METHODS FOR PROCESSING COPPER-NICKEL RAW MATERIALS IN THE ARCTIC

A. Goryachev¹, D. Makarov¹

¹Institute of North Industrial Ecology Problems – Separate subdivision of the Federal State Budgetary Institution of Science of the Federal Research Center «Kola Science Center», Apatity, Russian Federation

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Abstract

The different genesis of copper-nickel objects requires the use of different technologies for their enrichment. A scheme has been proposed for processing copper-nickel ore tailings, first by granulating the tailings with sulfuric acid, storing them at below-zero temperatures, and then followed by heap leaching of granules was proposed. The effect of different ratios of tailings to binder during granulation on the subsequent recovery of the metals was considered. At a ratio of S:L = 6:1, 44.4% nickel and 8.9% copper were recovered during the 40-day experiment. For ore processing, the efficiency of heap leaching with a 2% H₂SO₄ solution using technogenic ores from the Nud Terrasa was considered and Allarechensk deposits ores was studied, as no additional ore preparation was required. At the end of the experiment, 12.8% nickel and 10.2% copper were recovered from the Nud Terrasa ore, and 10.2% nickel and 4.4% copper were recovered from the ore of the Allarechensk technogenic deposit. The ore from the Nud II deposit and a rich sample of the Allarechensk ore were processed by low-temperature roasting with ammonium sulfate. From the ore of the Allarechensk technogenic deposit, 91.5% of nickel and 94.8% of copper were recovered. The results obtained may be of significant practical interest, especially in the Arctic zone.

Key words: low-temperature roasting; heap leaching; sulfuric acid granulation; copper; nickel; Arctic zone.

1. Introduction

The economy of the Murmansk region (north-western part of the Russian Federation) is dominated by the mining industry, and the copper-nickel industry plays a significant role in the economic development of the region. Most of the sulfide copper-nickel ore deposits and occurrences are located in the western part of the region, a smaller part – in the central part, and in the eastern part only deposits with minor copper-nickel mineralization are known [1]. A number of deposits considered promising for processing by alternative enrichment methods are associated with the ore-magmatic systems of Monchegorsk pluton. the Monchegorsk pluton consists of two branches. One branch is represented by the Nittis-Kumuzhya-Travyanaya massif, the other – by the Sopcha and Nud-Poaz massifs. At the Nud II and Nud Terrasa deposits, a nested disseminated type of mineralization is developed, the sulfide matrix of the ore is formed by pyrrhotite, that contains ingrowths of pentlandite [2]. From the technological point of view, the Allarechensk technogenic deposit, located in the Pechenga region, is also of interest. This object is a rock dump formed as a result of the primary Allarechensk deposit development. During the development of a primary deposit, overburden and host rock piled up to form a stockpile, the volume of rocks in the stockpile reached 6,700 thousand m³. The main ore-forming minerals are: pyrrhotite, pentlandite, chalcopyrite and magnetite.

In addition to a significant number of deposits in the region, large stocks of copper-nickel enrichment waste have also accumulated. For example, JSC «Kola GMK» currently operates a tailing pile at the enrichment plant in the city of Zapolyarny. The tailing dump covers an area of approximately 1,033 hectares and receives about 7 million tons of waste annually. During its operation, about 330 million tons (or 226 million m³) of tailings have accumulated. The tailingss are characterized by the predominance of the <0.1 mm fraction, a significant proportion being the <0.044 mm fraction [3]. The mineral composition of the tailings is dominated by serpentines (60%), and also includes pyroxenes, amphiboles, talc, chlorite, quartz, and feldspars. The main ore minerals are magnetite, pyrrhotite, pentlandite, and chalcopyrite. When processing copper-nickel ores, the loss of nickel with tailings is about 25% of the initial content in the ore.

*Corresponding author: a.goryachev@ksc.ru
[4]. Thus, the processing of finely dispersed tailings is of particular practical interest. The interest in sulfide-containing enrichment wastes is also due to the need to reduce the impact on the environment, in particular – water bodies pollution with metal ions. Non-ferrous metal and iron sulfides are oxidized to sulfuric acid during waste storage, while heavy metals are converted into water-soluble salts.

