



# Heap Leaching and Perspectives of Bioleaching Technology for the Processing of Low-Grade Copper-Nickel Sulfide Ores in Murmansk Region, Russia

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## Abstract

*Explored reserves are reducing. Cut-off grade sulfide ores from both abandoned and currently developed deposits, overburden rock while being a major source of non-ferrous metals, pose a serious environmental hazard if unprocessed. Reasonable utilization of rock waste dumps and low-grade ore is beneficial both from environmental and economical viewpoints. New techniques are designed to increase the selectivity and completeness of the disclosure of sulfide minerals, even in low-grade ores and mining waste. Among the variety of approaches is providing a bioleaching.*

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

## Introduction

The existing decrease in explored reserves, the increase in volume of complex ores supposed for processing and the growth of refuse ores and processing wastes of non-ferrous metals issue the challenge to develop new technologies of copper and nickel extraction and recovery.

Bioleaching should be pointed out among other approaches. The naturalness of the process based on chemico-biological processes provides almost complete recovery of valuable components (above 90%) and is the chief advantage of the method. The process initiation and intensification in difficult climate conditions is one of the disadvantages. Indeed, the Murmansk region located behind the Polar Circle is characterized by low-grade deposits and the most part of potentially processable wastes are higher than 67° northern latitude.

## Review of bioleaching methods

The underground, heap and tank leaching are the promising methods for processing of rebellious materials. Let's consider the heap leaching intensification by introducing microorganisms into the process.

The technology of heap leaching consists of the following. A solution containing a sulfuric acid, oxidizer (oxygen, iron (III) ions, etc.) and microorganisms (for example, *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, etc.) is applied on the heap surface or inside. The solution is spread evenly on the surface or inside

the heap mass by means of basins, drainage channels and perforated pipes or through pulverizing. The return solution enriched by non-ferrous metals is collected by the channels or pipes and forwarded for further processing (Svetlov et al., 2015; Khalezov, 2013).

Bioleaching is a rather young method for recovery of valuable elements compared to heap leaching on a global scale. There used to be some know-how in the USSR though they failed to receive any commercial introduction. For example, a pilot plant for underground leaching of copper with bacterial reconditioning of solutions was established in 1964 in Degtyarskiy mine (the Urals) (Polkin et al., 1982). Though, it should be noted that so far none of the leaching methods has become a part of mining technology during actual mining activities (Khalezov, 2013). There is a good deal of groundwork in this field in contemporary Russia and the leaching experience of the world mining leaders is being adopted. At the same time, there is a series of technological problems which are also studied (Kashuba and Leskov, 2014). This work suggests a review of the current world-wide practices (Watling, 2008). The study gives consideration to research and development issues of technology adoption as well as economic efficiency of bioleaching applied at copper-nickel deposits Mount Sholl and Sherlock Bay (Pilbara region, Western Australia), Jinchuan (Gansu Province, the Northern China) and Talvivaara (Sotkamo, Finland).

The Mount Sholl and Sherlock Bay deposits, Australia. Two large objects are located on the West of the continent:

- the Mount Sholl deposit, containing, %: Ni 0.67, Cu 0.92, Fe 11.1 and S 4.05;
- the Sherlock Bay deposit, containing, %: Ni 0.4, Cu 0.09 and Co 0.02.

BioHeap™ technology is applied in Radio-Hill (the Mount Sholl deposit). The technology belongs to the mining company and is based on registered warm-weather bacterial culture, oxidizing primarily sulfur. The molecular analysis showed that the bacterial mixture contains representatives of genus *Sulfobacillus* (bacteria) and *Thermoplasma* (archaea) (Hunter et al., 2007; Watling, 2008).

Sulfide minerals make up to 15% of the ore volume and are finely disseminated. The pentlandite (Fe, Ni)<sub>9</sub>S<sub>8</sub> particle size is -2+0.03 mm. There are about 60–70% of chalcopyrite (CuFeS<sub>2</sub>) grains with the size of -100 μm. Besides, 50% of sulfides are concentrated in inert silicate minerals.

