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Selective Leaching of Zinc from Copper-Zinc Concentrate

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Abstract—Biooxidation of copper-zinc concentrate with the use of consortia of mesophilic and moderately thermophilic acidophilic chemolithotrophic microorganisms was studied. Pyrrhotite, sphalerite, and chalcopyrite were the main sulfide minerals of the concentrate. The possibility in principal of complete selective leaching of zinc from sulfide concentrate coupled with minimal recovery of copper (less than 20%) was demonstrated. Selective leaching of zinc could be caused by galvanic interactions between minerals of the concentrate during the biooxidation. The results can be used as the basis for the development of the technologies for production of grade copper concentrate not containing zinc from sulfide copper-zinc concentrate obtained from refractory ores.

Keywords: leaching, acidophilic microorganisms, biohydrometallurgy, nonferrous metals, sulfide concentrate
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INTRODUCTION

The reserves of copper-zinc ores in exploited mineral deposits are being gradually depleted. The delay of exploration of new deposits requires the processing of low-grade and refractory ores. For example, about 70–75% of the resource base of mining and processing combines of the Urals region is represented by refractory ores, which cannot be treated with traditional flotation flowsheets to obtain conditioned concentrates suitable for further metallurgical processing. Collective copper-zinc concentrates can be obtained comparatively easily and cheaply, whereas their further separation is associated with technical difficulties and high financial costs.

The development of methods for the processing of collective copper-zinc sulfide concentrates by bioleaching with acidophilic chemolithotrophic microorganisms is a relevant issue. Biotechnologies for the treatment of sulfide mineral raw materials based on the application of microorganisms for the leaching of nonferrous metals and recovery of noble metals are widespread around the world [1, 2]. They are economically more attractive and have relatively little impact on the environment than traditional pyro- and hydrometallurgical technologies. The technology of biooxidation of sulfide concentrates is based on destruction of the crystal lattice of sulfide minerals due to oxidation by acidophilic chemolithotrophic microorganisms. The chemistry of the processes of biooxidation of sulfide minerals can be expressed by the following equations:

$$\mathrm{MeS} + 2\mathrm{Fe}^{3+} = \mathrm{S}^0 + \mathrm{Me}^{2+} + 2\mathrm{Fe}^{2+}, \qquad (1)$$

$$4\mathrm{Fe}^{2+} + 4\mathrm{H}^+ + \mathrm{O}_2 = 4\mathrm{Fe}^{3+} + 2\mathrm{H}_2\mathrm{O}, \qquad (2)$$

$$2\mathrm{S}^0 + 2\mathrm{H}_2\mathrm{O} + 3\mathrm{O}_2 = 2\mathrm{H}_2\mathrm{SO}_4, \qquad (3)$$

where Me is metal.

Reactions (2) and (3) provide regeneration of the active oxidant, ferric sulfate, for leaching in sulfuric acid media, which destructs the lattice of sulfide minerals according to equation (1).

The selective oxidation of ore minerals in collective concentrates is a promising method for their processing. Positive results in this field can make it possible to produce conditioned sulfide monoconcentrates of nonferrous metals, which can be processed by traditional metallurgical methods. This approach for treatment of collective sulfide minerals can simplify ore-dressing flowsheets and prevent losses of nonferrous metals with the wastes of concentration and metallurgy.

The goal of the present work was to study biooxidation of collective sulfide concentrate with the use of consortia of chemolithotrophic acidophilic microorganisms and to reveal the possibility of selective zinc leaching.

MATERIALS AND METHODS

Sulfide concentrate. Collective copper-zinc concentrate produced under industrial conditions from sulfide ore of Tarnier deposit (Russia) on the mining and processing combine was the object of the study. Sulfide minerals chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and pyrrhotite (FeS) were the main ore minerals. The chemical composition of the concentrate was revealed at the N.M. Fedorovsky All-Russia Scientific Research Institute of Mineral Resources (Russia). The total content of sulfur and sulfur of soluble sulfates was revealed by gravimetric method with a BP-221S analytical balance (Sartorius, Russia-Germany). The contents of copper, zinc, and iron were determined on an AAnalyst-800 atomic absorption spectrophotometer (Perkin Elmer, United States). The calcium content was determined by the titrimetric method, and the silicon content was determined by a KFK-3 photometer (Russia). The concentrate contained the following (%): copper—10.1, zinc—7.36, iron—36.1, total sulfur—34.5, sulfur of soluble sulfates—1.78, silicon—0.83, calcium—<0.1.

