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Processing of Sulfide Copper-Nickel Ores from the Deposits in Murmansk Region by Heap Leaching

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Abstract: The feasibility of processing low-grade copper-nickel ores by heap bioleaching was investigated. It was found that an iron-oxidizing strain of acidophilic microorganisms, *Acidithiobacillus ferrivorans*, is effective in the leaching of sulfide ores from the deposits in Russia's Murmansk region. Sulfide mineralization of the studied mineral feeds was described using the methods of X-ray phase analysis and optical microscopy. In the process of leaching, the pH and Eh values and the concentrations of ferric and ferrous iron, nickel, and copper ions were monitored. By the end of the experiment, 16.5% of nickel and 7.5% of copper was recovered from the ore of the Allarechensk technogenic deposit, while 22.5% of nickel and 12.7% copper were recovered from the ore of the Nud II deposit. By silicate analysis of the solid phase, patterns of ore chemistry change were described during the process of bioleaching.

Keywords: bioleaching; sulfide ores; non-ferrous metals; technogenic waste; acidophilic microorganisms



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1. Introduction

One of the most important areas of ongoing research is developing fundamentally new methods for the concentration of sulfide minerals in Russia's Arctic. Major resources of key minerals are concentrated in Russia's Murmansk Region, and multiple sulfide copper-nickel deposits have been found there. The nickel province of the Kola Peninsula is located in the eastern part of the Baltic Shield [1].

The Murmansk region is characterized by harsh climatic conditions, with an average annual temperature of 0.2 °C. The average annual air temperature decreases from 0 °C on the coast of the Barents and White Seas to −2 °C in the inland areas of the peninsula and down to −3–4 °C in mountainous areas [2]. The region's ecosystems are fragile and have relatively low resilience to anthropogenic impact. In this context, the intensive development of the mining industry in the region has led to a significant deterioration of the natural environment. Changes are observed in the surface water hydrochemistry, the chemical composition of bottom sediments and soils, and the structural and functional organization of biotic communities [3].

One of the reasons for these transformations is the pollution of ecosystems with ions of copper and nickel, caused by the incomplete development of copper-nickel deposits and the accumulation of concentration tailings [4]. To minimize the negative impacts, new technology needs to be developed that can efficiently process low-grade ores and industrial waste.

Microorganism bioleaching of minerals is an evolving technology with an important potential to add value to the mining industry with the capacity to offer economic, social, and

attractive environmental benefits to all associates. Bioleaching is a simple, environmentally friendly, and cost-effective method of processing sulfide mineral feeds [5–7]. This is due to the fact that sulfide deposits are a natural habitat for acidophilic microorganisms that oxidize iron and sulfur [8]. This method is promising in terms of processing various mineral feeds—low-grade ores, tailings dumps, fine concentration tailings, and other industrial waste-containing non-ferrous and precious metals. This process has been successfully applied in practice in a variety of climatic conditions in regions such as the South American Andes, the Arctic, and tropical regions.

Heap bioleaching has performed well in the subarctic zone, where the average annual temperature is 1.3 °C [9,10]. Polymetallic ore from the Talvivaara deposit was processed using indigenous communities of microorganisms that are capable of actively oxidizing sulfides at high concentrations of nickel (2.5 g/L), copper (0.3 g/L), aluminium (10 g/L), zinc (4 g/L), magnesium (1.2 g/L), and cobalt (0.08 g/L). The process was run year-round, which allowed the operation to function for several years. Later, due to a process leak and environmental pollution, the operation had to be shut down.

The purpose of this study was to establish the possibility of processing Murmansk Region's low-grade sulfide ores, and anthropogenic mineral feeds using the method of heap bioleaching.

2. Materials and Methods

Sulfide copper-nickel ores from the Allarechensk technogenic deposit (TD) and the Nud II deposit were used in this study. The Allarechensk technogenic deposit is located in the Pechenga district of Russia's Murmansk region and is a rock dump composed of the mining waste from the primary Allarechensk sulfide copper-nickel deposit. The rock dump holds 6.7 million m³ of rock, mainly gneisses, granite gneisses, amphibolites, and mineralized host rocks. In the Allarechensk TD, the currently prevailing ore type is disseminated ores held in serpentinites.

