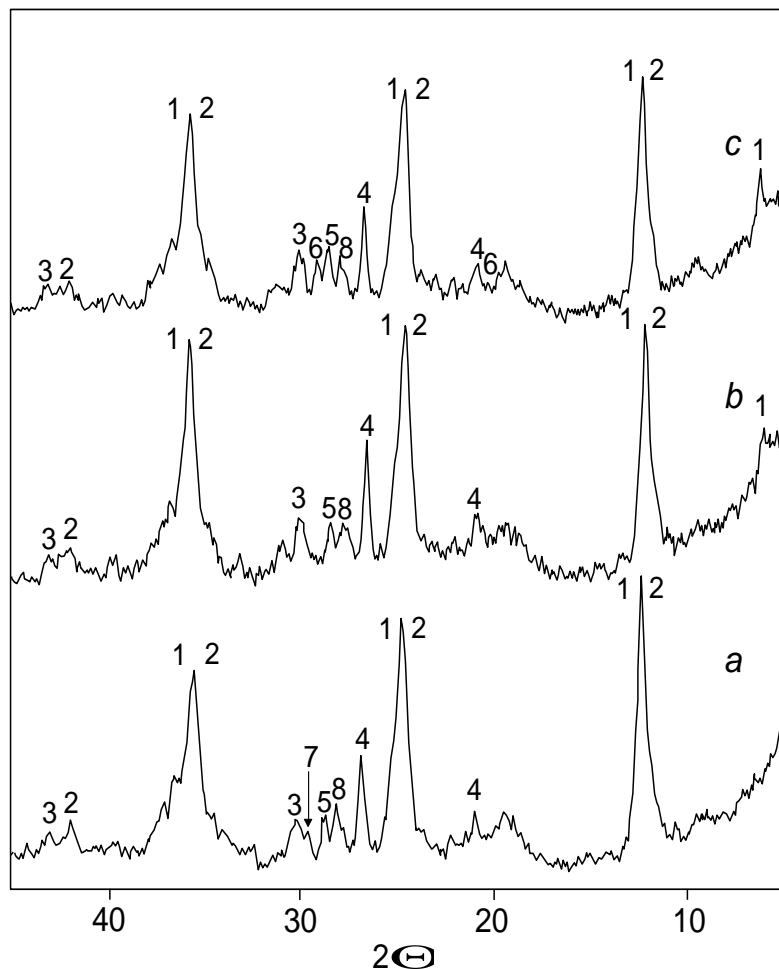
In our earlier laboratory experiments, we conducted percolation leaching of copper-nickel ore dressing tailings with sulphuric acid [25]. The pellets were prepared using Portland cement in the quantity of 3-5%. However, the cement stone yielded to sulphoaluminate corrosion as a result of which the pellets often failed by loss of strength. This limits the possibility of industrial leaching by 100 days.

However, pellet sulphatization, with sulphuric acid as a binder, can still be viable due to the availability of excess sulphuric acid turned out by the "Kola MMC" JSC enterprises.

At the first stage, we experimented with producing pellets at a liquid-to-solid (L/S) ratio of 3:1, the binding agent being  $H_2SO_4$  solutions with concentrations of 10, 20 and 30%. The pellet diameter in the experiments was 0.8-1 cm. Since their compressive strength was, respectively, 2.79, 0.71 and 0.61 MPa, the  $H_2SO_4$  concentration in further experiments was 10%. The tailings contained, %: Ni 0.17, Cu 0.07, Co 0.01.

Percolation leaching was performed with 1% sulphuric acid in columns with the diameter of 45 mm during 110 days. The pellets were preliminarily moistured with water to saturation. The pellet weight was 150 g. The interval between spraying was 2-3 days; each time the acid volume was 25 mL.

The solid phase X-ray diffraction analysis show that the tailings mainly consist of serpentine (Fig. 3). The quantity of mineral phases, assessed by the ratio of intensities of main reflexes, indicates to the presence of magnetite (17%), quartz (16%) and feldspar (10%). There were traces of pyroxenes and amphiboles (~3%) and sulphide of non-ferrous metals – pentlandite and chalcopyrite. The diffractograms prior to and after leaching differed in the absence of sulphide reflexes and also higher chlorite contents, especially in the bottom column strata. There emerged several undetectable phases. It was found that the coating on pellets from the column upper strata consisted of a mixture of sulphate phases: white, semi-transparent hexahydrate  $MgSO_4 \cdot 6H_2O$ , colourless epsomite  $MgSO_4 \cdot 7H_2O$ , where magnesium may be partially isomorphously substituted for iron, nickel and cobalt, and also gypsum  $CaSO_4 \cdot 2H_2O$ , forming rounded aggregates of needle-shaped crystals. All this suggests that the sulphuric acid solution interacted not only with sulphide minerals but also with silicates, serpentine in the first place. As for the chemically inert quartz, feldspar and magnetite, they did not dissolve during the experiments, their relative content in pellets remaining unchanged in the bottom strata and increased in the upper.



