Effect of organic nutrients on bioleaching of low-grade copper concentrate at different temperatures

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Abstract. The goal of the present work was to study the effect of different organic nutrients (yeast extract and molasses) on the biooxidation of copper concentrate containing chalcopyrite, tennantite, sphalerite, and pyrite in batch experiments at different temperatures (of 40 to 55°C). For the experiments, representatives of microbial groups predominant in biohydrometallurgical processes, bacterium of the genus *Sulfobacillus*, *Acidithiobacillus caldus*, and archaea of the genus *Acidiplasma*, were used. It was shown that both temperature and addition of organic nutrients in the medium affected the activity of the bioleaching. In the same time, the effect of organic nutrients was significant only at high temperatures (50 and 55°C). In all experiments, biooxidation rate decreased at the highest temperature, 55°C. Since among the strains used in the study, only *A. caldus* MBC-1 is autotroph, which is able to provide the population with organic nutrients and is not active at 55°C, at this temperature it was not able to maintain activity of other strains. Therefore at 55°C, biooxidation activity strongly depended on the presence of organic nutrients. Despite temperature and presence of organic nutrient affected activity of concentrate biooxidation that was revealed by the differences in pH, Eh values and iron ions concentrations in the medium, copper, zinc and arsenic extraction rates depended on these factors to a lesser extent.

1. Introduction

Despite most of copper production in the world is provided by pyrometallurgical processing of sulfide ores containing chalcopyrite (CuFeS₂) and other sulfide copper minerals, alternative technologies are developed and commercialized to extract copper from low-grade raw materials, which may also contain harmful impurities that impede successful copper extraction [1, 2]. These approaches include different hydrometallurgical technologies including autoclave and biological oxidative leaching [3–6]. These processes are based on oxidative disruption of sulfide minerals allow recovering non-ferrous metals into the liquid phase, which then may be treated to extract metals, for example, using SX/EW methods [6].

To improve the efficiency of bioleaching processes, properties of microorganisms involved in sulfide minerals oxidation as well as mechanisms of interaction of microorganisms and sulfide minerals have been extensively studied [7, 8]. It was shown, that biohydrometallurgical processes in industrial scale are always carried out by mixed microbial population formed during long-term adaptation to the conditions under which mineral raw materials are treated and activity of microorganisms in these populations may depend on different factors [7–10]. For example, it was
revealed that activity of microbial populations performing biooxidation depended on availability of carbon sources including both carbon dioxide and organic nutrients [7–10]. It is known that mixed microbial populations performing biooxidation processes include auto-, mixo-, and heterotrophic microorganisms. In this case, autotrophs maintain activity of mixo- and heterotrophs in the populations releasing exometabolites [10]. In the same time, it was shown that addition of organic nutrients including yeast extract may increase rate of biooxidation of sulfide concentrate [9]. Thus, addition of different carbon sources may be considered as promising approach to increase the efficiency of biooxidation processes.

The goal of the present work was to study the effect of different organic nutrients (yeast extract and molasses) on the biooxidation of copper concentrate in batch experiments at different temperatures. For the experiments, representatives of microbial groups predominant in biohydrometallurgical processes, bacterium of the genus Sulfbacillus, Acidithiobacillus caldus, and archaea of the genus Acidiplasma, were used.

2. Materials and methods

Tables 1 and 2 show chemical and mineral compositions of the concentrate, respectively. According to state standards of Russian Federation (GOST R 52998-2008), this concentrate is low grade.

### Table 1. Chemical composition of the concentrate.

|   | Fe  | Cu  | Zn  | As<sub>total</sub> | S<sub>total</sub> | S<sub>sulfide</sub> | S<sub>sulfate</sub> | S<sup>0</sup> |
|---|-----|-----|-----|------------------|----------------|-------------------|-------------------|--------|
|   | 27.4| 18.1| 6.2 | 1.7              | 35.9           | 33.2              | 2.5               | 0.2    |

### Table 2. Mineral composition of the concentrate (based on XRD data).

|   | Pyrite (FeS<sub>2</sub>) | Chalcopyrite (CuFeS<sub>2</sub>) | Tennantite (Cu<sub>12</sub>As<sub>8</sub>S<sub>13</sub>) | Sphalerite (ZnS) |
|---|--------------------------|-------------------------------|---------------------------------|------------------|
|   | 30                       | 40                            | 15                              | 15               |

