Effect of Organic Nutrients and Elevated Temperature on Bioleaching of Sulfide Copper Concentrate

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Abstract. The goal of the work was to study the effect of addition of organic carbon source required for microorganisms oxidizing sulfide minerals in the nutrient medium on the rate of copper concentrate bioleaching. The concentrate containing 31.6% Fe, 19.2% Cu, and 2.9% Zn was bioleached in a batch mode for 30 days using mixed culture of acidophilic microorganisms. In the first reactor, biooxidation was performed at 45°C without additional carbon sources. In the second and in the third reactors, biooxidation was performed at 45°C and 55°C and nutrient medium was supplemented with 0.02% of yeast extract. Biooxidation without yeast extract allowed extracting 47 and 92% of copper and zinc. During biooxidation at 45°C using the medium supplemented with yeast extract, 54 and 94% of copper and zinc were extracted. During bioleaching at 55°C, 48% and 84% of copper and zinc were extracted. Thus, yeast extract allowed increasing copper bioleaching rate at 45°C, but temperature increase up to 55°C led to decrease in bioleaching efficiency. It may be explained by the fact that yeast extract increased activity of acidophilic microorganisms, which may consume organic carbon sources, while high temperature may inhibit some microorganisms and, therefore, does not allow increasing bioleaching rate.

1. Introduction
Biohydrometallurgical treatment (bioleaching) of sulfide copper ores with acidophilic microorganisms has been successfully used for copper extraction worldwide and currently provides about 5% of world copper production [1–3]. Main reason to use bioleaching for copper extraction is possibility to treat copper ores, which are inappropriate for pyrometallurgical processing due to the low copper content, specificity of mineral composition, which impedes obtaining high-grade copper concentrates, and high content of different impurities, which decrease copper extraction rate and quality of the copper produced [1, 4].

As biohydrometallurgical technologies are mainly process low-grade copper ores, heap bioleaching is usually used in copper industry due to the low capital and operating expenses [4–6]. The role of heap bioleaching in copper production may increase in the future due to the decline in average copper content in ores and decrease in the resources of conventional copper ores [4–6].

Thus, the main advantages of heap bioleaching are low requirements for the quality of raw materials as well as low costs of metal production [3, 7]. In the same time, heap bioleaching provide low rate of metal extraction and does not provide effective copper extraction from some refractory minerals, for example, chalcopyrite (CuFeS₂), the most abundant copper sulfide mineral [2, 8, 9].
Therefore, the development and commercialization of alternative approaches is required to increase the rate and efficiency of biohydrometallurgical treatment of copper ores. Tank bioleaching has been successfully applied for processing sulfide concentrates and provides higher rate of metal extraction in comparison to heap bioleaching. In the same time, this technology is mainly used for treatment of gold-bearing sulfide concentrates due to relatively high costs related to use complex equipment for stirring, temperature maintaining, and aeration [10–12]. It was shown that tank bioleaching may be successfully used for processing cobalt, nickel, and low grade copper-zinc concentrates [1, 5, 12–14]. As copper minerals, including chalcopyrite, are often refractory to biooxidation with acidophilic microorganisms, different methods to increase copper bioleaching rate in tank bioleaching have been proposed. As parameters of tank bioleaching processes in contrast to heap bioleaching may be regulated, different approaches to increase their efficiency may be used. For example, it was shown that copper extraction rate in tank bioleaching processes may be increased by temperature increase or using high chloride concentrations [15, 16].

In our previous work we studied possibility to increase the efficiency of tank biooxidation of sulfide gold-bearing concentrate containing pyrite and arsenopyrite by addition of organic carbon source (yeast extract) required for the constructive metabolism of acidophilic microorganisms oxidizing sulfide minerals at different temperatures [17]. As many of microorganisms involved in biooxidation of sulfide concentrates gaining energy by oxidizing ferrous iron and sulfur compounds may also consume organic nutrients as carbon sources [1, 18, 19], addition of organic compounds in nutrient medium used for bioleaching made it possible to increase both pyrite and arsenopyrite biooxidation rate, as well as gold extraction rate [17]. Thus, it was shown that use of organic nutrients may be a promising approach to increase the efficiency of tank bioleaching of pyrite-arsenopyrite concentrate; therefore, it also may be used to increase the efficiency of chalcopyrite concentrate bioleaching as it may enhance the activity of microorganisms performing bioleaching.

The goal of the present work was to study the possibility to increase the rate of copper concentrate bioleaching by addition of organic carbon source required for acidophilic microorganisms oxidizing sulfide minerals and temperature regulation.

The experiments were performed using mixed culture of moderately thermophilic microorganisms, as moderate thermophiles are usually predominate in industrial bioleaching processes [12, 13, 20]. In the same time, it should be noted that moderately thermophilic acidophiles used in biohydrometallurgical processes are usually able to utilize organic compounds as carbon source and addition of organic nutrients are usually added in the media during their laboratory cultivation [21]. In mixed microbial populations performing bioleaching in the reactors, organic compounds required for some microorganisms are synthesized by autotrophic members of microbial populations that makes it possible to maintain activity of mixotrophic and heterotrophic acidophiles. Nevertheless, use of additional organic carbon sources may provide higher oxidizing activity of microorganisms [17–19].