Considerable nickel recovery (90%) was achieved within a short time span, i.e. less than a year. Copper recovery was more slowly and was about 50% over the same period. The mineralogical analysis of the ore mass after leaching showed that chalcopyrite (CuFeS<sub>2</sub>) had been oxidized, though copper re-deposited and dissolved only after the chemical conditions had changed. The dissolution and re-repositioning of copper in the ores of the Mount Sholl deposit was experimentally verified (Hunter et al., 2007). After passing into solution of 60% of nickel the copper recovery rate raises, which can be related to electrochemical properties of the minerals (Hunter, 2002).

It was shown by the example of the Sherlock Bay deposit that the disseminated sulfide copper-nickel ores are bioleachable using salt-resistant bacterial culture and highly mineralized mine waters (Williams, 2006). The leaching studies demonstrate good results. Nickel recovery is 88% during 400 days.

The technology has some advantages and first of all high leaching rate due to the presence of chlorine ions in the mine waters.

The Jinchuan deposit, China. Nickel reserves in China are about 6.7 mln. tons and are concentrated mainly in copper-nickel sulfide ores (91%). About 80% of nickel-containing sulfide reserves are concentrated in the ores of the Jinchuan deposit, Gansu province, the Northern China. Pilot heap leaching of non-ferrous metals was conducted here by a leading nickel, cobalt and PGM producer of China (Non-ferrous metals Company, the city of Jinsuan, JNMC, <http://www.jnmc.us/>). The test object had the similar technical regulations as in Radio Hill and had enforced aeration and watering, though without the registered bacterial mixture BioHeap™ (Watling, 2008).

Bacteria were used for leaching in the subsequent works of Chinese researchers at this object (Qin et al., 2009). Simultaneously the works deal with the issue of the oxidized waste water management.

The ores contain, %: Ni 0.6, Cu 0.3, Co 0.026 and Fe 10.4. The ore samples are represented by the following sulfide minerals, %: pyrrhotine (Fe<sub>1-x</sub>S) ~ 3.3, pentlandite ((Fe,Ni)<sub>9</sub>S<sub>8</sub>) ~ 1.6, chalcopyrite (CuFeS<sub>2</sub>) ~ 0.8, pyrite (FeS<sub>2</sub>) ~ 0.5 and violarite ((Fe,Ni)<sub>3</sub>S<sub>4</sub>) ~ 0.2. The basic rock minerals are: olivine (~ 37%), antigorite (~ 30%), chlorite (~ 7%), talc (~ 6%) and tremolite (~ 6%). There are magnetite (~ 3%) and chromite (~ 0.4%) in small amounts.

It should be noted that the composition of nonmetallic minerals of this deposit is close to the composition of processing tailings of Pechenganikel smelter (Kola Mining and Metallurgical Company, SC), namely there are high concentrations of antigorite, chlorites and talc in them. This study object is interesting also because it is located in the North West of China, the area with cold weather conditions. The microorganisms used for bioleaching are represented by a mixture of mesophilic bacteria, consisting of the bacteria collected at the tailing dump of the Non-ferrous Metals Company, and a strain *L. ferrooxidans* (DSM 2391), purchased at the German collection of microorganisms and cell cultures (DSMZ – Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH).

The period of studies was 350 days including 80 days for preliminary acid leaching and 270 days for bioleaching. The following recovery was achieved, %: Ni 84.6, Co 75.0 and Cu 32.6. Due to rather high concentrations of magnesium in rock minerals the acid consumption was 600 kg per ton of ore.

The financial viability of the project depends directly on the price of the acid.

Complex deposit Talvivaara, Finland. Being the largest sulfide copper-nickel deposit in Europe (Riekola-Vanhanen, 2007), the complex deposit Talvivaara in the city of Sotkamo, Finland, is geographically located in the conditions very similar to those in the Murmansk region and served an example of heap leaching in the Far North.