**Fig. 3.** XRD patterns of Cu-Ni tailings (a) and pellets after leaching: top of column (b), bottom of column (c). 1 – chlorite; 2 – serpentine; 3 – magnetite; 4 – quartz; 5 – talc; 6 – gypsum; 7 – sulphides (pentlandite, chalcopyrite), 8 – feldspar.

The dynamics of metal leaching in the experiment is given in Fig. 4.

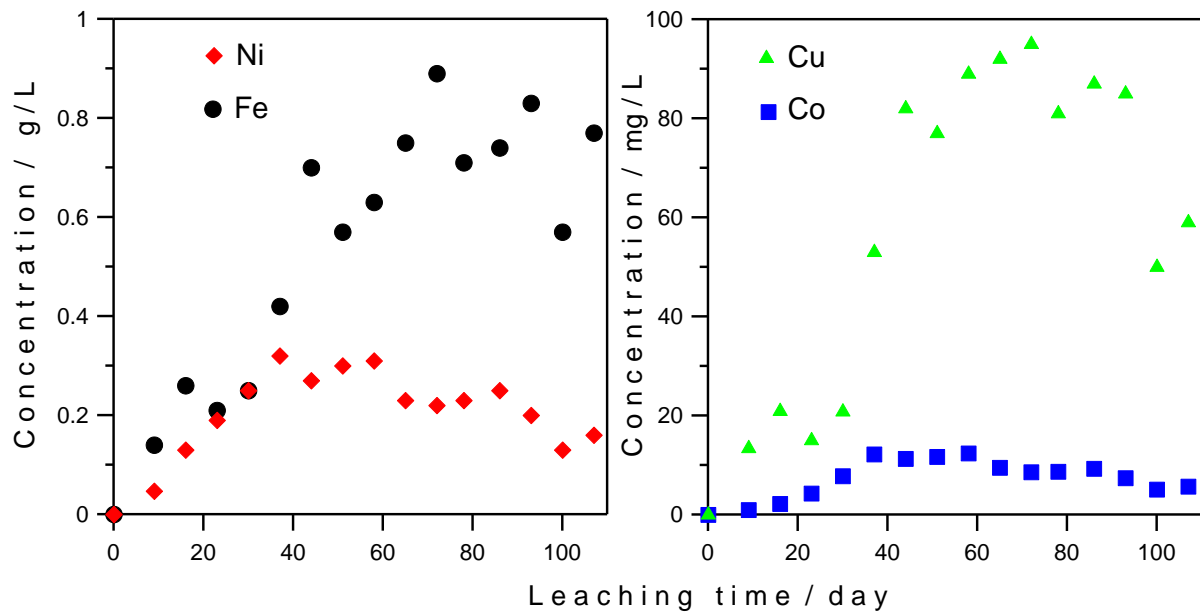


Fig. 4. Metal concentrations in product leaching solutions of copper-nickel ore dressing tailings.

It can be seen that the process is fairly intensive, the nickel concentrations in solution stably varying over the range of 0.1 to 0.35g/L, which is satisfactory for industrial processing on the condition of solution circulation. With silicate minerals partly dissolved, the iron concentration reached 0.9 g/L, which means that with proper engineering solutions it can be isolated from product solutions. Copper concentrations were also relatively high; the levels of cobalt extraction were also stable. Fig. 5 demonstrates the kinetics of metal leaching from pelletized copper-nickel ore dressing tailings. As always, nickel was extracted most readily. The yield of nickel to solution after 110 days was about 60%. The indices for copper were lower (~44%) due to it being incorporated in chalcopyrite [2]. The cobalt low extraction (~41%) was likely to be caused by cobalt department, which is partly present as an isomorphous impurity in magnetite. The obtained dependencies of non-ferrous metals extraction were as follows:

$$\epsilon_{Ni} = 0.6329 \tau - 4.6459, (R^2 = 0.9891); \tag{4}$$

$$\epsilon_{Cu} = 0.4682 \tau - 6.9116, (R^2 = 0.9871); \tag{5}$$

$$\epsilon_{Co} = 0.4484 \tau - 4.737, (R^2 = 0.9808), \tag{6}$$

where  $\epsilon_{Me}$  is the metal extraction, %;  $\tau$  is the leaching time, days.

