

Article **Options for Increasing the Rate of Bioleaching of Arsenic Containing Copper Concentrate**

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Abstract: In the present work the effect of alkaline sulfide leaching (ASL) on the extraction of copper and zinc from low-grade copper concentrate containing chalcopyrite, tennantite, sphalerite, and pyrite during batch and continuous bioleaching experiments was studied. It was demonstrated that ASL and further bioleaching may be a promising approach for treatment of copper–zinc concentrates containing tennantite as this approach allows increasing copper extraction degree in comparison to one-stage bioleaching by 1.6–2.3 times. Thus, ASL was shown to be effective for pretreatment of tennantite containing concentrates to improve bioleaching for copper extraction. At the same time, ASL led to decrease in zinc extraction by 1.4–1.5 times. Therefore, the development of combined hydrometallurgical processes including ASL and bioleaching for effective metal leaching requires further studies to avoid negative effect on zinc extraction.

Keywords: biohydrometallurgy; chalcopyrite; tennantite; sphalerite; sulfide leaching; two-stage processes

1. Introduction

Arsenic is a toxic metalloid that is a widespread component of different mineral raw materials, as well as mining and metallurgical wastes. Its presence in ores, concentrates, and dressing wastes poses a problem due to harmful environmental effects $[1-5]$ $[1-5]$. There are various arsenic minerals, but the most common arsenic-bearing minerals important from the point of view of mineral processing and metallurgy are arsenopyrite (FeAsS), which is common in gold-bearing sulfide ores, as well as enargite $(Cu₃AsS₄)$ and tennantite $(Cu_{12}As_4S_{13})$, widespread at some copper deposits.

Processing of sulfide concentrates with a high arsenic content, including copper ones containing such minerals as enargite ($Cu₃As₄$) and tennantite ($Cu₁₂As₄S₁₃$), requires the use of special gas purification systems to decrease the emission of highly toxic volatile arsenic oxides (As₂O₃ and As₄O₆), which makes their processing less cost effective [\[4,](#page-11-2)[5\]](#page-11-1). In addition, some copper concentrates with a high arsenic content also contain fine-grained intergrowth of copper and zinc minerals with pyrite [\[5\]](#page-11-1), which impedes the efficiency of their pyrometallurgical processing. Thus, the composition of some sulfide copper–zinc ores does not allow the production of concentrates conditioned for pyrometallurgical processing, and therefore, the development of novel technologies for processing polymetallic copper concentrates with different impurities (i.e., zinc, arsenic, antimony) are promising $[4,5]$ $[4,5]$. These methods include different hydrometallurgical process, for example, bioleaching based on activity of iron- and sulfur-oxidizing acidophilic microorganisms [\[4](#page-11-2)[–23\]](#page-12-0) and other oxidative leaching processes [\[4](#page-11-2)[–6,](#page-11-3)[24–](#page-12-1)[31\]](#page-12-2).

Currently, biohydrometallurgical technologies (heap bioleaching) are widely applied in copper production for the processing of low-grade copper ores, and approximately 5%

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of the global copper production is provided by heap bioleaching [\[7](#page-11-4)[,11\]](#page-11-5). Tank (reactor) bioleaching is not economically viable for the processing of low-grade ores; therefore, it is mainly used for processing gold-bearing concentrates [\[7,](#page-11-4)[11\]](#page-11-5).

In industrial practice, one of the main advantages of tank biooxidation over pyrometallurgy is possibility of effective and environmentally friendly treatment of gold-bearing concentrates containing arsenic, mainly in the form of arsenopyrite [\[1](#page-11-0)[,7\]](#page-11-4). Biooxidation provides destruction of gold-bearing minerals without formation of toxic gas emissions containing arsenic. Despite gold-bearing concentrates being the main type of products treated using tank biooxidation, it has been shown that reactor bioleaching can also be successfully used for extraction of copper and zinc $[8]$, as well as other non-ferrous metals $[9,10]$ $[9,10]$, from sulfide concentrates. It has been shown that tank bioleaching may be successfully used for nickel and cobalt extraction form sulfide concentrate containing arsenic, making it possible to avoid arsenic emission into the atmosphere when processing this concentrate [\[10\]](#page-11-8). Thus, it has been shown that bioleaching may be used to process sulfide concentrates containing arsenic to avoid problems due to arsenic emission with gases.