For efficient processing of the above-mentioned copper-nickel raw materials and technogenic formations, the development of alternative enrichment methods is required, since physical enrichment methods – flotation, gravity, and magnetic separation are ineffective for processing such raw materials. It has been established that the implementation of an enrichment technology is determined by the characteristics of the copper-nickel raw materials – the mineralogical composition and the initial content of the valuable component. Heap leaching method seems to be promising for the processing of substandard raw materials, in particular, industrial wastes whose content of non-ferrous metals does not exceed 1% [5,14]. Successful industrial trials of metals recovery from copper-nickel ores by heap leaching were carried out by Talvivaara Mining Company plc, Finland. This method has been used to recover nickel, cobalt, zinc, copper, manganese and uranium, providing experience with heap leaching under severe climatic conditions. As studies show, it is advisable to grind the ore to a particle size of <8 mm before heap leaching [6]. On the other hand, in the case of enrichment tailings, the accumulated experience justifies the need to enlarge the material in order to increase the filtration properties of the heap [7].

The difficult climatic conditions both in the Murmansk region and the entire territory of the Russian Arctic make it difficult to operate the heap all year round. The annual air temperature drops from 0 °C on the coast of the Barents Sea and the White Sea to -2 °C in the central part of the Kola Peninsula and to -3-4 °C in the mountainous areas. Therefore, it is advisable to carry out preliminary preparation (granulation) of technogenic formation material before a long period of below-zero temperatures, storage of the granules during winter time and subsequent leaching in the warm season [8, 11].

In the case of copper-nickel ores containing non-ferrous metals >1%, as well as rough concentrates, the method of low-temperature roasting of the ore with ammonium sulfate seems to be promising. Conducted studies on the roasting of copper-nickel raw materials with ammonium sulfate \((NH_4)_2SO_4\) allowed to establish that metal sulfides and oxides can react with the formation of water-soluble sulfates [15]. Previously, this compound was used to recover manganese from low-grade carbonate manganese ore, to process spent lithium-ion batteries, and to process converter slag to recover nickel, cobalt, and copper. The processing of substandard and low-grade sulfide and mixed ores by low-temperature roasting followed by water leaching can be considered as a promising and environmentally friendly process. This process is characterized by a high degree of metal recovery, the selectivity of the reactions occurring during the roasting process, energy efficiency and low cost [9, 10].

2. Experimental

In the Murmansk region, a significant amount of copper-nickel raw materials and technogenic formations of various genesis have been accumulated, for the processing of which there is no unified approach, which requires the study of different approaches to a specific type of raw materials. Taking into account the significant differences in the composition and properties of copper-nickel objects, each of them has its own enrichment scheme. In the course of the research, methods of processing the following copper-nickel objects were considered: a) copper-nickel ores enrichment tailings of the Kola GMK JSC, b) ores of the Nud Terrasa and Nud II deposits, c) ores of Aliarechensk technogenic deposit (hereinafter referred to as TD).

During the experiments on the processing of copper-nickel tailings, sulfuric acid granulation of tailings was carried out, followed by leaching according to the scheme: grinding of raw materials → granulation of raw materials using sulfuric acid → irrigation of the obtained granules with an oxidizer → storage of granules for six months → heap leaching of granules [11]. Content of metals in tailings, %: Ni – 0.20, Cu – 0.07, Fe – 14.1. During the experiment, the tailings were granulated using an experimental granulator FL015-1K02 («Dzerzhinsk-technomash» LLC, Dzerzhinsk, Russia). A 30% sulfuric acid solution was chosen as a binder, the S/L ratio – 4:1, 6:1, 9:1. The resulting granules were 3-4 mm in diameter and 1-1.5 mm thick (Figure 1). The granules were irrigated with a 0.5% sulfuric acid solution containing the Fe\(^{3+}\) oxidizer in an amount of 2 g/L, the ratio of granules and oxidizer = 5:1. The application of the oxidant was followed by a storage step in which excess moisture was removed and the granules gained strength. The goal set in the work is to develop an approach for tailings processing adapted to the Arctic climatic conditions.
For this reason, an assessment was made of the below-zero temperatures effect on the process of storing granules with subsequent leaching during the warm period. The samples were first stored in a freezer at -15 °C for six months. The granules obtained after storage were processed using the heap leaching method. To simulate the process of heap leaching, the granules were placed in glass percolators with a diameter of 45 mm. The load weight was 180 g, the height of the granular layer was 110 mm. The granular layer was supplied with distilled water with a volume of 50 ml five times a week for 20 days. This was followed by sulfuric acid leaching stage, during which 50 ml of a sulfuric acid 2% solution was applied to the surface of the heap with the same frequency. The heap leaching duration was 40 days at a temperature of +19 °C [11].