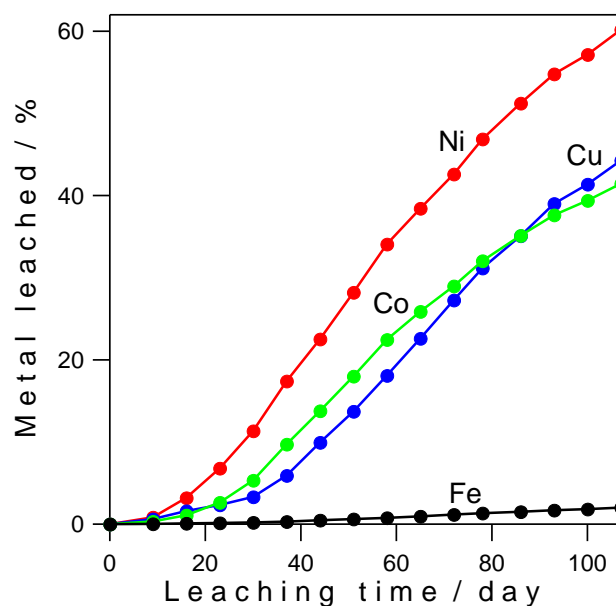


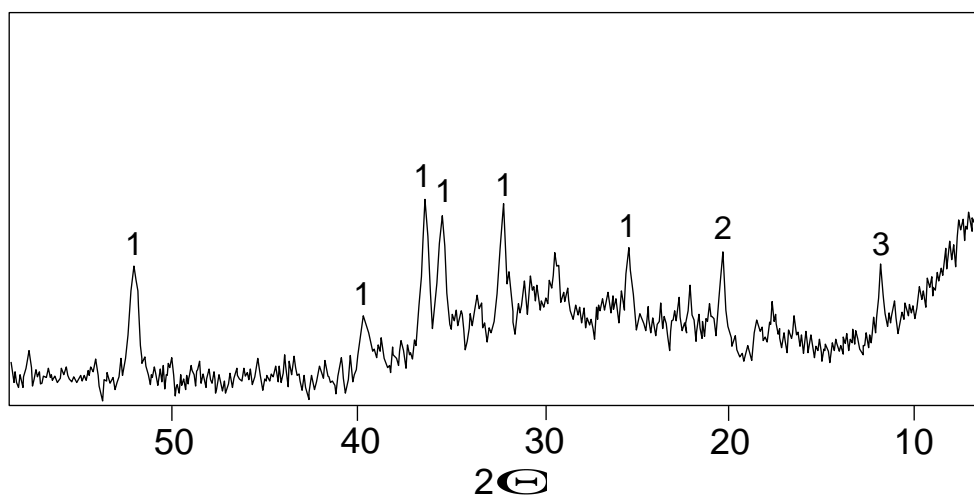
Fig. 5. Kinetics of metal leaching from copper-nickel ore dressing tailings.

## 4.2 Copper-nickel smelting slag

Sulphides of non-ferrous metals are within the silicate matrix of slag (Fig. 2), so for the better access of leaching reagent to minerals it's necessary to grind granules of slags with following pelletizing of crushed slags in the agglomerators.