The bulk of the ore in the Allarechensk TD is found in the range of 10–150 mm. The grades of nickel, copper, and cobalt in the disseminated ores vary, respectively, from 7.9%, 4.9%, and 0.12% (in high-grade ores) to 0.2%, 0.12%, and 0.008% (in low-grade ores). Average grades found in the rock dump: nickel 1.57%, copper 1.34% and cobalt 0.021%. As the grade of commercial minerals decreases, the proportion of silicate nickel tends to increase. For instance, in high-grade ores, silicate nickel accounts for 11% of the total nickel, while in low-grade ores, its share is 25%.

The Nud II deposit lies in the norite rocks of the eastern part of Monchepluton and is associated with the spread of the critical horizon. The ore minerals found in the Nud II deposit include pyrrhotite (40–50%), chalcopyrite (20–30%), pentlandite (10–15%), and pyrite (5–10%). In addition, magnetite is present in noticeable quantities (10–30%). Allarechensk TD and Nud II deposits are characterized by the fact that both high-grade and run-of-mine ores support conventional concentration methods. Low-grade ores incur great losses during flotation due to the high proportion of silicate nickel.

For laboratory experiments on heap bioleaching, a psychrotolerant iron-oxidizing acidophilic strain, *Acidithiobacillus ferrivorans* NO-37, was chosen. This microorganism was isolated from the dump effluent of the Allarechensk TD. A characteristic feature of the strain is the temperature range of oxidation of sulfide minerals from 4 to 37 °C, with an optimal temperature of 20–30 °C [11].

The ore was ground to a size range of 2–5 mm and then loaded into glass columns with a diameter of 2.7 cm. The weight of the ore sample from the Allarechensk TD was 800 g, while the one from the Nud II deposit was 200 g. The experiments were carried out using a mineral nutrient medium containing nitrogen and phosphorus salts (g/L): (NH₄)₂SO₄–3.0; KCl–0.1; MgSO₄ × 7H₂O–0.5; K₂HPO₄–0.5, FeSO₄–44.22, with initially approximately 1 × 10⁸ cell/mL of the microorganisms. The ore in the columns was irrigated with a solution at an S:L ratio of 4:1 for 80 days, and the ambient temperature was 19 °C.

Throughout the experiment, the pH and Eh values of the pregnant liquors and the concentrations of ferric and ferrous iron, nickel, and copper ions were monitored. The pH and Eh values were measured using an I-160MI ion meter (Izmeritelnaya tekhnika Co. Ltd., Moscow, Russia). The concentrations of Fe^{3+} and Fe^{2+} were measured by titration using Trilon B. The concentration of nickel and copper in the pregnant liquors was measured by atomic absorption spectrometry with electrothermal atomization (by following the standard PND F 14.1:2:4.140-98). The measurement error did not exceed 5%. The recoveries were calculated based on the concentrations of metals in pregnant solutions and the initial content of metals in the ore sample.

These measurements made it possible to assess the activity of the microorganisms responsible for the bioleaching process since the oxidation of sulfide, iron, copper, and nickel ions accumulate in a liquid medium, forming sulfuric acid. This, in turn, leads to a decrease in pH and a high concentration ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions, which is typical for active bioleaching processes and leads to an increase in Eh. In addition, the recovery of non-ferrous metals was calculated from the concentration of metals in the liquid phase.

Ore chemistry was studied using an ELAN 9000 DRC-e inductively coupled plasma mass spectrometer (PerkinElmer Inc., Waltham, MA, USA). The mineral compositions of the primary and experimental samples were measured by powder X-ray diffraction techniques using the DRON-2.0 instrument (JSC Burevestnik, Saint Petersburg, Russia) with a $\text{Cu-K}\alpha$ radiation source.

3. Results and Discussion

X-ray phase analysis revealed that in the initial Allarechensk TD ore, the predominant sulfide minerals are pyrrhotite and pentlandite, while chalcopyrite is less common (Figure 2a). The ore is characterized by a significant proportion of silicates represented by amphibole and serpentine. Reflections of the same sulfides are characteristic of the Nud II ore. A higher chalcopyrite content was observed in the Nud II ore compared to the Allarechensk TD ore (Figure 4a). Reflections of serpentine and amphibole were observed among nonmetallic minerals.

Using microscopic analysis, it was found that the disseminated sulfide in the low-grade copper-nickel ores is represented by both individual sulfide grains and intergrowths thereof (Figure 1). The main ore minerals are pyrrhotite, pentlandite, and chalcopyrite. Magnetite is often found in combination with these, as shown in Figure 1a. Finely disseminated sulfides (pyrrhotite, pentlandite) were also found in silicates (Figure 1b–d).