2. Materials and methods

Tables 1 and 2 show chemical and mineral composition of the concentrate, which was used in the study.

| Table 1. Chemical composition of the concentrate. |
|-----------------------------------------------|
| **Content, %**                                 |
| Fe | Cu | Zn | S$_{\text{total}}$ | S$_{\text{sulfide}}$ | S$_{\text{sulfate}}$ | S$^0$ |
|----|----|----|-------------------|-------------------|-------------------|------|
| 31.6 | 19.2 | 2.9 | 34 | 32.3 | 1.7 | < 0.01 |
Table 2. Mineral composition of the concentrate (based on XRD data).

| Mineral Composition | Content, % |
|--------------------|-----------|
| Pyrite (FeS₂)      | 14        |
| Pyrrhotite (FeS)   | 14        |
| Chalcopyrite (CuFeS₂) | 67       |
| Sphalerite (ZnS)   | <5        |
| Quartz (SiO₂)      | <5        |

Biooxidation was performed in a batch mode in stirred tank reactors that contained 1 L of pulp. Mineral nutrient medium used for the experiments with initial pH of 1.5 containing (g/L) (NH₄)₂SO₄ – 0.75; KCl – 0.05; MgSO₄ × 7H₂O – 0.125; K₂HPO₄ – 0.125. The experiments were conducted at aeration of 4 min⁻¹ and a stirring speed of 500 rpm. The duration of the experiments was 30 days. Pulp density was 20% (200 g of the concentrate and 1 L of mineral nutrient medium). Mixed culture of moderately thermophilic acidophiles, properties of which are shown in table 3, was used for the bioleaching. The initial number of each strain in the liquid phase of the pulp was about 1 × 10⁸ cells/mL. In the first reactor (control), biooxidation was performed at 45°C without organic carbon sources (i.e. under autotrophic conditions, where carbon dioxide contained in air, was the sole carbon source). In the second and in the third reactors, nutrient medium was supplemented with 0.02% of the yeast extract (YE), which is used for the cultivation of mixo- and heterotrophic acidophiles as organic carbon source, in the beginning of the experiments as well as on the 10th and 20th days, and bioleaching was performed at 45°C and 55°C, respectively.

Table 3. Properties of the strains used for the bioleaching.

| Microorganism                      | Oxidation | Optimum temperature / upper limit, °C | Carbon source       |
|-----------------------------------|-----------|--------------------------------------|---------------------|
| Acidithiobacillus caldus MBC-1    | − +       | 45/53                                | CO₂                 |
| Sulfobacillus thermosulfidooxidans | + +       | 50/60                                | CO₂, organic compounds |
| Acidiplasma sp. MBA-1             | + +       | 50-55/63                             | Organic compounds   |

The pH, Eh of the pulp as well as metal (Fe³⁺, Fe²⁺, Cu, Zn) concentrations were monitored. The pH of the pulp was adjusted using CaCO₃ or H₂SO₄ to maintain the pH value in the range from 1.0 to 1.7. The concentrations of Fe²⁺ and Fe³⁺ ions were determined using the rhodanide method based on formation of a purple coordination complex of ferric iron ions Fe³⁺ and rhodanide SCN⁻ spectrophotometrically (at 475 nm). The concentration of copper and zinc were determined using a Perkin Elmer 3100 flame atomic absorption spectrometer (Perkin Elmer, USA). The rates of copper and zinc leaching from concentrate were calculated by the concentration of Cu and Zn ions in liquid phase. Sulfur content in the solid residues was measured using the phase method.

3. Results and discussion

Table 4 and figures 1 and 2 show the results of the experiments. It was shown that under different conditions, some differences in liquid phase parameters and, therefore, in metal extraction rates were observed. Despite this, it should be noted that differences in bioleaching conditions affected mainly iron leaching, while copper and zinc bioleaching depended on experimental conditions to a lesser extent.
Figure 1. Changes in liquid phase parameters during the bioleaching: a – pH, b – Eh, c – Fe$^{3+}$ concentration, d – Fe$^{2+}$ concentration.
During bioleaching of the concentrate, iron, copper, and zinc concentrations in the liquid phase increased due to the biooxidation of sulfide minerals, while pH decreases due to the production of sulfuric acid due to the oxidation of sulfur compounds. The Eh value affected mainly by the ratio of Fe$^{3+}$/Fe$^{2+}$ ions reflects iron-oxidizing activity during the bioleaching of sulfide concentrates. As sulfuric acid and calcium carbonate are used to adjust the pH level, their consumption also reflects biooxidation activity. Thus, these parameters are used to evaluate microbial activity during sulfide concentrate bioleaching.

