Comparison of Bio- and Ferric Leaching for Beneficiation of Bulk Copper-Nickel Sulfidic Concentrate

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Abstract. Processing of sulfidic raw materials, including bulk concentrates of nonferrous metals, is a problem of current importance in metallurgy and waste recycling. In this study, leaching with a chemical ferric iron reagent was compared to two bio-approaches to process a bulk copper-nickel concentrate: (1) ferric leaching with a solution obtained by microbial oxidation and (2) stirred-tank bioleaching using an active acidophilic microbial community. The results of both the chemical and bio-processes indicated nickel dissolution, while copper was accumulated in leach residues. After short-term high-temperature leaching with the chemical or bio- solution (Fe³⁺, 10 g/L), the nickel content in solids decreased by 0.7 and 2.6%, respectively, while the copper content slightly increased (by 1.5–3.2%). Bioleaching at 40°C was characterized by a considerably higher efficacy of the process: nickel leaching reached 86.7%, and the copper content increased by ~5% in the bioleach residue. Based on these results, ferric leaching can be considered an inefficient method for selective nickel removal, while bioleaching may be a promising cost-effective approach characterized by relatively low environmental hazards to obtain a high-grade copper product. Moreover, ferric leaching with the bio-solution can improve the grade of nonmetallic sulfidic concentrates due to additional selective nickel extraction.

1. Introduction
Processing of sulfidic raw materials, including bulk concentrates of nonferrous metals, is a problem of current importance in metallurgical and waste recycling industries. Bulk copper-nickel concentrates are among raw materials that can be used for subsequent industrial production of selective concentrates [1, 2].

Although separation of bulk sulfidic concentrates is difficult due to the textural and structural properties of raw materials, different approaches can be used for selective bioleaching of readily oxidized sulfide minerals. Improved efficiency of beneficiation of nonferrous metal sulfidic concentrates has been previously shown for the pressure oxidation of a sphalerite-chalcopyrite concentrate, which resulted in a decrease in the zinc content from 22.2 to 0.5%(wt.) and an increase in the copper content from 12.2 to 26.0%(wt.) [3]. Selective zinc removal from the bulk copper-zinc concentrate has been previously demonstrated with a two-step biohydrometallurgical method. It included the following steps: (1) generation of ferric iron solution using an acidophilic chemolithotrophic microbial community and (2) subsequent leaching with a ferric sulfate-containing solution obtained in the first step. As a result, the zinc content decreased from 7.36 to 0.5%(wt.), and the refractory mineral chalcopyrite was concentrated in solids [4–5]. Bioleaching may be another promising method to obtain selective concentrates from bulk sulfidic concentrates of nonferrous metals [6]. This method has been successfully applied for the extraction of...
nonferrous (including precious) metals in the metallurgical industry for decades [7]. It is based on the oxidative activity of acidophilic microorganisms and considered an efficient and economically viable bio-approach with relatively low environmental hazards [8–9]. Stirred-tank biooxidation of sulfidic concentrates for gold recovery [10], as well as heap and underground leaching of copper and uranium [7, 11–12], have been widely used.

Pentlandite-chalcopyrite concentrates contain both refractory and readily oxidized minerals. While nickel is gradually leached from pentlandite, chalcopyrite is very stable in ferric sulfate solutions [13]. During bioleaching of copper-nickel concentrates, the products of chalcopyrite and pentlandite oxidation (S\(^0\) and Fe\(^{2+}\)) are oxidized by acidophilic microorganisms to sulfuric acid and ferric iron as final products [11, 14].

The goal of this study was to compare three methods used to process a copper-nickel sulfidic concentrate containing similar amounts of nonferrous metals: chemical leaching using a commercial reagent of ferric iron to two bio-approaches. The bio-methods were (1) ferric leaching with a ferric sulfate bio-solution obtained via microbial oxidation of ferrous sulfate reagent and (2) stirred-tank bioleaching using an active thermoacidophilic microbial community.