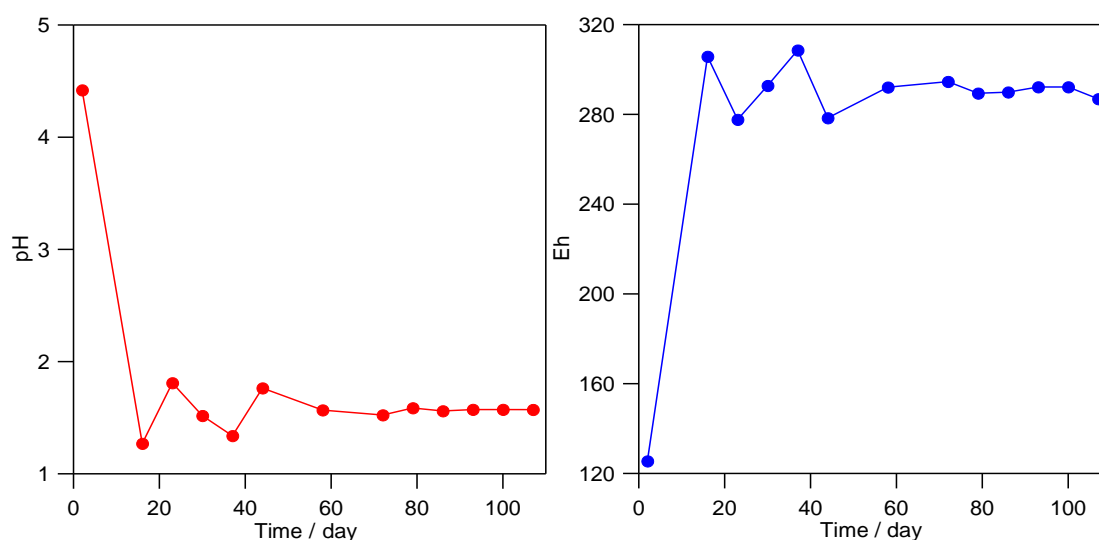
Leaching experiments were performed with pellets which were produced from crushed to  $-40\ \mu\text{m}$  slags in a slurry with a ratio of solids to liquid = 3: 1. 10%  $\text{H}_2\text{SO}_4$  solution was used a binder. The diameter of pellets for leaching was 0.8-1 cm, compressive strength of them was 2.14 MPa. The slag contained, %: Ni 0.155, Cu 0.115, Co 0.09 Percolation leaching was performed with 1% sulphuric acid in columns with the diameter of 45 mm during 110 days. The pellets were preliminarily moistened with water to saturation. The pellet weight was 150 g. The interval between spraying was 3-5 days; each time the acid volume was 25 mL.

According to XRD the total content of the crystalline phase in pellet samples is insignificant (Fig. 6). Halo in the corners  $2\Theta$   $20\text{-}40^\circ$  indicates the presence of the glass phase. X-ray diagnosis of a single grain from covering on the surface of the pellets was revealed hexahydrate  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  that was presented units icy white translucent and transparent grain phase of isostructural watevillite  $\text{Na}_2\text{Ca}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ .



**Fig. 6.** XRD patterns of Cu-Ni slag after leaching. 1 – olivine; 2 – hexahydrate; 3 – undiagnosed phase.

Values of pH and Eh of the solutions after reaction with the slag are sufficiently stable throughout the experiments (Fig. 7). The first point on the graphs corresponds to the moisture saturation pellets.