It should be noted that tank bioleaching has been shown to be able to be successfully used to extract copper from concentrate containing an excess of zinc [\[8\]](#page-11-6), which may decrease copper extraction during pyrometallurgical operation, increasing slug viscosity [\[32\]](#page-12-3).

As it has been shown that bioleaching may be promising for the processing of sulfide concentrates with high arsenic content, including those containing copper and zinc, the goal of the present work was to study the process of reactor bioleaching of arsenic-containing copper–zinc concentrate in batch and continuous mode, as well as the effect of alkaline sulfide leaching (ASL) pretreatment on metal extraction during bioleaching.

In our previous works, we studied reactor bioleaching of similar copper concentrates [\[33](#page-12-4)[–37\]](#page-12-5). It was shown that tennantite, which contained a significant fraction of copper in studied products, is refractory to bioleaching. Therefore, one-stage bioleaching under different conditions did not make it possible to reach high copper extraction degree. Additionally, we used ASL to remove arsenic from different tennantite concentrates in our previous study, which demonstrated high efficiency [\[36](#page-12-6)[–38\]](#page-12-7). It is known that ASL transforms tennantite according to the following equation [\[4,](#page-11-2)[38,](#page-12-7)[39\]](#page-12-8):

$$
Cu12 As4S13 + 6N aHS + 6NaOH \rightarrow 5Cu2S + 2CuS + 4Na3AsS3 + 6H2O
$$
 (1)

Thus, after ASL treatment, arsenic is removed from tennantite concentrates, while copper remains in solid phase in the form of copper sulfides. In our previous works [\[36](#page-12-6)[,37\]](#page-12-5), we demonstrated that ASL made it possible to increase copper extraction from tennantite concentrate in batch experiments. In the present work, we studied bioleaching of lowgrade copper concentrate with higher tennantite content than in previous experiments in continuous mode as industrial bioleaching is performed in continuous mode, and only continuous laboratory-scale experiments can provide an indication of real bioleaching performance of different concentrates.

2. Materials and Methods

2.1. Flotation Concentrate

The concentrate sample was provided by Ural Mining Metallurgical Company (Verknaya Pyshma, Russia). The contents of the main elements (Fe, Cu, Zn, As, S) in the concentrate was determined using the phase analysis method [\[40\]](#page-12-9) and are presented in Table [1.](#page-1-0)

Table 1. Main element contents in the concentrate.

Sulfur content was determined in the testing laboratory "Gintsvetmet-Analytics" (Moscow, Russia) according to the methods described in [\[41\]](#page-12-10). Sulfide sulfur content was determined by sample decomposition with mixture of concentrated nitric and hydrochloric acids and further gravimetric determination with barium chloride. Sulfate sulfur content was determined by sodium carbonate extraction and further gravimetric determination of sulfate content with barium chloride. S^0 content was determined by carbon tetrachloride extraction and further spectrophotometric measurement.

Mineral composition of the concentrate was determined using a DRON-2 diffractometer (Burevestnik, St. Petersburg, Russia). Chalcopyrite (CuFeS₂), tennantite (Cu₁₂As₄S₁₃), sphalerite (ZnS) and pyrite ($FeS₂$) were shown to be the main sulfide minerals of the concentrate (Figure [1\)](#page-2-0). A similar concentrate sample obtained from the same ore was used in our previous study, but the main element contents in the concentrate samples differed slightly [\[35\]](#page-12-11).

Figure 1. X-ray diffraction pattern of the samples: (a) concentrate, (b) sulfide leaching residue. Py: pyrite; Sph: sphalerite; Tn: tennantite; Ccp: chalcopyrite; g: gypsum; Q: quartz. pyrite; Sph: sphalerite; Tn: tennantite; Ccp: chalcopyrite; g: gypsum; Q: quartz.

2.2. Microbial Population

We used a mixed population of iron- and sulfur-oxidizing acidophilic bacteria and archaea with a predominance of *Acidithiobacillus caldus*, *Sulfobacillus benefaciens*, *Leptospirillum ferriphilum*, *Ferroplasma acidiphilum*, *Cuniculiplasma divulgatum*, and *Acidiplasma* sp. as inoculum to perform bioleaching experiments. The population was used in our previous experiments to perform biooxidation of different sulfide concentrates [\[15](#page-11-9)[,20](#page-12-12)[,35\]](#page-12-11). Cells of the mixed population were separated from a mixed liquid phase sample of the pulp, which was obtained during biooxidation of copper–zinc concentrate under different conditions [\[35\]](#page-12-11), by centrifugation in 500-mL tubes (9500 rpm, 15 min) using Sigma 4–15 centrifuge (Sigma, Osterode am Harz, Germany). Biomass resuspended in mineral medium was inoculated in the reactors in such a way that initial total cell number in the pulp was about 1×10^8 cells/mL.