2. Methods and Materials

The object of this study was a copper-nickel sulfidic ore concentrate from the Shanuch deposit (Kamchatka territory, Russia). The copper-nickel concentrate contained chalcopyrite, pentlandite, violarite, pyrrhotite, and pyrite, as well as the following gangue minerals: jarosite, plagioclase, chlorite, and quartz. The concentrate contained the following main minerals: CuFeS\(_2\) (31%), Fe\(_{1-x}\)S (4%), FeS\(_2\) (4%), (Ni,Fe)\(_9\)S\(_8\) (15%), and FeNi\(_2\)S\(_4\) (11%). The content of the main elements was as follows (%): Cu, 10.9; Ni, 9.45; Fe, 21.3; Co, 0.25; S, 26.8; Ca, 0.91; Si, 7.28. The particle size distribution of the concentrate had a P\(_{80}\) of 44 μm.

The mineralogical composition (Figure 1) was determined using X-ray diffraction with a DRON-2 diffractometer (Burevestnik, St. Petersburg, Russia) and polarizing microscopy with an Olympus BX51 microscope (Olympus, Tokyo, Japan). The relative mineral phase amounts were estimated using the Rietveld refinement of the XRD patterns [15].

![Figure 1. X-ray diffraction patterns of the copper-nickel concentrate (Cp, chalcopyrite; Pn, pentlandite; Vo, violarite; Py, pyrite; Po, pyrrhotite; S, sulfur; Jrs, jarosite).](image-url)

A solution of commercial chemical reagent of Fe\(_2\)(SO\(_4\))\(_3\)·7H\(_2\)O (Ferrix-3, Finland) that contained ferric iron (9.9 g/L Fe\(^{3+}\)) and ferrous iron (0.56 g/L Fe\(^{2+}\)) was used for the chemical tests. The reagent was dissolved in the Silverman and Lundgren 9K medium [16], pH 1.15 (adjusted with 98.5% sulfuric acid), and the obtained solution was used for high-temperature chemical ferric leaching of the studied concentrate.
A community of acidophilic chemolithotrophic iron-oxidizing bacteria (\textit{Acidithiobacillus ferrooxidans} and \textit{Leptospirillum} spp.) was used to prepare a leaching solution for high-temperature leaching with the bio-solution. The lixiviant was prepared via biooxidation of the FeSO\textsubscript{4}·7H\textsubscript{2}O commercial reagent (Laverna, Russia) in the 9K medium at 30°C. During biooxidation, the pH value was maintained at 1.4 by the addition of 98.5% sulfuric acid. The obtained solution contained 10 g/L of Fe\textsuperscript{3+}; it was supplemented with 98.5% sulfuric acid to pH 1.15 and used for ferric leaching. The experiments of high-temperature leaching with the commercial reagent and biologically generated ferric iron solution were carried out in 500-ml reactors containing 200 mL of suspension. Stirring was conducted with an overhead four-blade stirrer (with blades inclined at an angle of 45°) at a rate of 500 rpm. The reactors were placed in a water bath at a constant temperature of 80°C. The duration of leaching was 5 h.

For the stirred-tank bioleaching experiment, an active acidophilic microbial consortium was obtained from the bioprocessing of the zinc-containing wastes [17]. The original community contained chemolithoautotrophic and mixotrophic iron- and sulfur-oxidizing strains of various species: \textit{Acidithiobacillus} (At.) ferrooxidans, At. thiooxidans, At. caldus, \textit{Leptospirillum} (L.) ferriphilum, \textit{Leptospirillum} spp., \textit{Ferroplasma} (F.) acidiphilum, \textit{F. acidarmanus}, \textit{Acidiplasma} sp., \textit{Sulfobacillus} (S.) thermotolerans, \textit{S. thermosulfidooxidans}, and \textit{Sulfobacillus} spp., as well as a heterotrophic bacterium \textit{Acidiphilium} (Ac.) multivorum capable of sulfur oxidation [18] and a heterotrophic archaean \textit{Cuniculiplasma} sp. [19]. To inoculate a reactor, this community was cultured in a 2.5-L flask containing 1 L of the 9K medium (total volume) supplemented with 0.01%(w/v) yeast extract under the conditions of intensive aeration (the air was supplied at a flow rate of 1 v/(v·min)) in a Redline R153 thermostat (Binder, Germany) for two days at 40°C. The total inoculum volume was 10%(v/v). Ferrous iron (Fe\textsuperscript{2+}, 5.4 g/L) in the form of FeSO\textsubscript{4}·7H\textsubscript{2}O and elemental sulfur (1%(w/v)) were added as energy sources. The initial pH was adjusted to 1.6. The obtained solution (pH 1.3) containing the active community of acidophilic microorganisms, Fe\textsuperscript{3+} (4.2 g/L), Fe\textsuperscript{2+} (1.2 g/L), and elemental sulfur (unoxidized part) was separated from the sulfur precipitate by filtration on a paper filter and used as inoculum for subsequent bioleaching.

