Possibility of Environment-Friendly Hydrometallurgical Treatment of Copper-Zinc Concentrate Containing Arsenic

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Abstract. Pyrometallurgical treatment of copper concentrates containing arsenic poses a problem due to the emission of toxic gaseous arsenic oxides. Therefore, the development of effective environment-friendly hydrometallurgical approaches allowing extracting metals from these concentrates without gas emission is a relevant issue. The goal of the present work was to study the effect of chloride on the bioleaching of Cu-Zn concentrate containing tennantite and solid residue of its alkaline sulfide leaching (ASL) in order to evaluate the possibility to improve bioleaching of Cu-Zn concentrates containing tennantite using ASL pretreatment and NaCl addition. In NaCl absence, bioleaching of the concentrate made it possible to extract 52 and 62% of Cu and Zn for 30 days. The addition of 100 mM NaCl allowed extracting 66 and 93% of Cu and Zn. In the same time, bioleaching of ASL residue made it possible to extract 74 and 66% of Cu and Zn, while NaCl addition to the medium inhibited Cu and Zn extraction during ASL bioleaching and 35 and 62% of Cu and Zn were leached. Thus, it was shown, that both ASL pretreatment and NaCl addition increased the rate of copper and zinc bioleaching from the concentrate, while NaCl addition to the medium led to inhibition of ASL residue bioleaching. Therefore, both methods can be considered as promising approaches to increase metal extraction from Cu-Zn concentrates containing tennantite but the effect of each factor should be studied in detail to develop effective technologies.

1. Introduction
The most of copper production is provided by pyrometallurgical processing of mineral raw materials containing the most widespread Cu sulfide mineral, chalcopyrite (CuFeS₂) [1]. The depletion of high-grade and easily processed ores leads to the necessity to extract Cu from different mineral raw materials including those containing toxic components, for example, As in such minerals as enargite or tennantite [2–6]. Pyrometallurgical processing of As-containing Cu ores and concentrates led to the production of toxic volatile As gaseous oxides [4]. Therefore, alternative approaches should be used to treat this type of raw materials. Alkaline sulfide leaching (ASL) is the hydrometallurgical process, which can be used for the treatment of copper concentrates containing As [5]. ASL with Na₂S at high temperatures (above 80°C) allows removing As destructing enargite and tennantite [5]. Cu and other non-ferrous metals are not dissolved during ASL, while As is transferred into the liquid phase. This method allows obtaining products with lower As content appropriate for pyrometallurgical processing. Tennantite disruption during ASL results in the formation of CuS and CuS₂ remained in solid residue. Other impurities such as Zn may also impede Cu production using pyrometallurgy. Cu concentrates with a high content of

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other non-ferrous metals are considered as raw materials for hydrometallurgical processing including autoclave leaching or tank bioleaching processes, which are suitable to treat low-grade and “dirty” concentrates [3, 6].

In earlier work [7], we studied tank bioleaching of the concentrate containing 1.70% of As in the form of tennantite as well as 6.22 and 7.30% of Cu and Zn. Bioleaching allowed extracting up to 17% Cu and 70% Zn that may be due to the Cu minerals are more resistant to bioleaching in comparison to sphalerite (ZnS) [9]. Tennantite was resistant to bioleaching [7]. In previous work [8], we studied the possibility to increase the efficiency of Cu-Zn concentrate bioleaching containing tennantite using ASL. Tank bioleaching of the concentrate and ASL solid residue made it possible to extract 21 and 37% of copper and 38 and 47% of zinc, respectively. Thus, the results obtained demonstrated that ASL pretreatment allows for increasing Cu and Zn extraction. At the same time, it was also shown that the presence of chloride ions made it possible to increase both Cu and Zn bioleaching from similar concentrate, and application of NaCl may be considered as the method to improve bioleaching of Cu-Zn concentrates [10]. Therefore, a combination of ASL pretreatment and NaCl application may be a promising approach to improve the leaching of Cu-Zn concentrates containing tennantite.

The goal of the present work was to evaluate the effect of the presence of chloride on metal extraction during the bioleaching of Cu-Zn concentrate and solid residue of its alkaline sulfide leaching [8] to evaluate the possibility of environment-friendly hydrometallurgical treatment of copper Cu-Zn concentrate containing As.