2.3. Alkaline Sulfide Leaching

Alkaline sulfide leaching (ASL) for tennantite destruction was performed in 2.5 L laboratory titanium stirred tank reactor equipped with RW 20 overhead stirrer (IKA, Staufen, Germany) and ED-5 heating circulator (Julabo, Seelbach, Germany) with U-shaped titanium heat exchangers under the following conditions: 95° C, pulp density (solid-toliquid ratio, S:L) 1:5, residence time 6 h, NaOH concentration 3.5 M, Na₂S concentration 1.5 M, stirring rate 500 rpm. ASL solid product was separated by filtration using N 840.3 FT. 18 vacuum pump (KNF, Witney, Germany) and dried at 70 ◦C using Binder FD53 thermostat (Binder GmbH, Tuttlingen, Germany). Content of the main elements in ASL residue was determined to evaluate arsenic leaching value, as well as possible losses of copper and zinc during ASL.

2.4. Experimental Setup and Biooxidation

To extract copper and zinc from the concentrate and ASL residue, batch and continuous bioleaching experiments were performed. Bioleaching was started in batch mode in 1 L laboratory reactors with a working volume of 1 L under the following conditions: stirring rate 500 rpm, aeration rate 5 L/min, temperature 40 °C, pulp density (solid to liquid ratio, S:L) 1:10, and duration of batch bioleaching 30 days. Then, both concentrate and ASL residue were leached in continuous mode in the same reactors and under the same conditions (pulp density, temperature, stirring rate, aeration). Residence time was 10 days, and the duration of continuous experiment was 45 days. TW-2.03 circulating water baths (Elmi, Riga, Latvia) and U-shaped titanium heat exchangers were used to maintain the temperature; RW20 overhead stirrers (IKA, Staufen, Germany) were used for stirring.

Mineral nutrient medium, containing the following salts (g/L) : (NH₄)₂SO₄—0.750, KCl—0.050, MgSO₄ × 7H₂O—0.125, K₂HPO₄—0.125, distilled water—1.0 L, was used for the bioleaching. This mineral medium has been successfully applied in bioleaching experiments [\[20,](#page-12-12)[35](#page-12-11)[,36\]](#page-12-6). Initial pH of the medium was 1.3.

2.5. Microbial Population Analysis

The compositions of the inoculum and microbial populations that formed during batch and continuous experiments were determined by the metabarcoding of the V3–V4 region of the 16S rRNA gene using the MiSeq system (Illumina, San Diego, CA, USA) as described in our previous works [\[15,](#page-11-9)[20,](#page-12-12)[35\]](#page-12-11). Samples for the analysis of microbial populations were collected at the end of batch experiments and twice at the end of continuous experiments. Thus, averaged results for the microbial population composition formed in continuous mode are shown.

Procedures for the biomass collection, DNA isolation, and sequencing and analysis of the data obtained were described in detail in our previous works [\[17,](#page-11-10)[30,](#page-12-13)[31\]](#page-12-2).

2.6. Sampling and Analysis

In the samples in liquid phase, pH and redox potential (Eh) were determined using a pH-150MI pH meter (Izmeritelnaya tekhnika, Moscow, Russia), and ferrous and ferric iron were measured by trilonometric titration [\[41\]](#page-12-10). Quantitative assessment of microorganisms was carried out by direct counts using an Amplival (Carl Zeiss, Jena, Germany) microscope equipped with a phase-contrast device. Cu and Zn concentrations in pulp samples were measured using a Perkin Elmer 3100 flame atomic absorption spectrometer (Perkin Elmer, Waltham, MA, USA). The degrees of extraction of copper and zinc were calculated on the basis of the concentration of Cu and Zn ions in the liquid phase.

2.7. Data Processing

The results obtained were processed using MS 15.0.459.1506 Excel 2013 software (Microsoft, Redmond, WA, USA). Average values of the parameters are shown.