Ore from the Nud Terrasa and Allarechensk TD deposits with a non-ferrous metal content of <1% was processed using the heap sulfuric acid leaching method. Samples of Nud Terrasa ore with Ni content of 0.42% and Cu 0.15% and Allarechensk TD ore with Ni content of 0.52% and Cu 0.74% were used for leaching tests. The ore was crushed to a fraction of -3+1 mm and placed in glass columns with a diameter of 27 mm. The weight of the ore loaded into the column was 220 g. Three times a week 25 ml of a 2% H₂SO₄ solution were fed into the columns containing the ore. The duration of the experiments was 80 days. The heap leaching modeling studies were conducted at an ambient temperature of approximately +19 °C.

In the course of experiments on low-temperature roasting, the copper-nickel ore was mixed with ammonium sulfate (chemically pure, GOST 3769-78) and the resulting mixture was ground in a BMU-100 ball mill (HT Machinery Co., Ltd., Harbin, China). Ore from two deposits was used for the study– Nud II deposit ore with a content of Ni 0.45% and Cu 0.39% and the Allarechensk TD ore with a content of Ni 5.8% and Cu 2.9%. The mixture was roasted for 240 minutes at various temperatures in a SNOL 3/11 muffle furnace («NPF Thermiks» LLC, Moscow, Russia). The roasting temperature was varied from 300 to 500 °C in steps of 50 °C. Heating to the desired temperature took 60 min [15,16]. After roasting, the mixture was cooled in the static air for 60 min. After that, the roasted mixture was dissolved in distilled water heated to +80 °C for 40 min with constant stirring at an intensity of 230 min⁻¹ using the overhead stirrer (MV-6, «NV-LAB» LLC, Moscow, Russia). In the pregnant solutions, during the experiments, the concentrations of non-ferrous metals in the solutions were measured by electrothermal atomization (ETA) atomic absorption spectrometry (AAS) (AA-700, Shimadzu Corp., Kyoto, Japan) according to the standard PND F 14.1:2:4.140-98. In the experiments on heap leaching, the pH values of solutions were controlled using an ionometer (I-160 MI «Izmeritelnaya Tekhnika» LLC, Moscow, Russia).

3. Results and discussions
3.1. Sulfuric acid granulation and heap leaching of copper-nickel tailings

During the copper-nickel tailings granulation, granules with a strength of >3.5 MPa were obtained. The most solid were the granules obtained at a ratio of S:L = 4:1, the strength of these granules was 4.7 MPa. However, the granules prepared at this ratio were also characterized by high caking (48%), expressed in the formation of large shapeless agglomerates. According to the physical properties, the ratio S:L = 6:1 was selected as optimal for granulation. Even long-term storage of the granules did not lead to their destruction and inhibition of the following leaching process.

To study the effect of the ratio of finely dispersed materials and binder in the granulation process on the subsequent recovery of copper and nickel in solution,
three samples of granules were taken, prepared at a ratio of S:L = 4:1, 6:1, 9:1, at a temperature of -15 °C and stored for six months. During aqueous leaching of the granules prepared at a ratio of S:L = 4:1, the pH value of the pregnant solutions varied from 3.11 to 5.29, the average pH value of the solutions was 4.10. Low pH values of the pregnant solutions at an early stage of aqueous leaching indicate the formation of highly concentrated areas of granules saturation with sulfuric acid. The average concentration of metals in the pregnant solutions was 72.4 mg/L nickel and 6.5 mg/L copper.