2. Materials and methods

Compositions of the concentrate containing pyrite (FeS₂), chalcopyrite (CuFeS₂), tennantite (Cu₁₂As₈S₁₃), and sphalerite (ZnS) and ASL residue obtained in previous work [8] are shown in table 1.

| Table 1. Chemical composition of the concentrate and ASL residue. |
|-----------------|-------|-----|------|-----|-----|-----|
|                | Fe    | Cu  | Zn   | AsTotal | STotal | Sulfide | Sulfate | S₀   |
| 27.4            | 18.1  | 6.2 | 1.7  | 35.9 | 33.2 | 2.5 | 0.2 |
| 28.2            | 17.8  | 6.4 | 0.2  | 35.9 | 34.6 | 0.8 | 0.5 |

The bioleaching was performed in Erlenmeyer flask with 100 mL of mineral nutrient medium containing salts of nitrogen and phosphorus ((g/L) (NH₄)₂SO₄ – 3.0; KCl – 0.20; MgSO₄ × 7H₂O – 0.5; K₂HPO₄ – 0.5) with initial pH of 1.5 supplemented with 0.02% of yeasts extract and 2 g of the concentrate or ASL residue on a rotary shaker at 50°C for 30 days. In one variant of the experiment, the nutrient medium was supplemented with 100 mM NaCl. The experiments were performed using the mixed culture of acidophilic microorganisms oxidizing ferrous iron and sulfur compounds (Sulfobacillus thermosulfidooxidans SH-1, Acidithiobacillus caldus MBC-1, and Acidiplasma sp. MBA-1) [11, 12]. All strains were inoculated in the medium so that the initial cells number of each strain was about 1×10⁷ cells/mL. The control experiments were performed under the same conditions using the same sterile medium without inoculation of microorganisms. Also, the experiment of oxidative leaching of the concentrate and ASL leaching with Fe₂(SO₄)₃ was performed. This experiment was performed under the same conditions as bioleaching but the nutrient medium used for the bioleaching was replaced with Fe₂(SO₄)₃ solution containing 50 mM of Fe³⁺ ions.

Parameters of the liquid phase were monitored to determine bioleaching activity and rate of metal leaching. The pH and redox potential (Eh) were measured using pH-150MI pH meter. The concentrations of Fe³⁺ and Fe⁶⁺ 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

Figure 1 and 2 demonstrate changes in liquid phase parameters during the concentrate and ASL residue leaching.

Figure 1. Changes in liquid phase parameters during the bioleaching of the concentrate: a – pH; b – Eh, mV; c – Fe$^{3+}$; d – Fe$^{2+}$; e – Cu, f – Zn, and g – As concentrations, g/L.

The determination of the parameters shown that both in the absence and presence of NaCl in the medium biooxidation was sufficiently active. In both variants, pH values decreased (figure 1a), while
Eh values increased but were higher in the variant without NaCl addition (figure 1b). Fe$^{3+}$ ion concentrations increased during the bioleaching (figure 1c). Fe$^{2+}$ ions were not detected during the bioleaching without NaCl. In the variant with NaCl, Fe$^{3+}$ concentration was 0.2 g/L on the 30th day of the experiment (figure 1d). This corresponded to the changes in Eh values during the bioleaching in NaCl presence, which decreased to the end of the experiment (figure 1b). Liquid phase parameters showed that in NaCl presence, FeS$_2$ oxidation was less active that was also shown in earlier work [13].

![Figure 2](image)

**Figure 2.** Changes in liquid phase parameters during the bioleaching of ASL residue: a – pH; b – Eh, mV; c – Fe$^{3+}$; d – Fe$^{2+}$; e – Cu, f – Zn, and g – As concentrations, g/L.

In contrast to iron leaching, Cu and Zn extractions levels were higher in the variant with NaCl addition (figure 1e and 1f and figure 3, bars 1 and 2). This may be explained by the fact that rates of
Chalcopyrite and sphalerite bioleaching are increased in the presence of chloride-ion [3, 8, 10]. At the same time, in NaCl presence, As leaching was lower at the end of the experiment (figure 1g). This corresponded to the fact that tennantite bioleaching may be inhibited in NaCl presence [10]. In sterile control, Cu and Zn leaching rates were significantly lower than during the bioleaching (figure 3, bar 3). This suggests that microbial activity played important role in Cu and Zn leaching despite metals might be partially leached abiotically. In the experiment with Fe$^{3+}$ solution, Cu and Zn extraction was as high as during the bioleaching (figure 3, bar 4). As concentrations were extremely low (figure 1g) that may be explained both by low leaching rate of tennantite with ferric iron and by secondary arsenic precipitation due to scorodite formation (FeAsO$_4$) due to high initial concentration of Fe$^{3+}$ ions [14].