Polymetallic ores of the deposit contain on average, %: Ni 0.27, Zn 0.56 and Cu 0.14, there are also pyrrhotine (Fe<sub>1-x</sub>S), pyrite (FeS<sub>2</sub>), sphalerite (ZnS), pentlandite ((Fe,Ni)<sub>9</sub>S<sub>8</sub>), violarite ((Fe,Ni)<sub>3</sub>S<sub>4</sub>), chalcopyrite (CuFeS<sub>2</sub>) and graphite (C). 70% of nickel are concentrated in pentlandite, the rest part is distributed among pyrite (8%) and pyrrhotine (21%). The silicate minerals include quartz, mica, anorthite and microcline. The bioleaching of ore at Talvivaara mine has been studied for two decades: starting from laboratory experiment in leaching columns and ending by a construction of a demonstration heap (Puhakka et al., 2007).

The microorganisms used in the technological process were selected from water samples of the Talvivaara deposit. The culture of microorganisms was improved and the volume was adjusted using elementary sulfur, ions of ferrous iron and finely crushed ore. Well-known acidophiles were found out: *At. ferrooxidans*, *At. thiooxidans*, *L. ferrooxidans*, *At. caldus* and heat-resistant *Sulfobacillus* (Halinen et al., 2007; Puhakka et al., 2007).

The ore agglomeration was carried out using the mixture of acid and inoculation, after that it was heaped. The pre material had size of -8 mm. The watering was carried out by a solution with pH=1.8 and rate 5 l/m<sup>2</sup>/h and the solution temperature varied within 4 and 20°C. The temperature inside the heap varied between 30 and 90°C, despite the cold weather (cold months were also included in the study cycle), the temperature of saturated leaching solutions was 40–50°C (Riekkola-Vanhänen, 2007).

The communities of microorganisms in the heap (observed through leaching analysis) varied during the beginning several months and afterwards the dominating communities stood out: *At. ferrooxidans* and *Desulfotomaculum geothermicum*; the following species were found out: *Thiomonas arsenivorans*, *Alicyclobacillus tolerans* and *Ferromicrobium acidophilum* (Halinen et al., 2007). The analysis of ore samples from the heap showed *At. ferrooxidans*, *At. caldus* and *F. acidophilum*. Uncultured clone of bacterium H70 was revealed in both leaching products and in ore samples as well. The number of cells varied between 105 and 108 cells/ml in the filtrate and between 105–107 cells/g of ore. The metal recovery during 500 days was the following, %: Ni 92, Zn 82, Co 14 and Cu 2. Low values of copper recovery are explained by electrochemical properties of minerals (Watling, 2008).

The Talvivaara mine was first one to start commercial production of heap leaching of copper-nickel ores. The production was launched in 2009 with the nickel recovery 735 t (Annual Report, 2013). Initially the increase in production capacity equal to 33000 t of nickel, 1200 tons of cobalt, 60000 tons of zinc and 10000 tons of copper per year was planned by the year 2010 (Watling, 2008). However, the maximum values of nickel recovery were achieved in 2011 and they were equal to the half (16087 t) of the planned values for the year 2010 (Annual Report, 2013).

The project was developed and launched during the years when the price of non-ferrous metals was high (Lodeishchikov, 2009). According to Information-analytical center “Mineral” unprecedented growth of process started in 2005, continued in 2006 and proceeded to the middle of 2007 (WEB source a).

The price was 52.2 thous. dollars per ton in May of 2007. However, the price reduced practically twice by

August and became 27.7 thous. dollars and by the end of the year reduced to 26 thous. dollars per ton. The average yearly price of refined nickel at London metal exchange for 2007 grew up compared to the year 2006 by 52.5% – from 24416 dol./t to 37230 dol./t. The likelihood of commercial success of the project was very promising.