Bioleaching. The experiments were performed in 250 mL conical flasks with 100 mL of the suspension in a thermostated rotary shaker at 170 rpm. The flasks contained the required amount of copper-zinc concentrate, 90 mL of 9K medium diluted five times [3] and supplemented with ferrous sulfate (up to Fe^{2+} concentration of 8.5 g/L), and 10 mL of the inoculum. The initial pH value was adjusted to 1.6 by the addition of 98.5% sulfuric acid.

Microorganism cultures. To perform the experiments, two consortia of acidophilic chemolithotrophic microorganisms were developed. The first consortium was mesophilic (30°C) and consisted of bacteria *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, and *Leptospirillum* spp. isolated from the deposits of pyritic flotation wastes of Svyatogor and Gaisky mining and processing combines situated in the Urals region. The second association was moderately thermophilic (38°C) and consisted of bacteria *Leptospirillum* spp., *Sulfobacillus* spp., *Acidithiobacillus caldus,* and archaea *Ferroplasma acidiphilum* isolated from sulfide concentrates of the Olimpiada deposit (Russia), as well as the Kokpatas and Daugiztau deposits (Uzbekistan). The consortia were used as inoculum to reveal the parameters of bioleaching (biooxidation) of the concentrate.

Analytical methods. The pH values were measured with a 150MA pH meter (Measurement technology, Russia). The concentrations of Fe^{3+} and Fe^{2+} in the liquid were determined by the colorimetric method with potassium thiocyanate [4] with a KFK-3 photometer (Russia) at a wavelength of 475 nm. The concentrations of copper and zinc ions were measured with a Perkin Elmer 3100 atomic-absorption spectrometer (Perkin Elmer, United States) with flame atomization.

RESULTS AND DISCUSSION

Based on the data on mineral composition of the studied collective refractory sulfide copper-zinc concentrate, it could be concluded that biooxidation by acidophilic chemolithotrophic microorganisms should result in the destruction of pyrrhotite (FeS), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$). The oxidation of sphalerite and chalcopyrite can be expressed by the following equations:

$$ZnS + 2Fe^{3+} = Zn^{2+} + S^0 + 2Fe^{2+}, \quad (4)$$

$$CuFeS_2 + 4Fe^{3+} = Cu^{2+} + 2S^0 + 5Fe^{2+}. \quad (5)$$

It is known that the oxidation kinetic of chalcopyrite and sphalerite in sulfuric acid solutions containing ferric iron are fundamentally different. The lattice energy of chalcopyrite is larger, and its oxidation is accompanied by the formation of passivating layers on a mineral surface consisting of products of the reactions including elemental sulfur, hydrated iron oxides, and secondary copper sulfides [5]. This leads to a high refractoriness of chalcopyrite to biooxidation in sulfuric acid solutions containing ferric iron.

The redox potential of the media in microbial processes of biooxidation usually reaches high values due to the predominance of ferric ions in medium and low concentrations of ferrous ions caused by high activity of iron-oxidizing microorganisms if any special methods to change the redox potential of the medium are not used. Furthermore, it is known that chalcopyrite oxidation is the most intensive at relatively low values of the redox (up to 450 mV) due to the reduction passivating layers formation [6, 7], whereas sphalerite destruction is intensified if oxidant concentration increases, i.e., when the redox of the medium increases [8].

The oxidation of multicomponent raw materials, as well as mixtures of minerals, is accompanied by galvanic interactions between the minerals that form a galvanic couple with the dissolving anode. For example, Galvanox® [9] and Geocoat® [10] processes for copper recovery are based on intensification of chalcopyrite oxidation by means of pyrite addition, which causes galvanic interactions between the minerals. According to the results of several studies, during the leaching of collective copper-zinc concentrates containing chalcopyrite, sphalerite, and pyrite in sulfuric acid solutions containing ferric iron, zinc is extracted in the solution more intensively than copper. At the same time, copper recovery in pregnant solution was comparatively high (up to 40%), which can be explained by galvanic interactions between chalcopyrite and pyrite [11, 12].

