Biological and acid leaching of low-grade sulfide concentrate containing Cu and Ni at different temperatures

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Abstract. In this study, the bioleaching of low-grade nickel-copper concentrate was carried out using the nutrient medium containing yeast extract (YE) at temperature range of from 40 to 60°C in order to study the dependence of biooxidation rate and Cu and Ni extraction levels on the temperature and the presence of organic compounds. Mixed culture of the strains \textit{Sulfobacillus thermosulfidooxidans}, \textit{Acidithiobacillus caldus}, and \textit{Acidiplasma} sp., moderately-thermophilic acidophiles, which oxidize sulfide minerals, was used in the experiments. Temperature and organic carbon source were shown to affect bioleaching. At 40–50°C, the influence of YE addition was insignificant. At 55 and 60°C bioleaching depended on YE presence. Nevertheless, microbial activity affected mainly iron leaching and allowed maintaining comparatively low pH of medium. Both Cu and Ni extraction rates almost not affected by biooxidation activity. Thus, the leaching of the base metals form the concentrate was mainly determined by abiotic factors (acidity and temperature). Regardless of this fact, bioleaching may play a significant role for processing of similar sulfide concentrates, since to maintain favourable pH, abiotic acid leaching could require a large amounts of H\textsubscript{2}SO\textsubscript{4}, while biooxidation provides sulfuric acid generation.

1. Introduction

Biohydrometallurgy that is globally used to process mineral commodities containing sulfide minerals makes it possible to gain base (Cu, Zn, Ni, Co) and noble metals (Au and Ag) \cite{1, 2}. Base metals from low-grade ores is usually extracted using heap and dump bioleaching as these approaches do not require high capital and operating expenses, while stirred tank reactor bioleaching is often used to process refractory gold-bearing sulfide (mainly pyrite-arsenopyrite) concentrates, since it requires higher costs compared to dump or heap processes \cite{1}. Despite this, reactor biohydrometallurgy has been successfully commercialized to treat substandard and low-grade concentrates of some base metals (Cu, Ni, Co), minerals composition and content of impurities in which does not allow to use pyrometallurgical processing \cite{3-5}.

Currently, studies are underway to expand the area of biohydrometallurgy application, both by developing approaches based on novel principles, and by involving new types of mineral sources in metal production using biohydrometallurgy. Cu and Ni-containing sulfide ores and concentrates, which are often also characterized by comparatively high content of platinum group metals (PGM) (Pt, Rh, Ru, Pd, Os, and Ir) are considered as promising mineral commodities for biohydrometallurgical treatment \cite{6-8}. Cu-Ni ores are usually processed by dressing allowing obtaining sulfide Cu and Ni concentrates, which then is treated by pyrometallurgical technologies. PGM are concentrated first in nickel (mainly) and Cu concentrates, and then in sludge produced.
by electrolytic Ni and Cu refining [6]. The sludge is then treated to produce high-grade PGM concentrates, which then are subjected to the further processing at the refining stage to extract platinoids. Since at present industry faces with the problem of exhaustion of reserves of Ni and Cu-Ni ores, from which valuable metals could be extracted by traditional processing, approaches that may be used for gaining both non-ferrous metals and PGM from low-grade ores including technogenic ones, as well as substandard concentrates, are actively developed. As shown in several works, the bioleaching and cyanidation are promising approaches to treat low-grade Cu-Ni concentrates containing platinoids [7, 8]. Cyanidation, which is commonly applied to extract Au and Ag, may also be used for leaching PGM [7, 8]. For example, Panda et al demonstrated column bioleaching allowed to extract 52% Cu, 95% Ni, and 85% Co from low-grade concentrate containing 0.36% Cu, 0.74% Ni, and 0.011% Co, while 20% Pt, 87% Pd, and 46% Rh were extracted by cyanidation of the bioleaching residue [7]. Thus, technologies that include stages of bioleaching and cyanidation, which have been successfully commercialized for Au-bearing ores and concentrates, might be successfully applied for the processing of substandard mineral commodities to gain copper, nickel, and PGM [1, 9].