Bioleaching of the concentrate was carried out under the batch conditions in a 2.0-L bioreactor with a working volume of 1.0 L. Inoculum was added to the bioreactor containing 10 g of the solid sample (1%(w/v) pulp density). The initial pH was adjusted to 1.1–1.2. The experiments were conducted with aeration at 4 v/(v·min) and a stirring rate of an overhead 8-blade Rushton turbine impeller of 500 rpm. Distilled water was added once a day to the bioreactor to compensate for evaporation losses. At the end of ferric leaching and bioleaching tests, the pulp was centrifuged at 2000 rpm for 5 min, and the residue was washed three times with distilled water and dried to constant weight. The pH and Eh were measured with a pH-150WI pH meter–millivoltmeter (Izmeritelnaya tekhnika, Russia). The concentration of the Fe\textsuperscript{3+} ions in the liquid phase was determined by the titrimetric method from the reaction with Na\textsubscript{2}-EDTA [20]. The total iron concentration was determined by the same method after the reaction of the sample with ammonium persulfate. The ferrous ion concentration was defined as the difference between the values for total and ferric iron. The concentrations of copper and nickel ions in solutions were determined using atomic absorption spectroscopy (AAS) (Perkin Elmer 3100, PerkinElmer, USA). Solids were analyzed by a wet chemical method, using 1:3 concentrated nitric acid: concentrated hydrochloric acid at the boiling temperature of the mixture, followed by AAS (Perkin Elmer AAAnalyst-800, PerkinElmer, USA) for metal analysis [21].

3. Results and Discussion

Three technological approaches to the processing of the copper-nickel bulk sulfidic concentrate were compared in this study. They were (1, 2) leaching with a ferric iron solution containing the commercial chemical reagent and leaching with the ferric iron bio-solution generated via oxidation of ferrous iron by an acidophilic microbial community (10.0 g/L Fe\textsuperscript{3+}, initial pH 1.15, 1% pulp density, 80°C, 5h), as well as (3) bioleaching using an active acidophilic microbial community in a bioreactor (5.0 g/L Fe\textsuperscript{3+}, initial pH 1.15, 1% pulp density, 40°C, 22 days). Figure 2 illustrates ferric leaching of the copper-nickel concentrate with the commercial reagent solution and biologically generated ferric iron solution at 80°C. Figure 3 shows changes in parameters during bioleaching in the bioreactor.
Figure 2. Extraction of nickel and copper ions into the liquid phase (a) and iron concentrations (b) during ferric leaching of the copper-nickel concentrate with commercial ferric iron reagent (chemical) and biologically generated ferric iron solution (bio) at 80°C and 1% pulp density. Abbreviations: Fe3+, ferric iron; Fe2+, ferrous iron.

Figure 3. Extraction of nickel and copper ions into the liquid phase (a) and changes in iron concentrations (b), as well as values of pH and redox potential (c), during bioleaching of the copper-nickel concentrate at 40°C and 1% pulp density. Abbreviations: Fe3+, ferric iron; Fe2+, ferrous iron.