Though in subsequent years there was a considerable reduction of price of non-ferrous metals. According to London metal exchange the average price of nickel in January-March of 2016 was 8500 dol./t. The tight economic situation at the world market resulted in bankruptcy of Talvivaara Group (WEB source b). Despite complicated economic end the company produced some interesting results which were practically verified and had strategic importance for further research and development works:

- the microorganisms used for bioleaching exist and develop in the initial ore, are endemic and accustomed to the environment, this increases the technology's efficiency;
- the company organized testing of metal depositing from the obtained technological solutions. The methods of recovery of nickel and subsidiary non-ferrous metals (cobalt, copper and zinc) were developed in cooperation with OMG Kokkola Chemicals (Finland), and its nickel activities belong to MMC NORILSK NICKEL;
- the tests demonstrated high quality of the products obtained by recovery from solution on an industrial scale (the pilot plants showed high values of metal recovery from ores – up to 98%) (Lodeishchikov, 2009).

### **Perspective objects for bioleaching of Murmansk region**

The development of technologies for recovery of minerals from low-grade copper-nickel ores and mining wastes of the Murmansk region is an urgent research task. At the initial stage there was a laboratory modeling of heap leaching of low-grade ores and technogenic formations. The results are presented in the article. The study objects were: the ores of the Allarechensk deposit dump, low-grade ores of copper-nickel deposits of Monchepluton (by the example of the Lake Moroshkovoe deposit) and the wastes of copper-nickel production and processing at Kola Mining and Metallurgical Company (Kola MMC), SC.

The Allarechensk deposit dumps. The Allarechensky Deposit Dumps TMF (technogenic mineral formation) is situated in the Pechenga district of the Murmansk Region, and is a dump of mine waste formed after opencast mining of the Allarechensky sulfide copper-nickel ore deposit was completed in 1971. The base minerals were nickel, copper and cobalt. The dumped

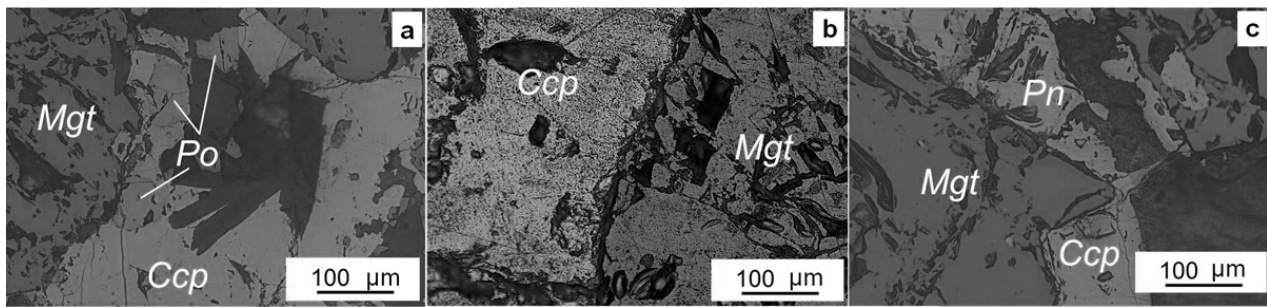


Fig. 1 The types of intergrowths of ore minerals at the Lake Moroshkovoe deposit: inclusions of chalcopyrite in magnetite (a); ingrowths of pyrrhotite in chalcopyrite (b); complex intergrowth of magnetite, chalcopyrite and pentlandite (c)

Rys. 1 Typy mineralizacji z złoży Lake Moroshkovoe: inkluzje chalkopirytu w magnetycie (a) wprysnięcia pirotynu w chalkopirytye, (b) kompleksowe inkluzje magnetytu, chalkopirytu, pentlandytu (c)