Therefore, the understanding of the patterns influencing the bioleaching of different Cu-Ni ores and concentrates should be performed to estimate how different factors affect bioleaching and to reveal the optimal conditions to extract different components to perform technological processes with maximum efficiency. Therefore, the aim of this work was to perform the bioleaching of low-grade Ni-Cu concentrate containing pyrrhotite, pentlandite, and chalcopyrite in batch experiments at temperatures of 40 to 60°C as this parameter is crucial for activity of acidophiles performing mineral destruction and metal leaching.

2. Materials and methods

Data on the content of the main chemical elements and minerals in the concentrate are presented in tables 1 and 2.

| Table 1. Content of the main chemical elements in Ni-Cu concentrate. |
|---------------------------------------------------------------|
| Content, %          | Fe | Cu | Ni | S_{total} | S_{sulfide} | S_{sulfate} | S^{0} |
|--------------------|----|----|----|-----------|-------------|-------------|-------|
| 32.7               | 0.7| 2.3| 20.9| 17.0      | 1.0         | 2.9         |

| Table 2. Mineral composition of Ni-Cu concentrate (XRD data). |
|---------------------------------------------------------------|
| Content, %          | Pyrite | Chalcopyrite | Pyrrhotite | Pentlandite | Chlorites | Plagioclase | Amphibole | Talc | Goethite |
|--------------------|--------|-------------|------------|-------------|-----------|------------|-----------|------|----------|
|                    | 5      | 5           | 35         | 5           | 5         | 30         | 5         | 5    | 5        |

Bioleaching experiments were performed with mixed culture of three extreme acidophiles, which oxidize ferrous iron and sulfur to gain energy for the growth (Acidithiobacillus caldus MBC-1, Sulfbacillus thermosulfidooxidans SH-1, and Acidiplasma sp. MBA-1), which we used in our previous studies in the experiments on the biooxidation of various minerals [10]. Erlenmeyer flasks with 100 mL of mineral nutrient medium containing (g/L) (NH_{4})_{2}SO_{4} – 3.0; KCl – 0.2; MgSO_{4} × 7H_{2}O – 0.5; K_{2}HPO_{4} – 0.5) and 2 g of the concentrate were used to carry out the experiments. The flasks were incubated on a rotary shaker (200 rpm) for 30 days at temperature range 40–60°C. As representatives of Sulfbacillus and Acidiplasma require organic carbon source for the growth, 0.02% yeast extract (YE) (mixotrophic conditions) was added into the medium to study the effect of organic nutrients on the concentrate biooxidation. In control, organic nutrients were not added (autotrophic conditions) [10]. Initial cell number of each strain was about 1 × 10^7 cells/mL.
Concentrations of Fe$^{3+}$, Fe$^{2+}$, copper, and nickel as well as pH and Eh were monitored to estimate bioleaching rate. The pH and Eh values were measured using pH-150MI pH meter (Izmeritel'naya Tehnika, Russia). Fe$^{2+}$ and Fe$^{3+}$ ions content in the liquid phase was determined spectrophotometrically using PE-5400VI spectrophotometer (Ecohim, Russia) at 475 nm using the rhodanide method. Cu and Ni concentrations were determined using a Perkin Elmer 3100 flame atomic absorption spectrometer (Perkin Elmer, USA). The rates of copper and nickel leaching were calculated by the content of these metals in the concentrate and concentration in the solution.

3. Results and discussion

Figures 1–3 present the results obtained.

Temperature and YE addition affected biooxidation activity at 55°C (figure 1), while at lower temperature (40–50°C) the effect of YE addition was insignificant. Liquid medium parameters demonstrated that in YE absence, biooxidation was more active at 40–50°C, while at 55 and 60°C, the process was suppressed that was reflected by pH, Eh, ferric and ferrous iron ion concentration changes during the bioleaching. At 55–60°C, pH level and Fe$^{3+}$ concentration were significantly higher than at 40–50°C while Eh values and Fe$^{3+}$ content were significantly lower than those at 55 and 60°C (figures 1A). Inhibition of biooxidation activity was observed only at 60°C, when YE was added in the medium, and the parameters of the medium observed under autotrophic/mixotrophic conditions differed insignificantly. At the case of YE addition, biooxidation activity at 55°C was high, and therefore medium parameters were close to those observed in the experiments at 40–50°C.

