

Perspectives for Heap Leaching of Non-Ferrous Metals (Murmansk Region, Russia)

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DOI: 10.29227/IM-2015-02-38

Abstract

The results of laboratory simulation of heap leaching of non-ferrous metals from dumps of the Allarechensk deposit, low-grade ore of the Nyud-II deposits, and processing wastes of the "Kola MMC" JSC are presented.

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 unfreed ore is beneficial both from environmental and economical viewpoints.

*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.*

Keywords: natural and anthropogenic sulphide-containing raw materials, non-ferrous metals, heap leaching

Introduction

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 (Khalezov, 2013). 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 (Khalezov, 2013). 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 (Chanturiya and Kozlov, 2014; Chanturiya et al., 2007, 2011). In recent years, there have been developed geochemical foundations for a geotechnology permitting to recover non-ferrous metals at negative temperatures and in permafrost (Ptitsyn,

1995; Yurgenson, 2009). These findings can be adjusted to objects in the Murmansk region.

Objects of research

The objects of research were:

- Ores of an anthropogenic deposit – dumps of the Allarechensk copper-nickel deposit (Pechenga area of the Murmansk region);
- Low-grade ores of the copper-nickel Nyud-II deposit (Monchegorsk area);
- Copper-nickel ore dressing tailings ("Kola MMC" JSC).

Dumps of the Allarechensk deposits are the represented by overburden, predominantly valueless, gneiss, granite-gneiss, amphibolites and, to different extents, various mineralized enclosing strata such as peridotite, olivinite, contact amphibolites, etc. The ore in the dumps can be referred to two morphological types: massive and disseminated. The main ore minerals found in both types are pyrrhotite, pentlandite and, more rarely, chalcopyrite, which are in a close paragenetic association with magnetite (Masloboev et al., 2014).

In the Nyud-II deposit, mineralized ores are represented by meso- and leucocratic norites and gabbro-norites occurring as alternating bands. The

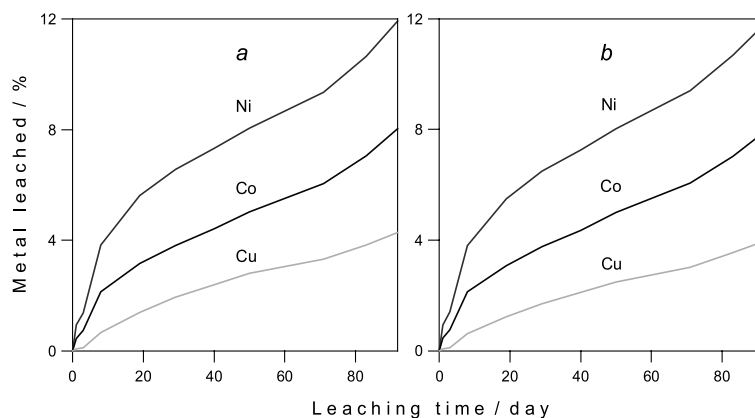


Fig. 1. Kinetics of metal leaching from dumps of the Allarechenskoye deposit with a 2% sulphuric acid solution (a) and H_2SO_4 plus oxidizer (b)

Rys. 1. Kinetyka ługowania metali z hałdy złoża Allarechenskoye z 2% roztworem kwasu siarkowego (a) i H_2SO_4 z dodatkiem utleniacza (b)

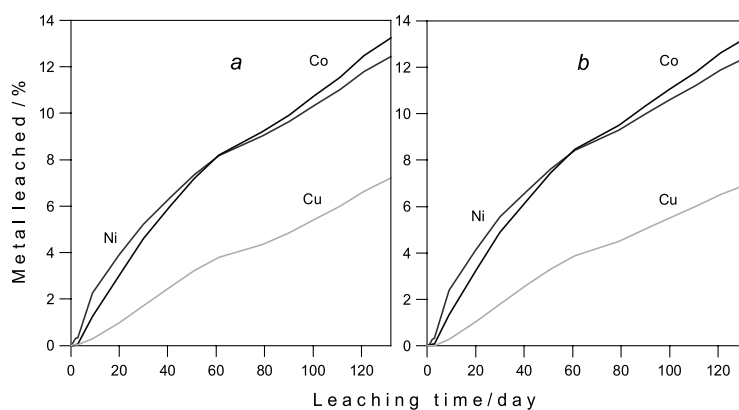


Fig. 2. Leaching kinetics of metals from Nyud-II ore with a sulphuric acid solution (a) and H_2SO_4 plus oxidizer (b)