3. Results

3.1. Alkaline Sulfide Leaching

The chemical composition of the ASL product is shown in Table [2.](#page-4-0) ASL extracted about 88% of arsenic from the concentrate. At the same time, the content of the metals changed insignificantly. The Fe, Cu, and Zn concentrations were extremely low in the ASL pregnant solution (5, 6, and 1.2 mg/L, respectively), i.e., these elements were almost not leached at all, while the As concertation in the solution was 3.6 g/L. ASL residue yield was 89%.

Table 2. Main element content in ASL residue.

XRD analysis demonstrated that tennantite was eliminated from the concentrate during ASL (Figure [1b](#page-2-0)). These results corresponded to Equation (1), according to which arsenic is dissolved during ASL, while copper and other metals remain in the solid phase in the form of CuS and $Cu₂S$ sulfides.

Thus, the results obtained in this section of the work are consistent with the data obtained previously in other works [\[4,](#page-11-2)[37](#page-12-5)[–39\]](#page-12-8), and ASL products in which arsenic content was significantly lower than in the processed concentrates were obtained.

3.2. Bioleaching

The results of bioleaching experiments in batch mode are shown in Figures [2–](#page-5-0)[4.](#page-7-0) The results obtained demonstrate the differences in the dynamics of leaching parameters during experiments with concentrate and ASL residue.

mode: pH and Eh (mV) values (**a**), concentrations of Fe³⁺ and Fe²⁺ ions (g/L) (**b**), concentrations of concentrations of mode: pH and Eh (mV) values (**a**), concentrations of Fe3+ and Fe2+ ions (g/L) (**b**), concentrations of **Figure 2.** Changes in the liquid phase parameters during the bioleaching of the concentrate in batch copper and zinc (g/L) (**c**).

mode: pH and Eh (mV) values (**a**), concentrations of Fe³⁺ and Fe²⁺ ions (g/L) (**b**), concentrations of $\mathcal{L}_{\mathbf{r}}$ parameters ($\mathcal{L}_{\mathbf{r}}$), concentrations of $\mathcal{L}_{\mathbf{r}}$, concentrations of $\mathcal{L}_{\mathbf{r}}$ **Figure 3.** Changes in the liquid phase parameters during the bioleaching of ASL residue in batch copper and zinc (g/L) (**c**).

Figure 4. Cu and Zn extraction from concentrate and ASL residue in bioleaching experiments. **Figure 4.** Cu and Zn extraction from concentrate and ASL residue in bioleaching experiments.

Prior to inoculation, concentrate and ASL residue were incubated in the reactor for days. During the first 5 days, the pH in both reactors increased, and sulfuric acid was 5 days. During the first 5 days, the pH in both reactors increased, and sulfuric acid was added to the pulp to maintain the pH level. Sulfuric acid consumption was 45 and 126 added to the pulp to maintain the pH level. Sulfuric acid consumption was 45 and 126 kg/t of the product in the experiment with the concentrate and ASL residue, respectively. Despite higher acid consumption, the pH level in the reactor with ASL residue was higher than that with the concentrate on the 5th day (2.56 and 1.65, respectively) (Figures [2a](#page-5-0) and [3a](#page-6-0)). This fact may be explained by the partial dissolution of copper and zinc minerals in the $\frac{1}{2}$ acid medium $[7,11,21,42-45]$ $[7,11,21,42-45]$ $[7,11,21,42-45]$ $[7,11,21,42-45]$ $[7,11,21,42-45]$. The larger pH increase in the reactor with the ASL residue might be due to the more active dissolution of CuS and Cu₂S sulfides in the acid medium in comparison to tennantite, which was proved by the results for copper dissolution
device the first 5 days of the health which was proved by the results of Giance 2001 200 Geneva dissolution during the first 5 days of the leaching before the inoculation (Figures 2c and concentrations in the pulp of the reactors differed 2.6-fold, and reached 0.88 and 2.30 g/L in the reactor with concentrate and ASL residue, respectively. Zinc concentrates prior in the reactor with concentrate and ASL residue, respectively. Zinc concentrates prior and 2.30 g/L in the reactor with concentrate and ASL residue, respectively. Zinc to the inoculation differed slightly, and reached 3.15 and 3.50 g/L in the reactor with concentrate and ASL residue, respectively. Iron ion concentrations were comparatively low reactor with concentrate and ASL residue, respectively. Iron ion concentrations were in both reactors, and the fraction of dissolved iron was lower than those of copper and zinc comparatively low in both reactors, and the fraction of dissolved iron was lower than (Figures [2b](#page-5-0) and [3b](#page-6-0)). This may be explained by the fact that the rates of dissolution of the those of copper and zinc (Figures 2b and 3b). This may be explained by the fact that the main iron-containing minerals in the concentrate (pyrite and chalcopyrite) in acid medium are insignificant $[7,11,21,42-45]$ $[7,11,21,42-45]$ $[7,11,21,42-45]$ $[7,11,21,42-45]$ $[7,11,21,42-45]$. during the first 5 days of the leaching before the inoculation (Figures [2c](#page-5-0) and [3c](#page-6-0)). Copper