The results obtained in the experiments with ASL residue differed from those obtained in the experiments with the concentrate (figures 2 and 3). According to the results shown in figure 2, bioleaching activity was high only in the experiment without NaCl. In this variant, pH decreased (figure 2a), while Eh was as high as during the concentrate bioleaching (figure 2b). Fe$^{3+}$ concentration gradually increased (figure 2c), while Fe$^{2+}$ was not detected (figure 2d). Cu extraction rate was significantly higher than during the concentrate bioleaching (figure 1e and 3, bar 5). At the same time, Zn extraction rate was insignificantly higher than in the experiment with concentrate (figure 1f and 3, bars 1 and 5). In contrast to the concentrate, NaCl addition inhibited bioleaching of ASL residue. Liquid phase parameters during ASL residue bioleaching slightly differed from those observed in sterile control (figure 2) with exception of pH and Fe$^{2+}$ concentration (figure 2a and 2d). The pH rapidly increased at the end of the experiment (figure 2a) that may be explained by the dissolution of Cu sulfides (CuS and Cu$_2$S) and sphalerite contained in the ASL residue accompanied with proton consumption [15]. Fe$^{3+}$ concentration was extremely low (figure 2c). At the same time, Fe$^{2+}$ concentration was comparatively high on the 10th day and reached 1.1 g/L (figure 2d). Then, Fe$^{2+}$ concentration decreased and Fe$^{2+}$ ions were not detected. This suggested that Fe$^{2+}$ may be oxidized due to microbial activity and abiotic oxidation, which may occur with a comparatively high rate at high pH values (figures 2a and 2d). Despite almost complete oxidation of Fe$^{3+}$, Fe$^{3+}$ concentration was low, which may be due to iron precipitation at high pH in the presence of high Na$^+$ concentration [16]. Cu and Zn leaching rates during the bioleaching of ASL residue in the presence of NaCl did not differ significantly from the sterile control (figures 2e and 2f, figure 3, bars 6 and 7). At the same time, NaCl presence should enhance chalcopyrite and sphalerite leaching. Probably, in this experiment, the formation of secondary iron-containing precipitates might lead to the passivation of mineral surfaces and inhibit further Cu and Zn extraction. In the experiment with Fe$^{3+}$ solution, Cu extraction from the ASL residue (figures 2e and 3, bar 8) was insignificantly lower than during the bioleaching (figure 3, bar 5) and insignificantly higher than during concentrate ferric leaching (figure 3, bar 4). Zn extraction from the ASL residue (figures 2f and 3, bar 8) was higher than during the ASL bioleaching (figure 3, bar 5) and during the concentrate ferric leaching (figure 3, bar 4).

**Figure 3.** Cu and Zn extraction after 30 days of the leaching: 1 – concentrate; 2 – concentrate + 100 mM NaCl; 3 – concentrate control; 4 – concentrate + 50 mM Fe$^{3+}$; 5 – ASL residue; 6 – ASL residue + 100 mM NaCl; 7 – ASL residue control; 8 – ASL residue + 50 mM Fe$^{3+}$.

4. Conclusions

ASL pretreatment as well as NaCl addition to the medium affected Cu and Zn extraction by bioleaching. This may be explained by the fact that tennantite is more refractory to bioleaching than copper sulfides...
(CuS and Cu₂S) formed during tennantite transformation during ASL as well as by the effect of chloride ion on chalcopyrite bioleaching. Zinc extraction was not significantly affected by ASL pretreatment, while it was enhanced by NaCl addition during concentrate bioleaching. At the same time, the presence of NaCl resulted in inhibition of ASL residue leaching. Thus, despite ASL pretreatment and NaCl addition allow to increase the bioleaching rate of Cu and Zn, the combination of these methods led to the decrease in metal extraction rates. Therefore, both methods may be considered as promising approaches to increase metal extraction from Cu-Zn concentrates containing tennantite but the effect of each factor should be studied in detail to develop effective environment-friendly hydrometallurgical technologies for the treatment of Cu-Zn concentrate with high As content.

5. References
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