Analysis of the mineral composition of the studied copper-zinc concentrate revealed that, in galvanic interaction between sulfide minerals (chalcopyrite, sphalerite, and pyrrhotite) during biooxidation, chalcopyrite possessing the highest electrode potential should act as a cathode, whereas sphalerite and pyr-

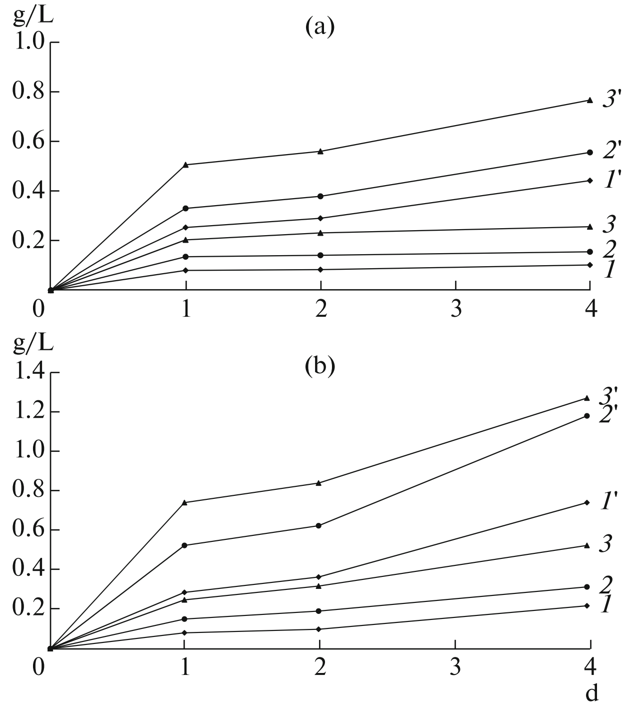

Fig. 1. Changes in the concentrations of copper (1, 2, 3) and zinc (1', 2', 3') during bioleaching of the concentrate by mesophilic (a) and moderately thermophilic (b) consortia at solid phase contents (%) 1 (1, 1'), 2 (2, 2'), and 3 (3, 3').

rhotite possessing a low electrode potential should act as dissolving anode [13, 14].

Considering the above, it can be concluded that sphalerite should be oxidized intensively during the biooxidation of the studied copper-zinc concentrate in sulfuric acid solutions containing ferric iron with acidophilic chemolithotrophic microorganisms, whereas chalcopyrite should be oxidized insignificantly.

It was supposed that the biooxidation of collective sulfide concentrate could make it possible to extract zinc in the liquid phase and obtain copper concentrate not containing zinc. It can allow the prevention of zinc losses with the slags during metallurgical processing of copper concentrates. Zinc and copper can be extracted from liquid phase as commercial products with the use of known hydrometallurgical approaches.

Biooxidation (bioleaching) of the copper-zinc concentrate was performed at different solid phase contents: 1, 2, and 3%. The changes in the concentration of nonferrous metals during bioleaching of the copper-zinc concentrate by the mesophilic consortium are shown in Fig. 1a; the changes in the Fe^{2+} and Fe^{3+} ions concentrations are shown on Fig. 2a.

Figure 1 demonstrates that the concentrations of nonferrous metals in the liquid phase depended on the duration of biooxidation and gradually increased. At the same time, the zinc concentrations were two to three times higher than the copper concentrations. An increase in the solid phase content did not always lead to a directly proportional increase in the concentration of nonferrous metals.

Analysis of the presented data revealed that rate of sphalerite bioleaching occurring according to Eq. (4) was higher than that of chalcopyrite bioleaching (5). This suggested that zinc could be removed from the copper-zinc concentrate.

The data on the behavior of iron cations during the bioleaching of the copper-zinc concentrate demonstrated that leaching of nonferrous metals was accompanied by biooxidation of Fe^{2+} to Fe^{3+}. Moreover, a decrease in the solid phase content resulted in an increase in the rate of Fe^{2+} oxidation and Fe^{3+} concertation. This suggested that the rate of biooxidation of Fe^{2+} ions (Eq. (2)) at a low solid phase content was higher than the oxidation of sulfide minerals (Eq. (1)) accompanied by reduction of Fe^{3+} to Fe^{2+}.