After leaching for 80 days, reflections of sulfides still appeared in the Allarechensk TD ore (Figure 2). That was due to the short duration of the experiment. After leaching for 80 days, we continued to record reflections of sulfides (Figure 2b), due to the short duration of the experiment. In the global industry practice, the process of heap bioleaching runs continuously for several years. Visually, the ore particles are sintered, covered with a crust (commonly iron hydroxides), and then begin to peel off and crumble. Chemically, sulfides transform into sulfates and hydroxides. This led to a certain decrease in the solution filtration intensity starting from the middle of the experiment.

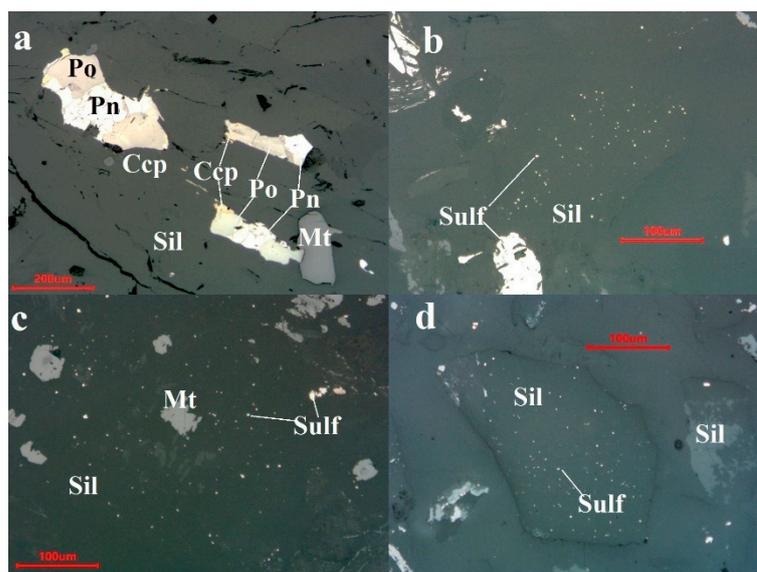


Figure 1. An example of low-grade disseminated sulfide copper-nickel ores of the Murmansk Region: (a) Large intergrowths of several sulfides and magnetite in a silicate; (b–d) large intergrowths of sulfides and finely disseminated sulfides in silicate. Images taken with reflected polarized light. Ccp: chalcopyrite; Mt: magnetite; Pn: pentlandite; Po: pyrrhotite; Sil: silicate mineral; Sulf: sulfide.

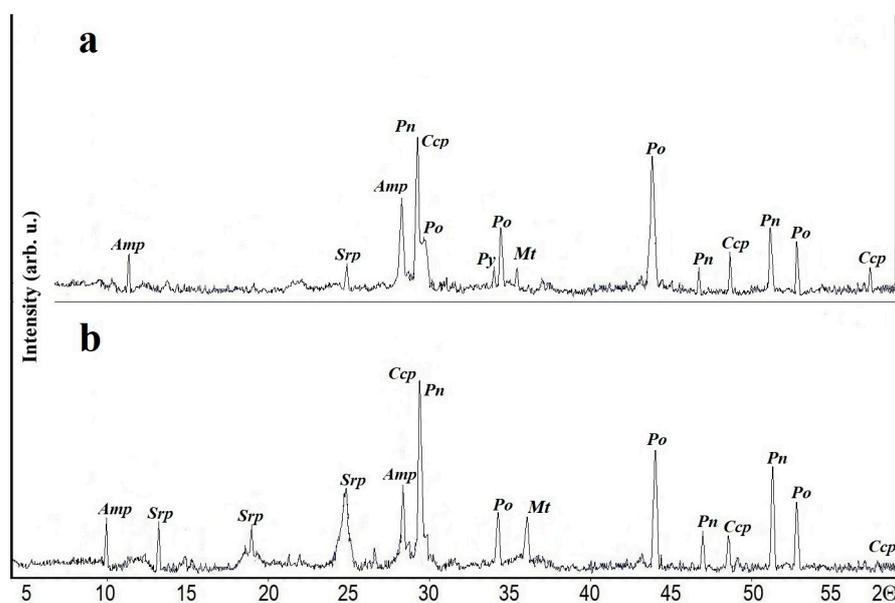


Figure 2. X-ray diffraction pattern of the Allarechensk TD samples: (a) feed ore; (b) ore after leaching. Amp: amphibole; Srp: serpentine; Po: pyrrhotite; Pn: pentlandite; Ccp: chalcopyrite; Mt: magnetite.