Acid leaching (sterile control) results (figure 2) demonstrated importance of the microbial activity for the leaching of only some components of the concentrate. In sterile control, pH values sharply increased, while Eh values were comparatively low. Fe$^{3+}$ cations content in the medium was low, while Fe$^{2+}$ cation content was high. Patterns observed demonstrated that in sterile control, iron-containing sulfides were dissolved in acid medium and this process led to the pH increase and accumulation of ferrous ions in the medium. Despite microbial activity affected leaching of iron sulfides (probably pyrite and pyrrhotite), the rates of Cu and Ni leaching in the presence of microorganisms were not higher in comparison to the sterile control (figures 1–3). This means that leaching of copper and nickel minerals depended mainly on acid leaching and electrochemical interactions of the minerals. Copper leaching depended on temperature, while YE presence partially inhibited copper extraction (figure 3A). Nickel extraction depended on experiment conditions at lower extent (figure 3B).

Thus, the results of the experiments performed in this work demonstrated that both organic nutrients addition and temperature affected activity of acidophiles performing bioleaching. At temperature from 40 to 50°C, YE addition effect was insignificant, since in this temperature range, autotrophic acidophile, *A. caldus* MBC-1, is active and could supply mixo- and heterotrophs (*S. thermosulfidooxidans* SH-1 and *Acidiplasma* sp. MBA-1) with organic compounds released in the medium as exometabolites [10, 11]. This made it possible to maintain comparatively high oxidative activity of mixed microbial culture in this temperature range. Higher temperature (55–60°C) inhibited *A. caldus* MBC-1, therefore, at 55°C bioleaching activity was determined by YE presence, which is consumed as carbon source by mixo- and heterotrophs performing sulfide mineral biooxidation [10, 11]. Microbial activity affected mainly iron leaching rate and led to the decrease in pH of the medium. Both copper and nickel leaching rates almost did not depend on biooxidation activity. This may demonstrate that leaching rate of these metals was mainly determined by abiotic factors, i.e. high acidity and temperature. Despite this, bioleaching may play key role for the processing of this type of concentrates as abiotic acid leaching requires high amounts of acid to maintain the pH required, while biooxidation provides sulfuric acid generation. Moreover, disruption of iron-containing sulfides (pyrite, pyrrhotite), which may be provided only by oxidative leaching, is required for successful deliberation of PGM and Au contained in Cu-Ni ores and concentrates [7, 8].
Figure 1. Liquid phase parameters: pH and Eh values as well as Fe^{3+}, Fe^{2+}, Cu, and Ni concentrations during bioleaching: A – control (autotrophic conditions); YE - yeast extract (mixotrophic conditions).
Figure 2. Liquid phase parameters: pH and Eh values as well as Fe$^{3+}$, Fe$^{2+}$, Cu, and Ni concentrations during acid leaching (sterile control): A – control (autotrophic conditions); YE - yeast extract (mixotrophic conditions).
Figure 3. Copper (A) and nickel (B) extraction rates (%) after 30 days of the leaching: A – control (autotrophic conditions); YE - yeast extract (mixotrophic conditions).

4. Conclusions
The experimental results demonstrated that non-ferrous metals (mainly nickel) may be extracted from the concentrate studied in our work both by biological and acid leaching, while iron removal was provided mainly by bioleaching. Bioleaching also provided maintaining pH level and $\mathrm{H}_2\mathrm{SO}_4$ generation. Thus, for the comprehensive processing of Cu-Ni concentrates bioleaching may be considered as promising method allowing both extracting non-ferrous metals and disrupting iron sulfides for subsequent PGM and Au extraction by cyanidation. In the same time, acid leaching provided comparatively high rate of Cu and Ni extraction.

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