The changes in the concentration of nonferrous metals during bioleaching of the copper–zinc concentrate with a moderately thermophilic consortium are shown in Fig. 1b; the changes in the concentration of Fe^{2+} and Fe^{3+} ions are shown in Fig. 2b. Comparison of the behavior of nonferrous metals during bioleaching revealed that the concentrations of nonferrous metal in the liquid phase were of 1.5 to 2 times higher in experiments with moderately thermophilic consortium than those in te experiments with the mesophilic consortium. The zinc concentrations in the liquid phase were two to three times higher than the copper concentrations in experiments with both mesophilic and moderately thermophiic consortia.

The data on the behavior of iron cations during the bioleaching of the copper–zinc concentrate with moderately thermophilic consortium demonstrated that ferrous iron was not completely oxidized. As in the experiments with the mesophilic microbial consortium, a decrease in solid phase content led to a more rapid decrease in Fe^{2+} ions concentration and increase in Fe^{3+} ions concentration. During bioleaching with the moderately thermophilic consortium, the divalent ferrous iron concentrations were higher and the trivalent ferric iron concentrations were lower than those in the experiments with mesophilic consortium at all studied solid phase contents. This suggested that reactions (4) and (5) resulted in reduction of Fe^{3+} to Fe^{2+} and the destruction of the crystal lattice of sphalerite and chalcopyrite occurred more rapidly at a higher temperature, which resulted in a more rapid accumulation of nonferrous metals in the solutions during bioleaching of the concentrate. At the same time, the biooxidation of Fe^{2+} to Fe^{3+} by the moderately thermophilic consortium according to Eq. (2) provided a Fe^{3+} ions concentration sufficient to oxidize sulfide minerals according to the reaction (1).

It should be noted that concentrations of nonferrous metals monotonically increased in 4 days of bioleaching and did not reach the maximum in either of the experiments. Thus, it was required to reveal the possibility of maximal zinc removal by means of an increase in the duration of the biooxidation. The results, which demonstrate an accumulation of nonferrous metals over 11 days of bioleaching of the copper-zinc concentrate, are shown in table.

Analysis of the behavior of zinc ions during bioleaching (table) at a solid phase content of 1% revealed that the maximal zinc concentration was reached after 7 days of bioleaching at 30°C and after 4 days at 38°C. At a solid phase content of 2%, the zinc was almost completely leached after 9 days of bioleaching with the mesophilic consortium and after 7 days of bioleaching with the moderately thermophilic. When the solid phase content was 3%, the zinc concentrations in all experiments were maximal after 11 days of bioleaching. At the same time, the concentration of copper ions in the liquid phase monotonically increased and reached the maximum after 11 days of bioleaching (at the end of the experiments). In all experiments the concentrations of nonferrous metals were higher in the variants with the moderately thermophilic consortium and most of the zinc was removed from the concentrate after 9 days of bioleaching at the maximal solid phase content.

It should be noted that the copper content in the copper–zinc concentrate was 1.5 times higher than the zinc content. Therefore, zinc could be completely removed from the copper concentrate, which should lead to an increased copper content in the studied product. To confirm this possibility, the recovery rates of the metals in the liquid phase after 4, 7, and 9 days of bioleaching were calculated. The results are shown in Fig. 3.

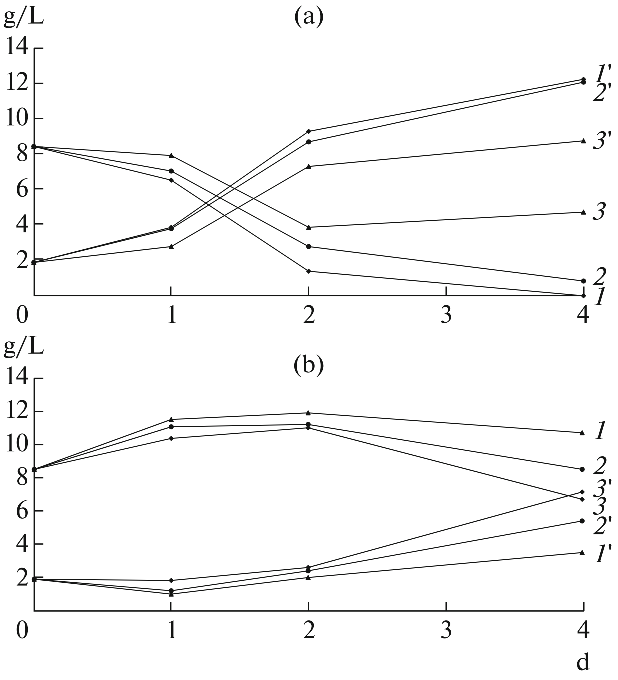

Fig. 2. Changes in the concentrations of ferrous (1, 2, 3) and ferric (1', 2', 3') iron during bioleaching of the concentrate by mesophilic (a) and moderately thermophilic (b) consortia at solid phase contents (%) 1 (1, 1'), 2 (2, 2'), and 3 (3, 3').