Bioleaching was performed using mixed culture of acidophilic microorganisms oxidizing ferrous iron and sulfur compounds (Acidithiobacillus caldus MBC-1, Sulfbacillus thermosulfidoxidans SH-1, and Acidiplasma sp. MBA-1) [9, 11]. A. caldus MBC-1 is autotrophic sulfur-oxidizer capable of growth at a temperature up to 53°C. S. thermosulfidoxidans SH-1 and Acidiplasma sp. MBA-1 are mixo- and heterotrophic microorganisms, respectively, which are active at 55°C. It is known that in microbial populations oxidizing sulfide ores and concentrates, autotrophic microorganisms including strain of A. caldus provide mixo- and heterotrophic microorganisms such as representatives of the genera Sulfbacillus and Acidiplasma, which require organic carbon source for stable growth, with organic nutrients realized into the medium as exometabolites [10, 12]. Therefore, the strains used in this study were selected in a such way to provide stable oxidizing activity of the mixed culture at different conditions. In the same time, the strains used in the study are representatives of the groups predominating in the processes of biooxidation of sulfide ores and concentrates at elevated temperatures [9–13]. All strains were inoculated in the medium so that initial cells number of each strain was about 0.5×10<sup>7</sup> cells/mL. The experiments were carried out in flasks with 100 mL of mineral nutrient medium containing salts of nitrogen and phosphorus ((g/L) (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> – 3.0; KCl – 0.2; MgSO<sub>4</sub> × 7H<sub>2</sub>O – 0.5; K<sub>2</sub>HPO<sub>4</sub> – 0.5) and 2 g of the concentrate on a rotary shaker (200 rpm) for 20 days at temperatures of 40 to 55°C. To evaluate the effect of different organic nutrients on the bioleaching concentrate, the medium was supplemented with 0.02% yeast extract (YE) or molasses (M) as carbon source (mixotrophic conditions). In control variant, the medium did not contain organic nutrients (autotrophic conditions).
Biooxidation of sulfide minerals results in the dissolution of iron, copper, zinc, and arsenic in the medium as well as to the generation of sulfuric acid. This, in turn, leads to the increase in Eh and decrease in pH. Thus, these parameters of liquid phase allowing to evaluate bioleaching activity and were monitored to access the effect of temperature and addition of organic nutrient addition on the bioleaching. The pH and redox potential (Eh) were measured using pH-150MI pH meter (Izmeritel'naya tehnika, Russia). The concentrations of Fe\(^{2+}\) and Fe\(^{3+}\) ions were determined spectrophotometrically using PE-5400VI spectrophotometer (Ecohim, Russia) at 475 nm using the rhodanide method. The concentration of Cu, Zn, and As were determined using a Perkin Elmer 3100 flame atomic absorption spectrometer (Perkin Elmer, USA). The rates of Cu, Zn, and As leaching from concentrate and ASL leaching residue were calculated by the concentration of these elements ions in the liquid phase.

3. Results and discussion
The results of the bioleaching tests are shown in figures 1–3.

It was shown that addition of organic nutrients significantly affected bioleaching activity at higher temperatures, while at lower temperatures the effect was insignificant. In the same, the effect of organic nutrients addition and temperature on the bioleaching of different components of the concentrate varied considerably.