Rys. 2. Kinetyka ługowania metali z rudy Nyud-II, w roztworze kwasu siarkowego (a) i H_2SO_4 z dodatkiem utleniacza (b)

principal ore minerals are pyrrhotite (90%), pentlandite, chalcopyrite and magnetite. There are also pyrite, mackinawite, violarite and molybdenite. The sulphides are impregnated, with ore pockets, shliers and veins (Pripachkin et al., 2013).

In copper-nickel ore dressing tailings of the Kola MMC JSC, 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 pyrrhoxene, amphiboles, talc, chlorites, quartz and feldspar (Chanturiya et al., 2004). The principal ore minerals are magnetite, pyrrhotite, pentlandite and chalcopyrite. The total content of sulphide minerals is 1–3%.

Results and discussion

Dumps of the Allarechensk copper-nickel deposit

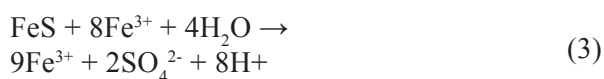
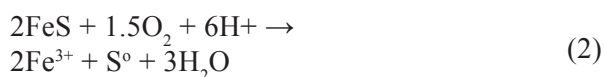
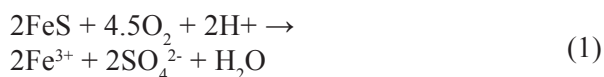
Previously we have studied the supergene leaching in sulphide minerals in dumps of the Allarechensk copper-nickel ore deposit (Masloboev et al., 2014). Oxidation was found to occur most vigorously in monoclinic pyrrhotite, yielding free sulphuric acid further affecting both pyrrhotite and the associated minerals, pentlandite in particular. This process results in the formation of violarite with a further increase in porosity and higher weathering rate. Another destructive element is natural bacterial leaching. There have been detected newly-formed nickel, cobalt and copper sulphates: retgersite $NiSO_4 \cdot 6H_2O$, moorhouseite $CoSO_4 \cdot 6H_2O$, beaverite $CoSO_4 \cdot 7H_2O$, and langite $Cu_4SO_4(OH)_6 \cdot 2H_2O$. It has been established that long exposure to weathering of coarse clastic sulphide-containing mining waste results in deterioration of initial properties, which in turn complicates the technology of separation of ore shells from rock mass and leads to still greater losses of valuable components during processing. Long

storage is also responsible for degradation of eco-systems on areas adjoining the dump (Masloboev et al., 2014).

In this work, interaction of impregnated ore of the fraction -3+2 mm with a leaching agent was studied in the dynamic regime in columns with a diameter of 40 mm and a temperature of $18 \pm 2^\circ\text{C}$ during 90 days. The ore of this fraction contained, %: Ni 0.52, Cu 0.74, Co 0.012. The reagents were a 2% sulphuric acid solution, the same solution with iron (III) sulphate acting as oxidizer. The oxidizer consumption was 80 g/t ore. First, the ore was saturated with water. At this stage no experiments with solution circulation were carried out. The ore weight was 150 g. Sulphuric acid in amounts of 10 mL was fed once in 3–4 days. The output solutions were analyzed using the atom-absorption spectrometry (AAnalyst 400 PerkinElmer).

Fig. 1 demonstrates the kinetics of metal leaching from ore samples. Quite predictably, leaching was the most intensive for nickel; the result for copper was much lower. After 90 days leaching without an oxidizer yielded, %: nickel 11.9, copper 4.3, cobalt 8.0. With an added oxidizer, the results were the following: nickel 11.8, copper 4.0, cobalt 7.9.