Inoculation led to a sharp increase in iron ion concentrations (Figures [2b](#page-5-0) and [3b](#page-6-0)), as the activity of iron-oxidizing microorganisms resulted in the destruction of iron-containing minerals. The concentration of ferrous iron ions in the pulp was low, and ferric ions prevailed in the solution, which showed the high oxidation activity of microorganisms. Ine Eh value also increased after inoculation, as this parameter in the solution depends on Fe^{3+}/Fe^{2+} concentration ratio (Figures [2a](#page-5-0) and 3a).

The dynamic of copper and zinc concentration differed between the reactors with concentrate and ASL residue (Figures [2c](#page-5-0) and [3c](#page-6-0)). In the experiment with concentrate, copper concentration gradually increased, and was close to its maximum (1.97 g/L) after 20 days of bioleaching. In the experiment with the ASL residue, the copper concentrate reached its maximum concentration on the 12th day of bioleaching (4.13 g/L) and then decreased to 3.50 g/L. Thus, in the experiment with the ASL residue, the copper leaching rate was significantly higher than in that with concentrate. At the end of batch experiments, the degree of copper leaching reached 36 and 58% in the experiments with concentrate and ASL residue, respectively (Figure [4\)](#page-7-0). In contrast to copper, zinc leaching was more active in the experiment with concentrate and was close to its maximum value after 5 days of bioleaching (5.15 g/L). In the batch experiment with ASL, zinc concentration slightly increased after inoculation and reached maximum after 8 days of bioleaching (4.12 g/L) , but then decreased to 3.51 g/L at the end of the experiment. At the end of the batch experiments, the degree of zinc leaching reached 64 and 44% in the experiments with concentrate and ASL residue, respectively (Figure [4\)](#page-7-0). Thus, the zinc leaching rate in the experiment with the ASL residue was lower than that in the experiment with concentrate. Additionally, zinc concentration in the experiment with ASL did not increase significantly, and the main fraction of zinc was leached before inoculation, while in the experiment with concentrate, the zinc concentration increased by 1.6 times after inoculation.

After the batch experiments, continuous bioleaching with a residence time of 10 days was started. The averaged parameters of the liquid phase of the reactors are shown in Table [3.](#page-8-0) The trends observed in the batch experiments were also revealed in continuous mode. Average copper concentration in the reactor with concentrate was 2.4 lower than that in the reactor with ASL residue, while the average zinc concentration was 1.4 times higher in the reactor with concentrate. In the experiments with concentrate, copper extraction was lower than in the batch mode, while zinc extraction was higher in the continuous mode (Figure [4\)](#page-7-0). In the experiment with ASL residue, copper extraction levels were similar in batch and continuous modes, while zinc extraction in the continuous experiment was higher.

Product	pH	Eh, mV $\frac{1}{2}$	Concentration, g/L			
			$Fe3+$	$Fe2+$	C_{11} ²⁺	$7n^{2+}$
Concentrate			1.07 ± 0.09 849 ± 15 17.50 ± 1.07 0.02 ± 0.05 1.52 ± 0.14 5.67 ± 0.19			
ASL residue			1.12 ± 0.05 854 ± 23 18.33 ± 2.1 0.04 ± 0.10 3.64 ± 0.14 3.96 ± 0.24			

Table 3. Parameters of the liquid phase of the pulp during continuous bioleaching (average value).