rocks are mainly barren gneiss, gneissic granite overburden and differently mineralized country rocks: peridotite, olivinite, contact amphibolite and others. The fine cut fraction contains blast-fragmented country and overburden rocks as well as quaternary fluvio-glacial and lacustrine–glacial deposits. The ore rocks in the dump are of two morphological types: solid and disseminated. The base minerals are pyrrhotite, pentlandite and less often chalcopyrite, which are tightly related paragenetically with magnetite. The prime concentrator of nickel is pentlandite. By the evidence of microprobe analysis, the average chemical composition of pentlandite in solid ore, %: Ni 35.3, Fe 30.8, Co 0.7, S 33.2, total 100.0, formula  $(\text{Ni}_{4.65}\text{Fe}_{4.26}\text{Co}_{0.08})_{8.99}\text{S}_{8.00}$ ; in disseminated ore, %: Ni 34.1, Fe 32.0, Co 0.6, S 33.0, total 99.7, formula  $(\text{Ni}_{4.50}\text{Fe}_{4.44}\text{Co}_{0.08})_{8.02}\text{S}_{7.98}$ . Despite the subarctic location of TMF, samples of water and ore contained thionic acidophilous iron- and sulfur-oxidizing bacteria. The bacteria were detected by inoculation of the Silverman and Lundgren medium 9K. The strains exhibited high oxidative activity, to 20–23 g/l  $\text{Fe}^{2+}$  per day (the specimens were 100 g in weight, with nickel content of 1.2–3.5%, grain size of – 10 mm, S : L = 1 : 3) (Masloboev et al., 2014).

The kinetics of metal leaching from the ore samples (the ore sample under study contained, %: Ni 0.52, Cu 0.74, Co 0.012) in laboratory conditions predictably demonstrates more intensive nickel leaching. The outlet solutions were analyzed by the atomic absorption spectrometry. The lowest leaching was shown by copper. After 90 days of leaching by the solution of sulfuric acid (2%) without the oxidizers, the metal recovery was, %: 11.9 nickel, 4.3 copper, 8.0 cobalt. (Svetlov et al., 2015).

The Lake Moroshkovoe deposit. The deposit is confined to the north-west-striking tectonic zone at the border of norites of the Nyud-Poaz massif and host meta-diorites. The Cu-Ni mineralization is located within the shear zone composed of actinolite-chlorite, actinolite and quartz-chlorite schists, which are the products of dynamic metamorphism of contact norites. The ore is

mainly disseminated, and occurs in lenses, veinlets and rarely in pockets up to 20 cm in size. High Ni content is typical of the ore composition. Nickel-bearing pyrite with pentlandite admixture predominates in the mineral composition (Pripachkin et al., 2013).

The mineralogical studies of the sample prepared for leaching shows that the magnetite forms hypidomorphic grains of grey color with a brown shade and makes up the most of the rock. Chalcopyrite is a mineral with bright yellow color forms irregularly shaped grains in interstices of magnetite (Fig 1a). Pyrrhotite inclusions can be often found in large grains of chalcopyrite (Fig 1b). Chalcopyrite forms intergrowths with pentlandite (Fig 1c).

The interaction of ore in fractions -3+2 mm with leaching agent in a dynamic mode in columns with the diameter 40 mm at the temperature  $18\pm 2^\circ\text{C}$  during 65 days was studied. The ore contained: %: Ni 0.72, Cu 3.09 and Co 0.039. 2% sulfuric acid was used as a reagent. Preliminarily, the ore had been watered before the leaching. There was no solution recycling. The water upload was 150 g. 10 ml of the acid were applied every 3–4 days. The return solutions from the columns were analyzed by atomic-absorption spectrometry.

The intensity of nickel and cobalt leaching is the same. Copper is leached out slowly. Apparently, this is connected to electrochemical properties of sulfide minerals (Svetlov et al., 2015). Chalcopyrite forming intergrowths with pentlandite plays the role of cathode areas where the oxidizers are reduces.

The acceptable values of copper recovery can be expected after oxidation of iron sulfides and nickel (Watling, 2008). The metal recovery was as follows, %: nickel 15.2, cobalt 14.9 and copper 2.4.

Copper-nickel ore processing tailings of Kola MMC SC. The tailing dump of Processing plant No.1 of Pechenganikel smelter in the town of Zapolyarniy of the Murmansk region has been operating since 1965. The volume of tailings is 250 mln.t. The particle-size and mineral composition of the tailings may vary within a certain range depending on the ore and the applied

technological process. At the same time fractions with the grain size  $-0.1$  mm dominate and in many cases up to 50% of grains have the size of  $-0.044$  mm. The processing tailings are dominated by serpentines ( $\sim 60\%$ ) (Makarov, 2004).