Note that the presence of oxidizer did not improve the metal extraction. Apparently, leaching of pyrrhotite with sulphuric acid occurring by the following reactions:



creates a sufficient quantity of Fe^{3+} intensifying the dissolution of non-ferrous metals. The slow transition of copper to solution is due to the low rate of chalcopyrite dissolution (Khalezov, 2013).

Ores of the Nyud-II copper nickel deposit

Interaction of Nyud-II ore of the fraction -3+2 mm with a leaching agent was examined in the dynamic regime in columns 40 mm in diameter at a temperature of $18 \pm 2^\circ\text{C}$ during 130 days. The ore contained, %: Ni 1.70, Cu 0.50, Co 0.07 (the experimental sample was taken from densely disseminated ore). Again, the reagents were a 2% sulphuric acid and an iron (III) sulphate solution as oxidizer. The ore was preliminarily saturated with

water. The experimental conditions did not provide for solution circulation. The ore weight was 150 g. The acid (10 mL) was fed every 3–4 days. Output solutions were analyzed by the method of atom-absorption spectrometry (AAnalyst 400 PerkinElmer). The solid phase was analyzed using X-ray diffraction (XRD) at a DRON-2 diffractometer (Cu $K\alpha$ radiation).

According to XRD, there was no qualitative difference between the output and input ore substances. There was observed a decrease in intensity of pyrrhotite reflexes relatively the silicate reflexes especially evident in the upper layer of the column. At the same time, the column walls acquired a thin green coating which composition was analyzed and found to be, for the most part, a newly formed sulphate belonging to the group of halotrichite $\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ (pickeringite $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$, and vupatkiite (Co,Mg,Ni) $\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$).

Fig. 2 presents the metal leaching kinetics from Nyud-II ore samples. Unlike the Allarechensk dumps, the metal easiest extracted in this case was cobalt. This may be due to the fact that cobalt is present in the ore only in sulphides, with a part of it incorporated in pyrrhotite. Copper was leached out poorly, as was the case with ore in dumps of Allarechensk deposit. After 130 days, the metal leaching with an oxidizer-free solution was as follows, %: nickel 12.4, copper 7.2, cobalt 13.2. With an oxidizer, the results were the following, %: nickel 12.4, copper 6.9, cobalt 13.3.

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 (Makarov D.V. et al., 2004) where filtration, blocked by a claylike artificial soil formed by chlorites and mixed layered formations with alternating chlorite and smectite layers, dwindled 100 fold (Makarov V.N. et al., 2005).

This problem can be addressed by granulating the materials with binders such as lime and Portland cement. Thus, in work (Rylnikova et al., 2008) 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

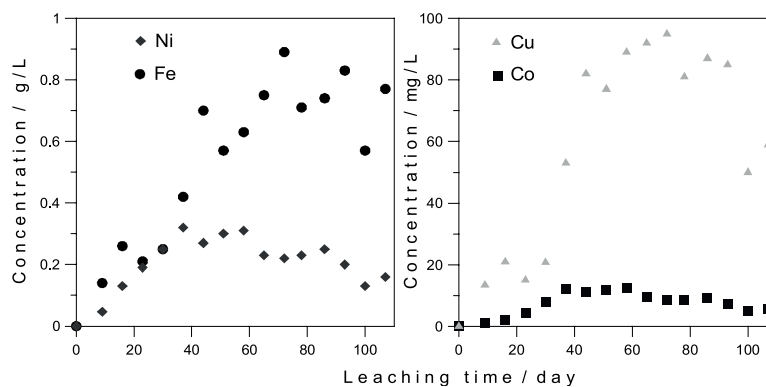


Fig. 3. Metal concentrations in product leaching solutions of pelletized copper-nickel ore dressing tailings
 Rys. 3. Zawartość metali w produktach ługowania peletów z odpadów miedziowo-niklowych