In the course of the experiment with tailings granulated at a ratio of 4:1, 12.3% nickel and 3.3% copper were recovered into solution during aqueous leaching. During the 2% H₂SO₄ leaching of granules, the average pregnant solutions pH value was 1.80. The average concentration of Ni ions in the solution was 107.8 mg/L, and that of copper was 19.6 mg/L. At the end of the experiment, 21.2% nickel and 10.2% copper were recovered. Thus, 33.6% nickel and 13.5% copper were recovered from tailings granulated at a ratio of S:L = 4:1 during 40 days of leaching, including the water and sulfuric acid stages (Figure 2a).

By reducing the binder consumption, the ratio S:L = 6:1 in the granulation stage the following results were obtained. The average pH value of pregnant solutions during aqueous leaching was 4.38, the values fluctuated in the range of 3.86 to 5.56 during the experiment. The average Ni concentration in the solution during the experiment was 129.5 mg/L, Cu – 6.8 mg/L. After water leaching, 27.5% nickel and 3.4% copper were recovered from the granules into the solution, while a significant portion of the granules did not change their original shape. During the 2% H₂SO₄ leaching, the average pH value of the pregnant solutions was 1.85. The average concentration of nickel in the solution over 20 days of sulfuric acid leaching was 82.9 mg/L, copper – 10.7 mg/L (Figure 2b). At the stage of leaching with a 2% sulfuric acid solution, 16.9% nickel and 5.5% copper were recovered at the end of the experiment. Thus, for a 40-day leaching, the total recovery was: 44.4% nickel and 8.9% copper [11].

![Figure 2](https://example.com/figure2.png)

*Figure 2* Metals recovery during leaching of tailings granules, obtained at a different ratio with binder (a), concentrations of copper and nickel ions in pregnant solutions during leaching of tailing granules, obtained at S:L ratio of 6:1 (b)

The granules obtained at the ratio S:L = 9:1 were characterized by relatively low strength. During the water leaching of the granules, the pregnant solutions pH value varied from 3.90 to 6.41, and the average value was 4.64, that is higher compared to the solutions obtained after leaching of the granules prepared at S:L = 4:1 and 6:1. The average nickel concentration in the solution was 89.1 mg/L, copper – 5.5 mg/L. After water leaching of the granules, 18.3% nickel and 0.1% copper were recovered. The average pH value of the pregnant solutions during leaching with a sulfuric acid was 1.87. When leaching with a sulfuric acid solution, the pregnant solutions average pH was 1.87. The average concentration of nickel in the solution was 77.2 mg/L, copper – 8.6 mg/L. During sulfuric acid leaching, 15.8% nickel and 4.4% copper were recovered from the granules [11]. Thus, 34.1% nickel and 4.5% copper were recovered from the tailings granulated at the ratio S:L=9:1 for the entire experiment.

The comparison of the results of granulation at different ratios of S:L allowed to establish that the granules obtained at a ratio of S:L = 4:1 are characterized by high caking, which does not provide proper contact with the leaching agent. A low solution filtration rate was noted during aqueous leaching of the granules. When using the ratio S:L = 9:1, softening of the granules occurs, leading to the effect of clogging and, as a result, to a deterioration in the filtration of the solution. Thus, the considered variants of the S:L ratios (4:1 and 9:1) are not
optimal due to the low quality of the obtained material and the relatively low level of metals recovery into solution during heap leaching stage. When the S:L=6:1 ratio was used, it was possible to obtain granules with better physical properties. In addition, the nickel recovery was highest for granules prepared in this ratio.

3.2. Sulfuric acid leaching of the Allarechensk TD and the Nud Terrasa ores

Processing of the ore of the Allarechensk TD and the Nud Terrasa deposits by the method of sulfuric acid heap leaching allowed obtaining the following results. The concentration of metals in the pregnant solutions during the processing of Allarechensk TD ore averaged 114.6 and 70.7 mg/L for nickel and copper, respectively (Figure 3b). The concentration of metals in the pregnant solutions decreased naturally with increasing duration of the experiment, and did not exceed 50 mg/L by the end of the experiment. For 100 days of leaching, 10.22% nickel and 4.44% copper were recovered from the ore (Figure 3a).