During the bioleaching, pH values fluctuated due to the biooxidation of sulfur compounds as well as due to sulfuric acid and calcium carbonate addition. To maintain pH level favorable for acidophilic microorganisms, sulfuric acid was added to the pulp of reactors 1 and 2 from the beginning of the experiment to the day 10. Then, the pH levels were low and maintained by calcium carbonate addition (figure 1). In the same time, in the reactor 3, sulfuric acid was added to the pulp up to the 20th day. Nevertheless, the pH was not stable and periodically increased (figure 1a). Sulfuric acid and calcium

![Graph showing changes in non-ferrous metals concentrations during the bioleaching: a - Cu, b - Zn.](image)

**Figure 2.** Changes in non-ferrous metals concentrations during the bioleaching: a - Cu, b - Zn.

**Table 4.** Results of bioleaching.

| Reactor | $T_\text{r}$, $^\circ\text{C}$ | YE addition | Cu extraction, % | Zn extraction, % | $S_{\text{sulfide}}$ oxidation, % | $\text{H}_2\text{SO}_4$ consumption, kg/t | $\text{CaCO}_3$ consumption, kg/t |
|---------|-----------------|-------------|-----------------|----------------|------------------|-----------------|-----------------|
| 1       | 45              | -           | 47              | 92             | 49               | 5.2             | 67.5            |
| 2       | 45              | +           | 53              | 94             | 55               | 10.3            | 112.5           |
| 3       | 55              | +           | 48              | 84             | 23               | 18.7            | 5               |
carbonate consumption (table 4) demonstrates clear difference between the reactors. Both sulfuric acid and calcium carbonate consumptions were the highest in the reactor 2. While in the reactor 3, calcium carbonate consumption was lower by an order of magnitude than in the reactors 1 and 3, while sulfuric acid consumption was several times higher. Thus, it may be concluded that biooxidation of sulfur compounds that leads to decrease in the pH in the reactor 2 was more intensive than in the reactors 1 and 3, while in the reactor 3, biooxidation intensity was probably low. In the same time, higher sulfuric acid consumption in the reactor 2 in comparison to reactor 1 may be explained by more active iron biooxidation in the reactor 2 (figures 1 c and d) that results in H⁺ consumption and increase in pH:

\[ 4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O. \]  

\[ (1) \]

Eh values in the reactors increased during the bioleaching and its changes reflected the changes in Fe³⁺/Fe²⁺ ratio (figures 1b, c, and d). Thus, in the reactor 3, Eh was comparatively low (figure 1 b) as Fe³⁺ concentration was lower and Fe²⁺ concentration was higher than in the reactors 1 and 2 (figures 1 c and d). In the reactors 1 and 2, Eh values were significantly high and exceeded 700 mV after 9 and 14 days of the bioleaching. Ferrous iron oxidation rates in the reactors 1 and 2 differed, but were comparable (figures 1 c and d).

Sulfide sulfur oxidation levels (table 4) confirmed the results of liquid phase parameters, as S_{sulfide} oxidation level was the highest in the reactor 2 and the lowest in the reactor 3.

Thus, differences in bioleaching conditions led to the differences in biooxidation rate. However, copper and zinc extraction rates depended on experimental conditions to a lesser extent (figure 2 and table 4). In the reactor 3, zinc extraction level was lower in comparison to the reactors 1 and 2, while copper extraction levels in the reactors 1 and 3 were almost equal. In the reactor 2, copper extraction was the highest, but the difference with the reactors 1 and 3 was about 5%.

Thus, the addition of organic nutrients into the medium made it possible to increase the intensity of sulfide concentration bioleaching and rate of sulfide sulfur biooxidation. In the same time, the increase in copper and zinc extraction levels was not significant.

4. Conclusions

Thus, organic carbon source made it possible to increase copper bioleaching rate at 45°C, but the increase in temperature up to 55°C led to decrease in bioleaching efficiency. It may be explained by the fact that addition of yeast extract led to the increase in activity of acidophilic microorganisms, which may consume both carbon dioxide and organic substances as carbon source, but high temperature may inhibit some microorganisms in microbial populations and, therefore, does not allow to increase bioleaching rates by increasing the temperature. Despite this, it should be noted that differences in bioleaching conditions affected mainly iron leaching, while copper and zinc bioleaching depended on experimental conditions to a lesser extent. These results may be explained by the fact that sphalerite (ZnS) is comparatively easily leached [22] and, therefore, may be actively bioleached regardless the conditions. In the same time, chalcopyrite bioleaching is determined by different factors, including temperature and Eh, but not only by the high activity of iron- and sulfur-oxidizing activity [2].

In our previous work, we studied the biooxidation of gold-bearing pyrite-arsenopyrite concentrate under the same conditions [17]. It was shown, that organic nutrients addition significantly affected both pyrite and arsenopyrite biooxidation and made it possible to increase gold extraction rate. Thus, the comparison of the results obtained in the present work with those obtained under the same conditions with other sulfide concentrate demonstrated that peculiarities of mineral biooxidation mechanism have a crucial role in the efficiency of different approaches, which may be proposed to improve bioleaching processes.

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