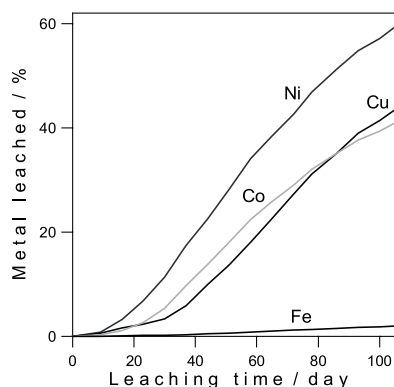


Fig. 4. Kinetics of metal leaching from pelletized copper-nickel ore dressing tailings
 Rys. 4. Kinytyka ługowania metali z granulatu z odpadów przeróbczych miedzi i niklu

dressing tailings with sulphuric acid (Masloboev et al., 2012). 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 ratio of S:L = 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 prelimi-

narily 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 mm.

The output solutions were analyzed using the atom-absorption spectrometry. The solid phase was analyzed using XRD.

The tailings mainly consist of serpentine. 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 isomorphous-

ly substituted for iron, nickel and cobalt, and also gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 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.

The dynamics of metal leaching in the experiment is given in Fig. 4. It can be seen that the process is fairly intensive, the nickel concentrations in solution stably varying over the range of 0.1 to 0.35 g/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. 4 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 (Khalezov, 2013). 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:

$$\varepsilon_{\text{Ni}} = 0.6329 \tau - 4.6459, (R^2 = 0.9891) \quad (4)$$

$$\varepsilon_{\text{Cu}} = 0.4682 \tau - 6.9116, (R^2 = 0.9871) \quad (5)$$

$$\varepsilon_{\text{Co}} = 0.4484 \tau - 4.737, (R^2 = 0.9808) \quad (6)$$

where ε_{Me} is the metal extraction, %; τ is the leaching time, days.

Conclusion

It has been established that sulphide-containing dumps of the Allarechensk copper-nickel ore deposit and low-grade ore of the Nyud-II deposit can be processed by heap leaching in the case optimal technologies are developed to intensify the sulphide mineral dissolution.

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 granules, where H_2SO_4 acts as a binder in tailing pelletizing, is recommended.

Acknowledgements

The work has been performed with support of RFFR (project №14-05-98804p_sever_a within the Programme №5 of the RAS Presidium. Grant of RF President "Scientific school of Academician V.A. Chanturiya" NSh-748.2014.5.

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Możliwości ługowania metali nieżelaznych z hałdy w Rejonie Murmańsk (Rosja)

Przedstawiono wyniki badań laboratoryjnych ługowania metali nieżelazowych z hałd złoża Allarechensk, ubogich rud w złożach Nyud-II, oraz przetwórstwa odpadów „Kola MMC” JSC.

Jak wiadomo, odpady o niskich zawartościach metali, których eksploatacja jest nieopłacalna, mogą stanowić poważne ryzyko dla środowiska. Dlatego rozsądna utylizacja składowisk odpadów jest korzystna zarówno pod kątem środowiskowym, jak i ekonomicznym. Tego typu naturalne i sztuczne źródła surowców mogą być przetwarzane z wykorzystaniem ługowania na hałdzie, gdzie roztwór kwasu siarkowego, utleniacz (tlen, jony żelaza (III) etc.) i mikroorganizmy (Thiobacillus Ferrooxidans, Thiobacillus Thiooxidans etc.) są dawkiowane zarówno na powierzchni, jak i wewnątrz hałdy. Równomierne dozowanie roztworu uzyskuje się przez system basenów, rynien, sieci rur połówkowych lub rozpylania. Wzbogacony roztwór wyciekający spod hałdy jest zbierany do rynien lub rur, a następnie podlega dalszej obróbce.

Słowa kluczowe: naturalne i antropogeniczne surowce zawierające siarczki, metale nieżelazne, ługowanie hałdy