During processing the Nud Terrasa deposit ore, the average nickel concentration in the solutions was 114.2 mg/l, copper – 32.7 mg/l (Figure 3c). At the end of the experiment, 12.80% nickel and 10.20% copper were recovered from the Nud Terrasa deposit ore. Thus, over the same period of heap leaching, the recovery of copper from the Nud Terrasa deposit ore was significantly higher. This indicates the need for additional activation of the grains surface of sulfide minerals of the Allarechensk TD ore, in particular, chalcopyrite, which is the main concentrator of copper.

![Figure 3](image)

**Figure 3** Metals recovery during sulfuric acid leaching of Allarechensk TD ore (a), concentrations of metals during leaching of Allarechensk TD (b) and Nud Terrasa ores (c) [11]

3.3. Low-temperature roasting of the Allarechensk TD and the Nud II ores

The processing of ores with a higher initial content of non-ferrous metals was carried out using ammonium sulfate. It is known that the process of thermal decomposition of ammonium sulfate occurs in the temperature range of 155-450 °C, so this compound can contribute to the intensive conversion of non-ferrous metal sulfides into the sulfate form during the low-
temperature roasting of the mixture. At atmospheric pressure, ammonium sulfate decomposes to form a melt based on NH$_4$HSO$_4$ hydrosulfate and an ammonia-enriched gas phase. It can be argued [12] that in the process of low-temperature roasting at temperatures of 300-500 °C for four hours, several ammonium compounds that make up the melt come into contact with ore particles (Figure 4). This condition is fulfilled only with the access of atmospheric oxygen. Experiments in an autoclave without constant air access showed that during low-temperature roasting for four hours, no melt formation occurs [13].

During the roasting of Nud II deposit ore and ammonium sulfate mixture with a particle size of <100 μm in a 1:2 ratio, it was found that with an increase in the roasting temperature, the recovery of metals during subsequent aqueous leaching increased. The minimal recovery of metals was noted at a roasting temperature of 300 °C, 12.5% of nickel was recovered, and less than 13.5% of copper. A significant increase in the recovery of metals was noted at a temperature of 400 °C, 33.6% nickel and 34.6% copper were recovered into solution during leaching. Further increase in the roasting temperature did not result in a significant increase in the recovery of metals. Taking into account the sharp increase in recovery after roasting the mixture at 400 °C, it was reasonable to consider ways to intensify the transition of metals into a water-soluble form at a given temperature [12]. An increase in the consumption of ammonium sulfate led to a more intensive metals recovery into solution. At a ratio of 1:7, by the end of the experiment, 56.7% nickel and 52.1% copper were recovered. To further increase the metals recovery, the mixture was ground to finer fractions before roasting. The recovery of the metals increased as the particle size of the mixture decreased. From the <40 µm fraction, 73.5% nickel and 72.1% copper were recovered (Figure 5a).

According to the results of experiments with the Allarechensk TD ore, at different roasting temperature, it was found that at a temperature of 300 °C, the minimum recovery of metals occurs in the studied roasting temperature range, 17.0% nickel and 18.9% copper were recovered during water leaching. As in the case of the Nud II ore, the increase in the roasting temperature led to an intensification of the recovery of metals into solution in the leaching stage. The highest recovery of nickel was observed at a temperature of 450 °C, with almost 44% going into solution. There was no significant increase in nickel recovery nickel when the temperature was
increased above 450 °C, probably due to the decomposition of ammonium sulfate at this temperature and the absence of prolonged contact of the reagent with sulfide minerals. Analysis of metal recovery using different ratios of ore and (NH$_4$)$_2$SO$_4$ (at a temperature of 400 °C) showed that the highest recovery of nickel was observed at a mass ratio of 1:7, with 79.0% of Ni recovered into solution. Copper recovery also tended to increase with an increase in the proportion of the reagent in the roasted mixture. In order to increase the recovery of non-ferrous metals into solution, the effect of the particle size was analyzed. The experiments were performed at an optimum temperature of 400 °C and ore: (NH$_4$)$_2$SO$_4$ ratio of 1:7. When the mixture was ground to a particle size of <50 µm, 87.1% nickel and 81.4% copper were recovered. Grinding to a particle size of <40 µm contributed to an increase in the recovery of non-ferrous metals, 91.5% nickel and 94.8% copper were recovered into solution (Figure 5b).