In the course of the bioleaching experiments on the Allarechensk TD ore, 16.5% of nickel and 7.5% of copper were recovered after 80 days (Figure 3c). The maximum concentration of nickel in the solution was noted on the 22nd day of the experiment, which amounted to 1557 mg/L, while the average concentration during the experiment was 680 mg/L (Figure 3a). The maximum concentration of copper was noted on the 30th day of the experiment (211 mg/L) with an average concentration of 84 mg/L. It should be noted that the concentration of nickel ions (Ni^{2+}) exceeded the concentration of copper ions (Cu^{2+}), which is primarily due to the fact that the chalcopyrite in the ore is more resistant to oxidation. In addition, the chemistry of the Allarechensk TD ore samples showed the intensive leaching of cobalt (Table 1), which is also of practical interest due to the significant

market demand for this metal. The only cobalt concentrator in the ores is pentlandite, in addition to violarite in oxidized ores.

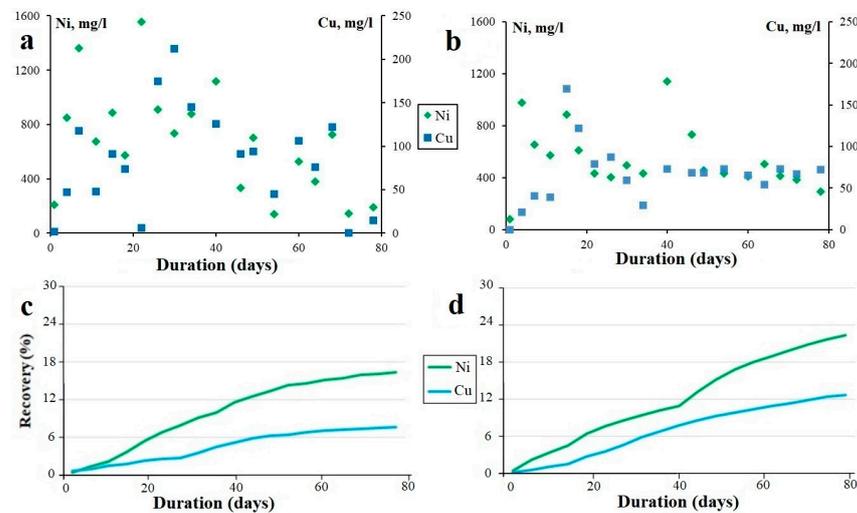


Figure 3. The concentration of metals in pregnant liquors during ore bioleaching: (a) Allarechensk TD, (b) Nud II. Recovery of metals into solution during the experiment: (c) Allarechensk TD, (d) Nud II.

Table 1. Chemical composition of the Allarechensk TD ore.

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	S	CaO	TiO ₂	Cr ₂ O ₃	Fe ₂ O ₃	CoO	NiO	CuO
Feed ore	0.07	9.38	1.68	14.0	29.8	1.10	0.43	0.15	30.3	0.41	5.41	4.93
Ore after leaching	0.06	8.64	0.61	12.9	26.7	0.98	0.39	0.13	27.1	0.37	4.72	4.80

The pH value of the pregnant liquors varied during the experiment from 1.9 to 2.2, while the redox potential ranged from 471 to 582 mV. The concentration of Fe³⁺ at the beginning of the experiment was 9.0 g/L and increased by the end of the experiment to 15.0 g/L, while the concentration of Fe²⁺ decreased from 3.0 g/L to 0.9 g/L. The content of sulfur in the ore sample decreased by 10.4%, which indicates the activity of microorganisms (Table 1).

In the course of bioleaching of the copper-nickel ore from the Nud II deposit, the maximum concentration of nickel in the solution was noted on the 40th day, which equivalently amounted to 1140 mg/L, while the average concentration of nickel in the solution during the experiment was 542 mg/L (Figure 3b). The maximum concentration of copper was noted on the 15th day of the experiment (169 mg/L) with an average concentration of 66 mg/L. The leaching kinetics of non-ferrous metals from the Nud II ore was characterized by a decrease in recoveries at the middle of the experiment, followed by an increase in the concentrations. Thus, the concentration of copper on the 35th day of the experiment decreased to 29 mg/L. Over the entire study period, 22.5% of nickel and 12.7% of copper were recovered from the ore (Figure 3d). The reflections of sulfides still appear after leaching (Figure 4). The extraction of the metals from pregnant solutions can be carried out following the example of the Talvivaara company, where hydrogen sulfide was used for the precipitation of the metal.