3.3. Microbial Population Analysis

The analysis of microbial population composition made it possible to evaluate the effect of the differences in mineral composition of oxidized product (concentrate or ASL residue) and in parameters of the liquid phase on certain various groups of acidophilic microorganisms (Figure [5\)](#page-9-0).

Analysis of the populations formed during batch bioleaching demonstrated that the composition of the formed populations differed from that of the inoculum. Bacteria of the genera *Leptospirillum* and *Acidithiobacillus*, as well as archaea of the genus *Cuniculiplasma*, prevailed in the inoculum. After batch bioleaching, microbial population compositions changed significantly in both experiments. Despite some differences in the microbial populations of the reactors with concentrate and ASL residue were revealed, similar trends were observed in both cases. The abundance of *Acidithiobacillus* decreased to minor values (0.06 and 0.01% in the reactors with concentrate and ASL residue, respectively), while the proportion of the genus *Leptospirillum* decreased, but remained significant (88% in the inoculum, 51 and 44.8% in the reactors with concentrate and ASL residue, respectively). In both reactors, abundance of the genus *Ferroplasma* increased from 0.13% to 38 and 54% in the reactors with concentrate and ASL residue, respectively. In the same time, abundance of the archaea *Cuniculiplasma* decreased in both cases (from 5% to 0.3 and 0.7%). In the reactors with concentrate, uncultivated archaea A-plasma were of the main groups (10%), while in the inoculum and in the reactor with ASL residue, these archaea were not detected.

It should be noted that the total cell number in the batch experiments differed between the reactors, reaching 1.73 and 1.09 \times 10 9 cell/mL in the reactor with concentrate and ASL residue, respectively.

Figure 5. Analysis of microbial populations performing bioleaching under different conditions **Figure 5.** Analysis of microbial populations performing bioleaching under different conditions (proportion of the 16S rRNA gene fragment). (proportion of the 16S rRNA gene fragment).

The shift to continuous mode also led to a change in microbial population The shift to continuous mode also led to a change in microbial population composiorders of magnitude and reached 31 and 20% in the reactor with concentrate and ASL residue, respectively. The abundance of the genus *Leptospirillum* increased (by 59 and 77%, respectively). Thus, in all samples analyzed, bacteria of the genus *Leptospirillum* were predominant. The abundance of the genus *Ferroplasma* in both reactors significantly decreased, while fractions of A-plasma archaea were similar in both reactors (2.5 and 2%, respectively). The abundance of the archaea *Cuniculiplasma* increased in the reactor with concentrate from 0.3 to 1.5% and decreased in the reactor with ASL residue from 0.7 to 0.19%. In the reactor with concentrate, bacteria of the genus *Sulfobacillus* were revealed, but were not detected in other samples.

Subsequence of the genus *Sulform* were not detected in other samples. tions. In both cases, the abundance of the bacteria *Acidithiobacillus* increased by two–three

Average total cell number in the continuous experiments differed in the reactors and
 $\frac{1}{2}$ and $\frac{1}{2}$ reached 1.49 \pm 0.34 and 1.72 \pm 0.32 \times 10⁹ cell/mL in the reactor with concentrate and ASL reciduo respectively. residue, respectively.

Thus, crucial differences between microbial populations on the reactors with concentrate and ASL residue were not revealed, while the shift from batch to continuous mode led to similar changes in the composition of microbial populations. At the same time, some groups, which were presented in the population during continuous bioleaching of the concentrate, were eliminated during continuous bioleaching of ASL residue.

t_{max} groups, which were presented in the population during continuous du bioleaching of the concentrate, were eliminated during continuous bioleaching of ASL **4. Discussion**

The results obtained in this study demonstrated that ASL leaching made it possible to ASL treatment led to a decrease in zinc extraction rate. In experiments with concentrate, zinc
leasting decree wee 1.7.2.7 higher than some maybe tien. Convergely in the summing rate with ASL residue, copper extraction degree was higher than zinc extraction by 10–14%. Copper and zinc extractions reached in the present work were comparable to those obtained in our previous work [35] in continuous bioleaching experiments at different temperatures (40–60 \degree C) with the concentrate similar in mineral and chemical compositions (10–27%) of copper and 41–82% of zinc were leached). The higher zinc extraction in experiments with concentrate is explained by the well-known fact that the sphalerite contained in the increase copper leaching rate both in batch and continuous experiments. At the same time, leaching degree was 1.7–2.7 higher than copper extraction. Conversely, in the experiments