Figure 5 Metals recovery during water leaching of roasted mixtures of Nud II ore (a) and Allarechensk technogenic deposit ore with ammonium sulfate (b) [13]

4. Conclusion

The conducted studies show the prospects of processing copper-nickel raw materials and technogenic formations of the Murmansk region by alternative methods of enrichment. Severe climatic conditions are not an obstacle to the use of the proposed enrichment processes.

Copper-nickel tailings can be processed by heap leaching. The principal possibility of using sulfuric acid granulation as a method for preliminary preparation of finely dispersed copper-nickel material before subsequent leaching was shown. The storage conditions of the ore material in winter with the conversion of the non-ferrous metals into a soluble form and the subsequent leaching in the summer period were simulated. Using this approach will significantly reduce capital and operating costs and make the processing of substandard raw materials profitable.

Laboratory tests of heap sulfuric acid leaching showed the effectiveness of the method for processing copper-nickel ores with substandard non-ferrous metal content. The leaching of non-ferrous metals from the ore of the Nud II deposit was particularly intense. This is probably due to the structural features of the ore from this deposit. When the ore was crushed, the sulfide grains opened up better and became available for leaching. The application of the method will make it possible to involve in the processing of currently unclaimed raw materials, providing additional economic benefits and minimizing the negative impact on the environment.

Empirically, the prospects for processing the ore of the Allarechensk deposit by roasting with ammonium sulfate were demonstrated. Roasting at 400 °C at a ratio of ore and ammonium sulfate = 1:7 can recover more than 80% of the target metals into solution. It should be noted that the temperature of 400 °C is lower than the temperature of traditional pyrometallurgical processes. In addition, there is a possibility of regenerating the reagent by collecting the off-gases – SO$_2$ and NH$_3$. Low-temperature roasting of sulfidic raw materials with ammonium sulfate, provided that the process is optimized, can also be considered promising for the processing of low-grade ores due to its high selectivity, relatively low energy consumption, and low cost. Comparing the metal recovery rate, as well as the expected energy costs, it can be argued that the heap leaching method is advisable for objects with a low content of non-ferrous metals, while the low-temperature roasting method offers a significant economic advantage when processing raw materials with a metal content of more than 1%.
Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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5. References


METODE ZA PRERADU BAKRO-NIKLOVIH SIROVINA NA ARKTIKU

A. Goryachev, D. Makarov

1Institute of North Industrial Ecology Problems – Separate subdivision of the Federal State Budgetary Institution of Science of the Federal Research Center «Kola Science Center», Apatity, Russian Federation


Izvod

Različita geneza bakro-niklovih sirovina zahteva upotrebu različitih tehnologija za njihovo obogaćivanje. Predložena je šema za preradu otpadne rude bakra i nikla tako što se sirovin pro granulira sumpornom kiselinom, čuva na temperaturama ispod nule, a zatim se luži hemijski. Ispitivan je uticaj različitih odnosa jatovine i veziva tokom granulacije na naknadno dobijanje metala. U odnosu S:L = 6:1, 44,4% nikla i 8,9% bakra dobijeno je tokom 40-dnevog eksperimenta. Za obogaćivanje rude proučavana je efikasnost hemijskog luženja sa 2% rastvorom H2SO4 korističenjem tehnogenih rud sa ležišta Nud Terrasa i Allarechensk, jer nije bilo potrebno dodatno obogaćivanje rude. Na kraju eksperimenta, 12,8% nikla i 10,2% bakra dobijeno je iz rude Nud Terrasa, a 10,2% nikla i 4,4% bakra je dobijeno iz rude tehgenog ležišta Allarechensk. Ruda sa ležišta Nud II i bogat uzorak rude Allarechensk prerađeni su niskotemperaturnim pečenjem sa amonijum sulfatom. Iz rude tehnogenog ležišta Allarechensk dobijeno je 91,5% nikla i 94,5% bakra. Dobijeni rezultati mogu biti od značajne praktične koristi, posebno u arktičkoj zoni.

Ključne reči: pečenje na niskoj temperaturi; hemijsko luženje; granulacija sumpornom kiselinom; bakar; nikl; arktička zona.