According to the data shown in Figure 2a, the rate of nickel dissolution in the liquid phase depended on the mode of ferric leaching, while the rate of copper dissolution was similar (9%). The maximum nickel dissolutions were 35 and 42% in the case of the chemical and biologically generated ferric iron solution, respectively. Analysis of the decrease in the Fe3+ concentration (Figure 2b), which resulted from the interactions with minerals, showed the following. Leaching of the copper-nickel concentrate by
chemical and biologically generated ferric solutions resulted in the residual Fe$^{3+}$ concentrations of 8.14 and 7.56 g/L, respectively. Based on these data, more active leaching of nickel was associated with a more active reduction of ferric ions during the leaching process. Table 1 summarizes the content of elements in the solids after ferric leaching in comparison with bioleaching, taking into account residue yields at the end of the process. More rapid dissolution of Ni in the case of ferric leaching with the biosolution, in comparison with the chemical solution, agreed with the content of Ni in the leach residues: 6.85 and 8.75%, respectively.

| Processing mode | Content in residue (wt.%) |
|-----------------|--------------------------|
| Bioleaching (22 days) | Cu: 15.6, Ni: 1.49 |
| Ferric leaching with bioreagent (5 h) | Cu: 12.4, Ni: 6.85 |
| Ferric leaching with chemical reagent (5 h) | Cu: 14.1, Ni: 8.75 |

Table 1. Content of elements in leach residues in different processing modes.

Bioleaching with the active microbial community that contained different iron and sulfur oxidizers, as well as heterotrophic microorganisms, showed a considerably higher efficacy of the process than ferric leaching. During the bioleaching, changes in the metal concentrations in the liquid phase, pH, and redox potential were monitored.

Figure 3a shows the dissolution of nickel and copper into the solution during bioleaching of the concentrates. Nickel extraction increased during all 22 days of bioleaching reaching 86.7%, with a higher rate of dissolution in the first four days. According to the nickel content in the bioleach residue, only 1.49% remained in the solids (Table 1). On day 22, no significant retardation of nickel extraction into the solution was noted. Thus, nickel recovery may be increased with an increase in the duration of bioleaching. Similarly, no inhibition of nickel bioleaching from the nickel concentrate has been reported by Sun et al. [22]. The microbial community showed high iron-oxidizing activity, resulting in the rapid oxidation of ferrous iron in the medium within the first 4–5 days of the bioprocess (Figure 3b). The obtained patterns agreed with changes in pH and redox potential (Figure 3c). The pH value increased at the beginning, which was associated with the rapid dissolution of some gangue minerals in the concentrate, as well as partial dissolution of pyrrhotite and violarite-pentlandite phase and chemical oxidation of these sulfides with ferric iron in the acidic solution. The activity of sulfur-oxidizing microorganisms caused a further decrease in pH, which was rapid within the next three days and proceeded at a slower rate until the end of bioleaching. The redox potential, which is primarily associated with the ratio of ferric and ferrous ions, increased rapidly and reached its maximum of ~950 mV (vs. SHE) after 5 days of bioleaching.

It is noteworthy that copper was in the form of chalcopyrite, which is known to be very stable in ferric solutions [13]. The patterns for copper dissolution in our study agreed with the previously determined pattern for the mineral dissolution during nickel concentrate bioleaching with At. ferrooxidans by Mason and Rice [23]: pyrrhotite > violarite > pyrite > pentlandite > chalcopyrite. Thus, copper recovery from chalcopyrite was low in all leaching experiments (Figures 2a and 3a). The content of copper was concentrated in solids after ferric leaching at high temperatures and bioleaching, reaching 15.6% in the latter case (Table 1). Bioleaching of chalcopyrite is known to be more efficient at a relatively low redox potential (<600 mV vs. SHE) [24]. Therefore, the redox potential that reached ~950 mV (vs. SHE) during bioleaching of the copper-nickel concentrate contributed to the selective nickel leaching.
4. Conclusions
To summarize our data on the leaching of the violarite-pentlandite-chalcopyrite concentrate in different modes, biolteching at 40 °C allowed efficient removal of nickel and benefitted the low-grade concentrate by increasing the copper content in it (Table 1). Therefore, biolteching may be a promising cost-effective approach characterized by relatively low environmental hazards for copper-nickel concentrate beneficitation to obtain a high-grade copper sulfide product. At the same time, high-temperature ferric leaching with the chemical solution or biologically generated solution containing ferric iron was not sufficient to remove nickel from the concentrate and to considerably increase the copper content in the leach residues. Nevertheless, treatment with the ferric bio-solution allowed better nickel dissolution than in the case of the chemical solution and may be potentially used to improve the grade of selective sulfidic concentrates.

5. References
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