concentrate is more easily leached than chalcopyrite and tennantite containing copper in the studied concentrate [\[7](#page-11-4)[,11](#page-11-5)[,15](#page-11-9)[,21](#page-12-14)[,33](#page-12-4)[,35](#page-12-11)[,42](#page-12-15)[,43\]](#page-12-16). The increase in the degree of copper extraction is explained by the fact that copper sulfides formed during ASL are less refractory to bioleaching that chalcopyrite and tennantite [\[4](#page-11-2)[,15](#page-11-9)[,21,](#page-12-14)[36,](#page-12-6)[42](#page-12-15)[–45\]](#page-13-0).

The decrease in zinc extraction rate cannot be unambiguously explained on the basis of the results obtained, and require further studies on the speciation of different elements in the concentrate and the ASL residue. It should be noted that similar trends were observed in our previous works [\[36,](#page-12-6)[37\]](#page-12-5) on the batch bioleaching of tennantite containing copper–zinc concentrate in flasks and stirred tank reactors. It was determined that ASL treatment led to an increase in copper extraction; but in some cases, zinc extraction was lower than that from untreated concentrate. Thus, the decrease in zinc extraction degree may be due to the interactions of different components of concentrate and pregnant solutions during ASL, for example, precipitation of some components on the surface of sphalerite that led to its passivation.

The decrease in degree of zinc extraction may also be explained by the decrease of the activity of microbial population due to the change in mineral composition of the concentrate during ASL leaching and, in turn, in the composition of the leaching pregnant solution. For example, microbial population could be partially inhibited by higher copper concentrate in reactor pulp. This may be confirmed by the lower rate of iron leaching and cell number in the batch experiment with ASL in comparison to that with concentrate (Figures [2](#page-5-0) and [3\)](#page-6-0).

An analysis of the microbial populations suggested that ASL treatment did not result in crucial changes in population composition, while the shift from batch to continuous mode led to similar changes in abundance of various microbial groups. Significant differences in average total cell number in the continuous experiments were also not observed. In both continuous experiments, the bacterial genera *Acidithiobacillus* and *Leptospirillum* were predominant groups in the populations, and probably played a key role in the bioleaching. At the same time, some groups that were presented in the population during continuous bioleaching of the concentrate were absent in the population during continuous bioleaching of ASL residues.

Bacteria of the genus *Sulfobacillus*, as well as archaea *Ferroplasma*, *Cuniculiplasma*, and A-plasma, were not observed in the population of the reactor in which the ASL residue was bioleached. The difference in the microbial population composition could also be a result of the change in zinc bioleaching rate. Previously, it has been shown that bacteria of the genus *Sulfobacillus* can actively oxidize sulfide minerals in bioleach reactor at a relatively low cell number (10⁷ cells/mL) [\[46\]](#page-13-1). Therefore, the absence of sulfobacilli in the population could lead to a decrease in the rate of sphalerite oxidation.

Thus, it was shown that copper leaching from the concentrate may be improved using ASL pretreatment both in batch and continuous experiments. Despite this, ASL treatment might decrease zinc extraction and, therefore, have a different effect on the leaching of different components. The results obtained should be used in further work on the improvement of treatment for arsenic-containing copper–zinc concentrate, which may be aimed at the development of promising approaches to process this type of product. For example, a possible flowchart may be based on a multistage leaching process, including preliminary zinc bioleaching, ASL, and further copper bioleaching from the product obtained.

5. Conclusions

In the present work, the possibility of using two-stage hydrometallurgical treatment including stages of ASL and bioleaching for the treatment of copper–zinc concentrate with high arsenic content was studied. It was shown that the studied approach may be promising as it made it possible to increase the copper extraction rate in comparison to one-stage bioleaching. ASL was shown to be effective for pretreatment of tennantite containing concentrates to improve oxidative leaching processes for copper extraction including bioleaching. The increase in copper extraction rate using two-stage leaching may allow avoiding the main disadvantage of bioleaching in terms of treatment of studied product, low copper leaching rate. At the same time, the development of combined hydrometallurgical processes including ASL and bioleaching for effective metal leaching requires further studies, as in the present work, ASL led to a decrease in zinc extraction. Modification of the proposed method is needed to address the problem of the decrease in zinc extraction rate.

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