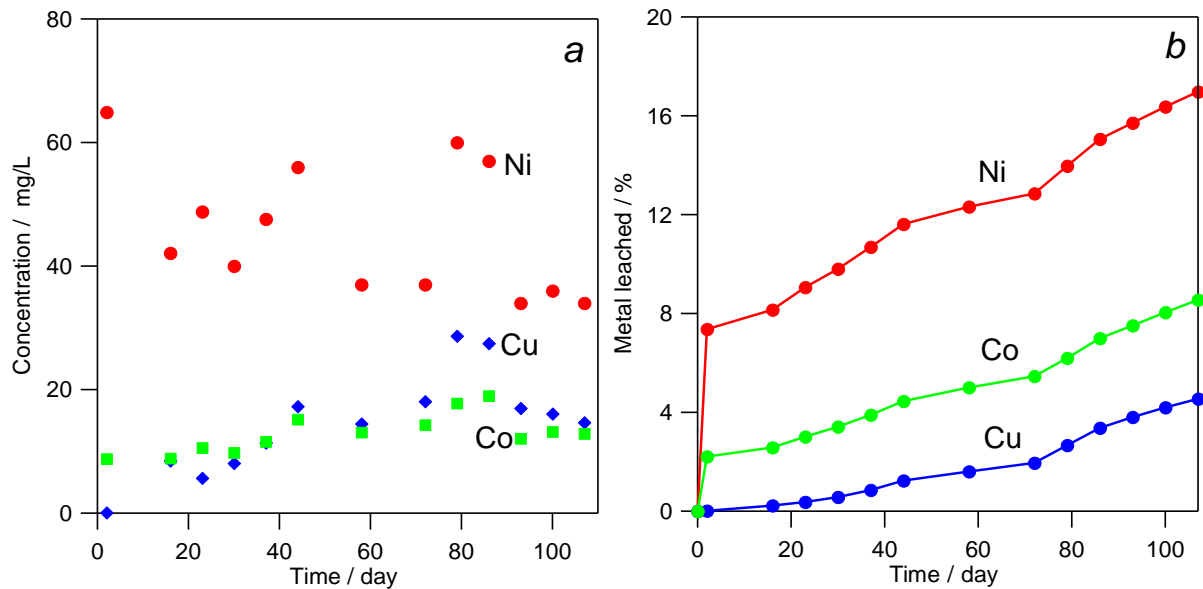


**Fig 7.** Eh (mV) and pH of column discharge solutions.

Concentrations of metals in the productive solutions are shown in Fig. 8a. Indicators are generally acceptable for industrial implementation of the method provided turnover and possible intensification of leaching by using oxidants. Fig. 8b demonstrates the kinetics of metal leaching from slag. The most



intensive, as expected, was leaching of nickel. The recovery of nickel to solution after 110 days was about 17%. For cobalt recovery was lower, only 8.6%. Much worse in comparison with other non-ferrous metals was leaching of copper (~4.6%).



**Fig 8.** Metal concentrations in product leaching solutions (a) and kinetics of metal leaching from copper-nickel slag (b).

**5. CONCLUSION**

Preliminary studies have made it evident that heap leaching is quite advantageous when re-extracting metals from pelletized copper-nickel ore dressing tailings of current production, or of lean additional concentrate of tailings flotation. Taking into account the availability of excess sulphuric acid turned out by the "Kola MMC" JSC enterprises, sulphatization of pellets, where H<sub>2</sub>SO<sub>4</sub> acts as a binder in tailing pelletizing, is recommended. Additional perspectives for non-ferrous metals recovery from the low grade materials gives an implementation of oxidants that will be the theme of the next report.

Bacterial leaching is also perspective direction in this way. It is planned to conduct the study of current microbial environment on man-made deposits, and to run enlarged leaching test using bacteria.

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**REFERENCES**

- [1]. Chanturiya V.A. and Kozlov A.P., Developing of a physical-chemical foundation and innovation technologies of high-level processing of anthropogenic minerals, *Gornyi Zhurnal (Mining Journal)*. (7), 79 (2014).
- [2]. Khalezov B.D., Heap leaching of copper and copper-zinc ores (domestic experience), *Ural Branch of RAS, Ekaterinburg*, 346 (2013).
- [3]. Watling H.R., The bioleaching of sulphide minerals with emphasis on copper sulphides – A review, *Hydrometallurgy*. 84(1-2), 81 (2006).
- [4]. Watling H.R., The bioleaching of nickel sulphides, *Hydrometallurgy*. 91(1-4), 70 (2008).
- [5]. Watling H.R., Elliot A.D., Maley M., van Bronswijk W. and Hunter C., Leaching of a low-grade, copper-nickel sulfide ore. 1. Key parameters impacting on Cu recovery during column bioleaching, *Hydrometallurgy*. 97(3-4), 204 (2009).
- [6]. Maley M., van Bronswijk W. and Watling H.R., Leaching of a low-grade, copper-nickel sulfide ore 2. Impact of aeration and pH on Cu recovery during abiotic leaching, *Hydrometallurgy*. 98(1-2), 66 (2009).
- [7]. Maley M., van Bronswijk W. and Watling H.R., Leaching of a low-grade, copper-nickel sulfide ore 3. Interactions of Cu with selected sulfide minerals, *Hydrometallurgy*. 98(1-2), 73 (2009).

