Two-stage leaching of copper-zinc concentrate containing tennantite

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Abstract. The goal of the present work was to evaluate the possibility to improve bioleaching of Cu-Zn concentrate containing tennantite by means of using alkaline sulfide leaching (ASL). Concentrate contained 18.1% Cu, 6.2% Zn, and 1.7% As. ASL allows removing arsenic by means of destruction tennantite (Cu₁₂As₅S₁₃) that results in the formation of dissolved thioarsenite and CuS and Cu₂S in solid residues. ASL was performed under the following conditions: 95°C, pulp density 20%, residence time 6 h, NaOH concentration 3.5M, Na₂S concentration 1.5M. ASL residue contained 17.8% Cu, 6.4% Zn, and 0.2% As. Biobleaching of the concentrate and ASL solid residue was performed in stirred tank reactor under the following conditions: 40°C, pulp density 10%, residence time 20 d. Cu extraction reached 21 and 37%, while Zn extraction was 38 and 47% during concentrate and ASL residue biobleaching. The results obtained demonstrated that ASL pretreatment of the concentrate containing tennantite led to significant increase in copper extraction. Therefore, two-stage leaching including ASL and biobleaching may be considered as promising approach for processing tennantite-containing products since it allows avoiding emission of toxic gases and providing comparatively high copper and zinc extraction.

1. Introduction

Most of world’s copper production (about 80%) is provided by pyrometallurgical processing of sulfide ores. Sulfide ores containing chalcopyrite (CuFeS₂), the most widespread copper sulfide mineral, as well as other sulfide copper minerals are usually treated by means of obtaining high-grade sulfide concentrates and further pyrometallurgical processing [1]. In last decades, copper industry has been faced with a problem due to the depletion of high-grade and easily processed ores [2]. This forces to extract copper from different substandard ores with low content or valuable metals or those, which contain toxic impurities (As and Sb) as well as other sulfide minerals, which impede production of high-grade copper concentrates [3–5]. Pyrometallurgical processing of these raw materials presents a number of challenges due to the loss of valuable products with ore dressing and metallurgical wastes as well as due to the production of toxic volatile products, for example, arsenic oxides As₂O₃ and As₄O₆ [4].

Existing challenges result in the necessity for development and commercialization of novel technologies for metal production. Hydrometallurgical approaches may be considered as alternative to pyrometallurgical technologies for metal extraction from substandard ores and concentrates. For example, oxidative leaching (autoclave leaching, tank bioleaching) may be used to extract copper and other non-ferrous metals from low-grade concentrates [3, 6]. These processes based on oxidative...
disruption of sulfide minerals allow recovering non-ferrous metals into solutions, which then used for obtaining metals, for example, using SX/EW methods [6]. Alkaline sulfide leaching (ASL) is another hydrometallurgical process, which can be used for treatment of certain types of copper concentrates [5]. ASL with sodium sulfide at elevated temperatures (above 80°C) allows performing removal of As and Sb by means of destruction of a minerals such as enargite (Cu₃AsS₄) and tennantite (Cu₁₂As₄S₁₃) as well as tetrahedrite ((Cu,Fe)₄Sb₅S₁₃) and stibnite (Sb₂S₃) [5]. Non-ferrous metals (Cu, Zn) are not dissolved during ASL and this method makes it possible to decrease As or Sb content in the concentrates and obtain products suitable for further processing. Enargite and tennantite disruption during ASL bioleaching results in the formation of dissolved thioarsenite or thioarsenate as well as CuS and CuS₂ in solid residues:

$$\text{Cu}_{12}\text{As}_4\text{S}_{13} + 6\text{NaHS} + 6\text{NaOH} \rightarrow 5\text{Cu}_2\text{S} + 2\text{CuS} + 4\text{Na}_3\text{AsS}_3 + 6\text{H}_2\text{O} \ (1)$$

In our previous work, we studied bioleaching of copper-zinc concentrate containing pyrite (FeS₂), chalcopyrite (CuFeS₂), tennantite (Cu₁₂As₄S₁₃), and sphalerite (ZnS) [7]. Tank bioleaching at 40°C in continuous mode for 10 d made it possible to extract 17% Cu and 70% Zn. Thus, bioleaching was comparatively effective for zinc extraction, while copper extraction rate was low. It may be explained by the fact that copper minerals may be comparatively resistant to bioleaching in comparison to sphalerite (ZnS) [8]. Tennantite was more resistant to bioleaching than chalcopyrite and arsenic and tennantite content in bioleaching residue was higher than in the concentrate. Thus, bioleaching did not make it possible to reach high efficiency of copper leaching and did not provide high rate of tennantite leaching [7]. Since copper sulfides (equation 1) formed during ASL are less refractory to bioleaching than primary sulfide minerals [3], ASL may allow increasing the rate of copper bioleaching.

The goal of the present work was to evaluate the possibility to improve bioleaching of copper-zinc concentrate containing tennantite by means of using preliminary ASL.