There are pyroxenes, amphiboles, talc, chlorites, quartz and field spars in great amounts. The main ore minerals are magnetite, pyrrhotine, pentlandite and chalcopyrite. The total composition of sulfide minerals is 1–3%.

With regard for the oversupply of produced sulfuric acid at Kola MMC and difficulties with its commercialization the sulfuric acid agglomeration is perspective where the acid is a binding agent. Granules were received with the correlation S:L=5-3:1 during experiments. The  $H_2SO_4$  solution with the acid concentration 10–30% was used as a binding agent. The diameter of granules for testing - 0.8–1 cm. The further studies were conducted using 10%-solution as a binding agent and with the correlation S:L=3:1.

Percolation leaching was carried out with 1–3% sulfuric acid in columns with the diameter 45 mm during 10 days. The granules were initially watered. The upload of pellets was 150 g. The interval between water applications was 2–3 days and the volume of applied acid – 25 ml. The tailings contained: %: Ni 0.17, Cu 0.07 and Co 0.01. The solutions from columns were analyzed by atomic-absorption spectrometry.

Nickel concentrations in the solution are stable and vary within the range 0.1–0.35 g/l. These indices are applicable for industrial method implementation under condition of recycling of solutions.

With regard for dissolving of the part of silicate minerals the iron concentrations reach 0.9 g/l. Thus, there is a need in a technical solution for selective removal of iron from pregnant solutions. Relatively high copper concentrations are remarkable. The cobalt values are also rather stable.

The kinetics of metal leaching from tailings of copper-nickel ore processing shows that nickel is leached

most intensively, which is predictable. About 60% of the metal from granules leached into the solution during 110 days. Copper indices are lower ( $\sim 44\%$ ) and are explained by the fact that copper exists in chalcopyrite (Makarov, 2005; Makarov, 2004). The rather low values cobalt ( $\sim 41\%$ ) are probably due to the metal existence in the form of isomorphous admixture in magnetite.

## Conclusion

The review of the international experience shows that heap bioleaching of low-grade copper-nickel ores can be realized on industrial scale and in severe climate conditions. The demand for such methods in future is obvious.

The mineralogical and technological studies of burden rocks of the Allarechensk deposit dumps and low-grade copper-nickel ores of Monchepluton by the example of the Lake Moroshkovoe deposit are performed. The studies show that the ores can be processed by heap bioleaching with twice lower expenses compared to tank leaching and with the duration of about one year.

The experiments on sulfuric agglomeration of copper-nickel ore processing tailings and grained slags are carried out. Granules are received with the correlation S:L=5-3:1. Percolation leaching of the tailings and slags is carried out by sulfuric acid with the concentration 1–3%. The experiments show that about 60% of nickel can be recovered from the tailings for 110 days.

It is necessary to find adequate technological solutions to intensify the dissolving of sulfide minerals, first of all, chalcopyrite. The viability of sulfuric agglomeration of both technogenic objects (tailings), and ores is apparent; as well as introduction of oxidizers and adapted endemic microorganisms into the solution.

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*Ługowanie haldy i perspektywy bioługowania dla przeróbki ubogich siarczkowych rud  
miedziowo-niklowych w rejonie Murmańska (Rosja)*

*Udokumentowane zasoby rudy są ograniczone. Rudy siarczkowe pozostałe w złożu po wydobyciu stwarzają poważne zagrożenie dla środowiska. Racjonalne wykorzystanie składowisk odpadów i rudy o niskiej zawartości metalu jest korzystne zarówno z punktu widzenia ochrony środowiska jak i ekonomiki.*

*Nowe techniki mają na celu zwiększenie selektywności i kompletności wykorzystania minerałów siarczkowych, nawet z rud o niskiej zawartości i odpadów górniczych. Wśród różnych technologii rozpatrywane jest bioługowanie.*

*Słowa kluczowe: naturalne i antropogeniczne minerały siarczkowe, metale nieżelazne, ługowanie haldy*