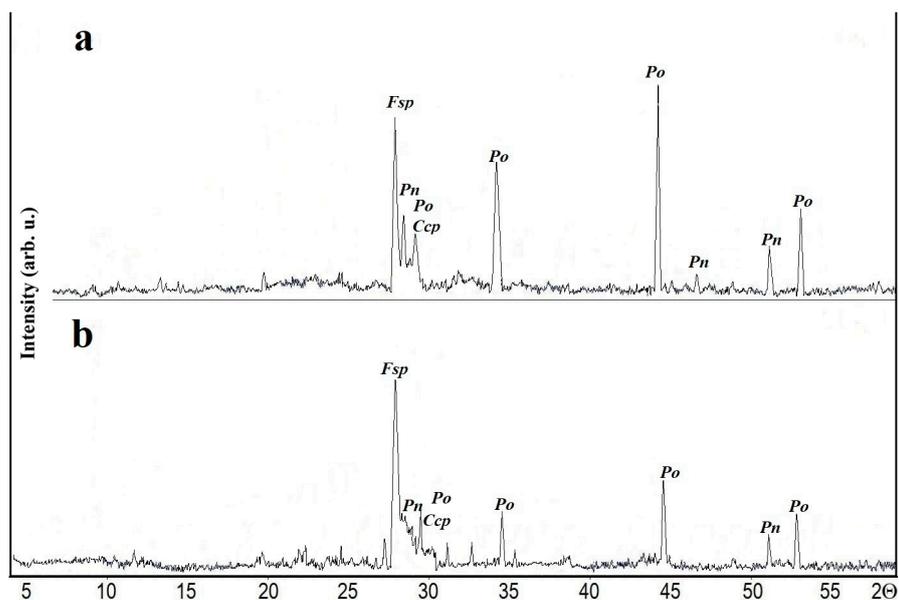


Figure 4. X-ray diffraction pattern of the Nud II samples: (a) feed ore; (b) ore after leaching. Fsp: feldspar; Po: pyrrhotite; Pn: pentlandite; Ccp: chalcopyrite.

The pH value of the pregnant liquors varied from 1.8 to 2.3, while the redox potential ranged from 488 to 608 mV. The concentration of ferric iron, which at the beginning of the experiment was 9 g/L, increased by the end of the experiment to 16.4 g/L, while the concentration of ferrous iron decreased from 1.9 g/L to 0.9 g/L. The sulfur content in the solid phase decreased by 34.6%, which is three times higher than in the Allarechensk TD ore (Table 2).

Table 2. Chemical composition of the Nud II ore.

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	S	CaO	TiO ₂	Cr ₂ O ₃	Fe ₂ O ₃	CoO	NiO	CuO
Feed ore	0.02	7.30	2.30	32.3	14.9	4.60	0.30	0.14	33.2	0.26	2.40	2.20
Ore after leaching	0.06	7.53	3.00	40.0	9.75	4.77	0.38	0.18	30.5	0.24	1.40	1.70

4. Conclusions

Laboratory tests demonstrated the high performance of heap bacterial leaching in the processing of natural and anthropogenic copper-nickel ores. The leaching of non-ferrous metals from the Nud II ore was particularly intense. This is probably due to the structural features of the ore from that specific deposit—when grinding, the sulfide grains unlocked better and became available for leaching. The bacterial strain used demonstrated its ability to function effectively at low pH values of the solution and high metal concentrations.

The main reason for the inhibition of the ore leaching process in the experiment can be attributed to particle sintering and clogging. This problem can be solved by mixing the ore layers in order to improve their permeability.

The use of the heap leaching method makes it possible to process mineral feeds, for which no market demand currently exists. The recovery of such minerals allows the acquisition of additional economic benefits with a reduction of their negative impacts on the environment.

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A.G.; writing—review and editing, E.Y., N.F., E.S., A.K., D.M. and A.G.; visualization, E.Y., N.F., E.S., A.K., D.M. and A.G.; supervision, N.F. and D.M.; project administration, E.Y. and A.G.; funding acquisition, D.M. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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