- [8]. Halinen A-K., Rahunen N., Kaksonen A.H. and Puhakka J.A., Heap bioleaching of a complex sulfide ore: Part I. Effect of temperature on base metal extraction and bacterial compositions, *Hydrometallurgy*. 98(1-2), 92 (2009).
- [9]. Halinen A-K., Rahunen N., Kaksonen A.H. and Puhakka J.A., Heap bioleaching of a complex sulfide ore: Part II. Effect of temperature on base metal extraction and bacterial compositions, *Hydrometallurgy*. 2009. 98(1-2), 101 (2009).
- [10]. Qin W., Zhen S., Yan Z., Campbell M., Wang J., Liu K. and Zhang Y., Heap bioleaching of a low-grade nickel-bearing sulfide ore containing high levels of magnesium as olivine, chlorite and antigorite, *Hydrometallurgy*. 2009. 98(1-2), 58 (2009).
- [11]. Zhen S., Yan Z., Zhang Y., Wang J., Campbell M. and Qin W., Column bioleaching of a low grade nickel-bearing sulfide ore containing high magnesium as olivine, chlorite and antigorite, *Hydrometallurgy*. 96(4), 337(2009).
- [12]. Yang C., Qin W., Lai S., Wang J., Zhang Y., Jiao F., Ren L., Zhuang T. and Chang Z., Bioleaching of a low grade nickel-copper-cobalt sulfide ore, *Hydrometallurgy*. 106(1-2), 32 (2011).
- [13]. Bhatti T.M., Bigham J.M., Vuorinen A., Tuovinen O.H., Chemical and bacterial leaching of metals from black schist sulfide minerals in shake flasks, *International Journal of Mineral Processing*. 110-111, 25 (2012).
- [14]. Chanturiya V.A., Bunin I.Zh., Ivanova T.A. and Khabarova I.A., Effect of high-power nanosecond electromagnetic pulses on disintegration process and physical-chemical properties of sulphide minerals and noble metal-containing beneficiation products, *Proceedings of the XII Balkan Mineral Processing Congress, Delphi, Greece*. Pp. 75-80, (2007).
- [15]. Chanturiya V.A., Samusev A.L., Minenko V.G., Koporulina E.V. and E.L. Chanturiya, Validation of the efficient application of the electrochemical water processing in ore heap leaching, *Journal of Mining Science*. 47(5), 675 (2011).
- [16]. Ptitsyn A.B., Geochemical prerequisites for heap leaching and underground leaching under permafrost conditions, *Journal of Mining Science*. 31(1), 75 (1995).
- [17]. Yurgenson G.A., The cryomineralogenesis of minerals in the technological massifs, *Mineralogy of technogenesis – 2009, Conference Proceeding, Institute of Mineralogy, Ural Branch of RAS, Miass*, Pp 61-75, (2009). (*In Russian*).
- [18]. Lindsay M.B.J., Moncur M.C., Bain J.G., Jambor J.L., Ptacek C.J., Blowes D.W., Geochemical and mineralogical aspects of sulfide mine tailings, *Applied Geochemistry*. 57, 157 (2015).
- [19]. Piatak N.M., Parsons M.B., Seal II R.R., Characteristics and environmental aspects of slag: A review, *Applied Geochemistry*. 57, 236 (2015).
- [20]. Masloboev V.A., Seleznev S.G., Makarov D.V. and Svetlov A.V. Assessment of eco-hazard of copper-nickel ore mining and processing waste storages, *Journal of Mining Science*. 50(3), 559 (2014).
- [21]. Chanturiya V.A., Makarov V.N., Makarov D.V. and Vasilieva T.N., Forms of nickel in storage tailings of copper-nickel ores, *Doklady Earth Sciences*. 399(8), 1150 (2004).
- [22]. Makarov D.V., Potapov D.S., Potapov S.S. and Svetlov A.V., Study of the environmental hazard and the potential ability to extract useful components from granulated slag of the "Pechenganickel" combine "Kola Mining and Metallurgical Company" JSC, *Ecology and Industrial Production*. 2, 54 (2013).
- [23]. Makarov V.N., Vasilieva T.N., Makarov D.V., Alkatseva A.A., Farvazova E.R., Nesterov D.P. and Lashchuk V.V., Potential environmental hazard of unexploited dumps of copper-nickel ore dressing tailings, *Chemistry for Sustainable Development*. 13(1), 85 (2005).
- [24]. Rylnikova M.V., Radchenko D.N., Ilimbetov A.F. and Zvyagintsev A.N., Pilot-scale approbation of leaching technology for copper-pyrite ore dressing wastes, *Mining Informational and Analytical Bulletin*. 2, 293 (2008).
- [25]. Masloboev V.A., Makarov D.V., Nesterov D.P., Mazukhina S.I., Bocharova I.V., Menshikov Yu.P. and Svetlov A.V., Geocological validation of mechanisms and parameters of physical-chemical processes facilitating the in-depth processing of complex sulphide ores and mining wastes, *Proceedings of the Murmansk State Technical University*. 15(2), 361 (2012).