2. Materials and methods

Chemical and mineral compositions of the concentrate are shown in tables 1 and 2. According to standards approved in Russia Federation, this concentrate may be considered as low grade, while arsenic content exceeds approved limits (GOST R 52998-2008).

| Table 1. Chemical composition of the concentrate. |
|-----------------------------------------------|
| **Content, %**                               |
| Fe    | Cu | Zn   | As_total | S_total | S_sulfide | S_sulfate | S⁰  |
| 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). |
|-----------------------------------------------|
| **Content, %**                               |
| Pyrite (FeS₂) | Chalcopyrite (CuFeS₂) | Tennantite (Cu₁₂As₄S₁₃) | Sphalerite (ZnS) |
| 30            | 40                        | 15                         | 15                          |

Alkaline sulfide leaching (ASL) was performed in titanium stirred tank reactor equipped with RW 20 overhead stirrer (IKA, Germany) and TW-2.02 heating circulator (Elmi, Latvia) under the following conditions: temperature 95°C, pulp density (solid-to-liquid ratio, S : L) 1 : 5, residence time 6 h, NaOH concentration 3.5M, Na₂S concentration 1.5M, stirring rate 500 rpm. ASL solid residue was separated by filtration using N 840.3 FT. 18 vacuum pump (KNF, Germany) and dried at 70°C. Chemical analysis of the residue was performed to evaluate the rate of arsenic leaching.

Batch bioleaching of the concentrate and ASL solid residue was performed in glass stirred tank reactor equipped with RW 20 overhead stirrer (IKA, Germany) and TW-2.02 heating circulator (Elmi, Latvia) under the following conditions: temperature 40°C, S : L 1 : 10, residence time 20 days, stirring
rate 250 rpm. The experiments were performed using liquid medium containing the following (g/L distilled water): (NH₄)₂SO₄, 0.75; KCl, 0.05; MgSO₄ · 7H₂O, 0.125; K₂HPO₄, 0.125. Mixed culture of acidophilic microorganisms, which was formed during long-term bioleaching of similar copper-zinc concentrate, was used as inoculum for bioleaching test [7]. Prior the inoculation, concentrate and ASL residue were incubated in the reactors for 3 days to stabilize pH values and initial pH values were adjusted to 1.5 by adding concentrated sulfuric acid. Cells of the mixed culture were collected by centrifugation in sterile 500-mL tubes (9500 rpm, 15 min) using Sigma 4-15 centrifuge (Sigma, Germany), resuspended in mineral medium, and inoculated in the reactors in such a way that initial cell number in the pulp was about 1 · 10⁸ cells/mL.

Parameters of liquid phase were monitored to evaluate bioleaching activity. The pH and redox potential (Eh) were measured using pH-150MI pH meter (Izmeritel'naya tehnika, Russia). The pH values during the bioleaching were adjusted by adding concentrated sulfuric acid and CaCO₃ to the medium. The concentrations of Fe²⁺ and Fe³⁺ ions were determined by trilonometric titration. The concentration of copper, zinc, and arsenic were determined using a Perkin Elmer 3100 flame atomic absorption spectrometer (Perkin Elmer, USA). The rates of copper, zinc, and arsenic leaching from concentrate and ASL leaching residue were calculated by the concentration of Cu, Zn, and As ions in liquid phase. The microorganisms were enumerated by direct count using Amplival phase contrast light microscope (Carl Zeiss, Germany).

3. Results and discussion

Chemical composition of ASL solid residue is shown in table 3. ASL made it possible to remove about 88% of arsenic from the concentrate. In the same time, content of other elements changed insignificantly. It should be noted that Fe, Cu, and Zn were not detected in ASL pregnant solution, while As concentration in the solution was about 3.2 g/L. These results corresponded to the equation (1), according to which arsenic is converted into the solution during ASL, while copper and other metals remain in solid phase. Despite this, small amounts of copper were lost, probably due to the losses during filtration.

| Table 3. Chemical composition of ASL residue. |
|---------------------------------------------|
| Content, %                                  |
| Fe  | Cu  | Zn  | As_total | S_total | S_sulfide | S_sulfate | S⁰ |
| 28.2 | 17.8 | 6.4 | 0.2      | 35.9    | 34.6      | 0.8       | 0.5 |

The results of the bioleaching tests are shown in figures 1–3. Biooxidation of sulfide minerals leads to the release of iron, copper, zinc, and arsenic into the solution as well as to the generation of sulfuric acid. The increase in Fe³⁺ ions and sulfuric acid concentrations in turn leads to the increase in Eh and decrease in pH values, respectively.