During bioleaching, pH gradually decreased almost in all variants (figure 1) that demonstrated active biooxidation of sulfur compounds during the concentrate bioleaching. In the same time, under autotrophic conditions, pH values increased at 50 and 55°C reaching 2.03 and 2.40 at the end of the experiment. That probably means that at 50 and 55°C sulfur oxidation was significantly suppressed. Eh values increased in most variants of the experiment and were in the range of 739 to 911 mV at the end of the experiment. At 55°C, Eh values were lower than those reached at other variants of the experiment (figure 1). The Eh was the lowest at 55°C under autotrophic conditions (639–654 mV). In the presence of YE in the medium, Eh values reached 875 mV after 10 days of the bioleaching but then decreased to 790 mV. In the presence of molasses, Eh increased at 55°C up to the 5th day of the experiments and then decreased to 739 mV. Changes in Fe\(^{3+}\) and Fe\(^{2+}\) concentrations corresponded to Eh values during the experiment. Fe\(^{3+}\) concentrations increased in all variants of the experiment with the exception of the bioleaching at 55°C under autotrophic conditions. Under autotrophic conditions Fe\(^{3+}\) concentrations sharply increased at 40 and 45°C, while at 50°C it increased at a slower rate and was 1.5–1.7 times lower than at 40 and 45°C. In the same time, in the presence of YE, Fe\(^{3+}\) concentrations were high at 40–55°C (2.41–2.67 g/L at the end of the experiment), and about 2.5 times lower at 55°C. In the presence of molasses, Fe\(^{3+}\) concentration was the lowest at 55°C (about 0.60 g/L), while at other temperatures it was high (2.02–2.77 g/L), despite at 50°C the rate of Fe\(^{3+}\) accumulation was lower than at 40 and 45°C. Fe\(^{2+}\) concentrations were low at the end of the experiment and did not exceed 0.21 g/L with exception of bioleaching at 55°C under autotrophic conditions and in the presence of molasses. Thus, the results of the experiments demonstrated that at higher temperatures (50 and 55°C) biooxidation activity was suppressed. In the same time, YE and molasses presence made it possible to decrease inhibitory effect of high temperature. This may be explained by the fact that organic nutrients added into the medium, maintained activity of mixo- and heterotrophs, while at 55°C activity of the autotrophic microorganism (A.caldus MBC-1) was inhibited, therefore, it was not able to maintain activity of mixo- and heterotrophs. It should be noted that, despite temperature and presence of organic nutrients affected activity of concentrate biooxidation that was reflected by the differences in pH, Eh values and iron ions concentrations in the medium, copper, zinc and arsenic extraction depended on these factors to a lesser extent (figures 2 and 3). Under autotrophic conditions, Cu extraction was the highest at 45°C, while at 55°C it was the lowest (figures 2 and 3) that corresponded to the results shown in figure 1. In the experiment with YE, Cu extraction rates differed insignificantly, while in the presence of molasses Cu extraction was the highest at 50°C. Under autotrophic conditions and in the presence of YE, zinc extraction rates differed insignificantly, while in the experiment with molasses it was the highest at 50°C.
Figure 1. Liquid phase parameters: changes in pH, Eh, Fe$^{3+}$, Fe$^{2+}$ concentrations during bioleaching: A – control (autotrophic conditions); YE - yeast extract; M – molasses.
Figure 2. Liquid phase parameters: changes in Cu and Zn concentrations during bioleaching and arsenic concentration after 20 days of the bioleaching: A – control (autotrophic conditions); YE - yeast extract; M – molasses.

Figure 3. Copper (A) and zinc (B) extraction (%) after 20 days of the bioleaching: A – control (autotrophic conditions); YE - yeast extract; M – molasses.

4. Conclusions
It was shown that both temperature and addition of organic nutrients in the medium affected the activity of the bioleaching. In the same time, the effect of organic nutrients was significant only at high temperatures (50 and 55°C). In all experiments, biooxidation rate decreased at the highest
temperature, 55°C. This may be explained by physiological properties of the microorganisms used in the experiments as well as by interactions between microorganisms. Among the strains used in the study, only *A. caldus* MBC-1 is autotroph, which is able to provide the population with organic nutrients. Since this strain is not active at 55°C, at this temperature it was not able to maintain activity of other strains. Therefore at 55°C, biooxidation activity strongly depended on the presence of organic nutrients. Despite temperature and presence of organic nutrients affected activity of concentrate biooxidation that was revealed by the differences in pH, Eh values and iron ions concentrations in the medium, copper, zinc and arsenic extraction rates depended on these factors to a lesser extent. This may be explained by the fact that leaching of copper and zinc minerals may also be determined not only by biooxidation but also by chemical abiotic leaching. Thus, the results obtained demonstrated that addition of organic nutrients made it possible to maintain activity of biooxidation at high temperature. Therefore, application of organic nutrients may be promising approach allowing to stabilize the activity of microbial population at high temperatures. Despite this, it should be noted that high rate of the biooxidation of some components of sulfide concentrate in some cases may not increase extraction rate of the target components.

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