Minerals of the concentrate are oxidized according to the equations (2)–(5) with the formation of different intermediates (S⁰, Fe²⁺ ions), which, in turn, are oxidized by microorganisms (equations (6)–(7)):

\[4\text{FeS}_2 + 15\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SO}_4\]  
(2)

\[\text{CuFeS}_2 + \text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2\text{S}^0 + 2\text{H}_2\text{O}\]  
(3)

\[\text{Cu}_2\text{As}_2\text{S}_3 + 8\text{O}_2 + 6\text{H}_2\text{SO}_4 \rightarrow 12\text{CuSO}_4 + 4\text{H}_2\text{AsO}_4 + 13\text{S}^0\]  
(4)

\[\text{ZnS} + 2\text{O}_2 \rightarrow \text{ZnSO}_4\]  
(5)

\[2\text{FeSO}_4 + \text{O}_2 + 4\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}\]  
(6)

\[2\text{S}^0 + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4\]  
(7)
Figure 1. Changes in liquid phase parameters during the bioleaching: a – pH and Eh, b – Fe$^{3+}$ and Fe$^{2+}$ concentrations, c – Cu and Zn concentrations, d – As concentration.
Figure 2. Changes in microbial cell number in liquid phase of the pulp of bioleach reactors.

Thus, the analysis of liquid phase parameters (pH, Eh, Fe\(^{3+}\), Fe\(^{2+}\), Cu, Zn, and As concentrations) may be used to evaluate the activity of concentrate biooxidation. During bioleaching, pH gradually decreased, while Eh and metal ions and arsenic gradually increased (figure 1). Prior the inoculation, pH was stabilized by means of incubation in the reactors and adjusted to 1.5 by means of addition of concentrated sulfuric acid. It should be noted that sulfuric acid consumption during incubation of ASL residue was higher in comparison to the concentrate: 99 and 36 kg/t, respectively. Higher sulfuric acid consumption may be probably explained by changes in mineral composition of the concentrate during ASL. ASL residue contained CuS and Cu\(_2\)S formed during tennantite transformation, which are more readily soluble in acidic solutions than chalcopyrite and tennantite. During further bioleaching, pH decrease rate in the reactor with concentrate was higher, but after 12 days of the bioleaching pH values in the reactors were similar (figure 1a). Eh values in both reactors increased and exceeded 900 mV after 15 days of the leaching (figure 1a). Changes of Fe\(^{3+}\) and Fe\(^{2+}\) ion concentrations corresponded to Eh changes (figures 1a and 1b). During preliminary incubation, about 1.5−2.5 g/L of Fe\(^{2+}\) ions accumulated in the liquid medium. After inoculation, concentrations of Fe\(^{2+}\) ions sharply decreased and were residual after 5 days of bioleaching. Concentrations of Fe\(^{3+}\) ions gradually increased up to 15 day and then changed slightly (figures 1b). In accordance with changes in Fe\(^{3+}\) and Fe\(^{2+}\) concentrations, Eh increased sharply after 2 days of the bioleaching (figure 1a). In general, changes in pH, Eh, and iron ions during bioleaching did not change significantly during the bioleaching. Rates of Zn leaching did not differ significantly in both reactors, but Zn concentrations during ASL residue leaching was slightly higher than during concentrate bioleaching (figures 1c). In the same time, significant differences in copper leaching rates were observed (figures 1c). During ASL residue leaching, copper concentrates were 1.5−1.7 times higher than during concentrate bioleaching. It should be noted that after 5 days of the bioleaching, copper concentrates did not increase. Arsenic concentrations during concentrate bioleaching were significantly higher than during ASL residue leaching as arsenic content in the concentrate was about 8 times higher than in ASL residue (figure 1d). Number of microorganisms during ASL bioleaching increased faster than during concentrate bioleaching but after 15 days cell numbers in liquid phase of the pulp were similar (figure 2).

Extraction levels of Cu, Zn, and As after 20 days of the bioleaching are shown in figure 3. Copper extraction reached 21 and 37% during concentrate and ASL residue bioleaching. In the same time, arsenic leaching during concentrate bioleaching was comparatively low. This may be explained by the fact that tennantite is more refractory to bioleaching than copper sulfides (CuS and Cu\(_2\)S) formed during ASL. Zinc extraction was higher during ASL residue leaching in comparison to the concentrate leaching, but this difference was lower that difference in copper extraction.
Figure 3. Copper, zinc, and arsenic extraction after 20 days of the bioleaching.

The results obtained demonstrated that ASL pretreatment of the concentrate containing tennantite led to a significant increase in copper extraction. It may be explained by the transformation of tennantite that is comparatively refractory to bioleaching [7] into copper sulfides, which are readily leachable [3]. It should be noted that ASL pretreatment affected mainly copper extraction that was reflected in the parameters of liquid phase during the bioleaching.

4. Conclusions
The results of the present work demonstrated that ASL may be a promising approach for treatment of copper-zinc concentrates containing tennantite as this method makes it possible to remove arsenic from the concentrate and transform tennantite into copper sulfides, which are less refractory to bioleaching. Thus, ASL may be considered as an effective method for pretreatment of tennantite containing concentrates to improve bioleaching. Therefore two-stage leaching including ASL and bioleaching may be considered as an alternative to well-known approaches for processing tennantite-containing technologies since it allows avoiding emission of toxic gases and providing copper and zinc extraction.

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