It was revealed (Fig. 3a) that 100% of zinc was leached by moderately thermophilic association after 4 days of bioleaching at a solid phase content of 1%, whereas the rate of copper leaching was 21.5%. Thus, the amount of zinc leached in the solution was about five times higher than the amount of copper. This demonstrated the high selectivity of zinc leaching. The rate of zinc and copper recovery was 74.3% and 12.6%, respectively, during bioleaching by the meso-

Changes in the concentrations of copper and zinc during bioleaching of the copper–zinc concentrate by mesophilic and moderately thermophilic consortia

Temperature, °C	Duration of leaching, days	Cu^{2+}, g/L			Zn^{2+}, g/L		
		solid phase content, %					
		1	2	3	1	2	3
30	4	0.127	0.220	0.270	0.55	0.979	1.18
	7	0.144	0.253	0.322	0.74	1.34	1.74
	9	0.157	0.272	0.344	0.74	1.40	1.86
	11	0.171	0.287	0.368	0.75	1.42	1.96
38	4	0.22	0.330	0.450	0.75	1.20	1.50
	7	0.256	0.370	0.510	0.75	1.46	1.80
	9	0.280	0.410	0.550	0.75	1.49	1.95
	11	0.310	0.450	0.620	0.75	1.50	2.10

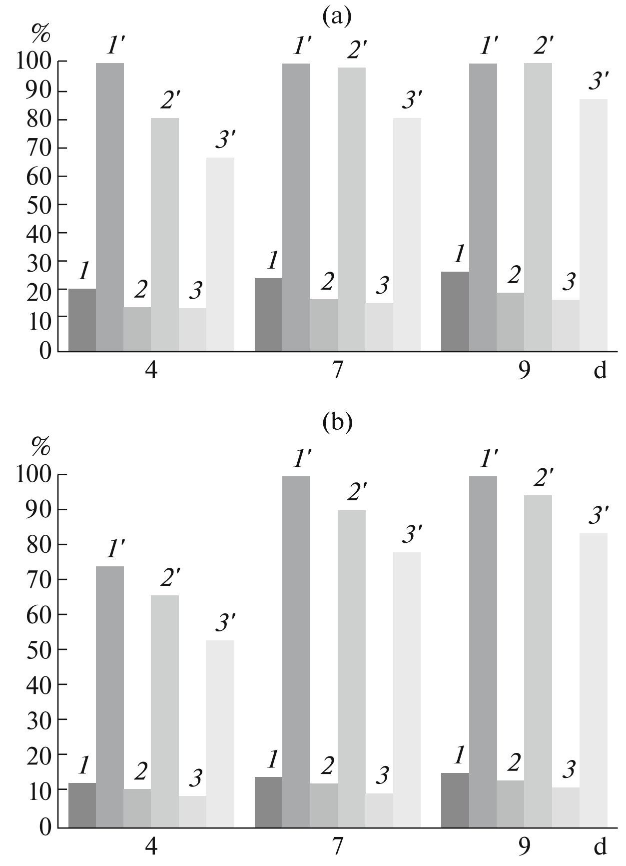

Fig. 3. Recovery of copper (1, 2, 3) and zinc (1', 2', 3') during bioleaching of the concentrate by moderately thermophilic (a) and mesophilic (b) consortia at solid phase contents (%) 1 (1, 1'), 2 (2, 2'), and 3 (3, 3').

philic microbial consortium under the same conditions (Fig. 3b). Complete zinc recovery was reached after 7 days of bioleaching.

At higher solid phase contents (2 and 3%), the zinc was almost completely leached after 9 days of bioleaching by the moderately thermophilic consortium, whereas the copper recovery rates were 18.2 to 20.3%. Bioleaching by the mesophilic consortium under the same conditions made it possible to recover 94.6 and 83.8% of the zinc and 13.4 and 11.4% of the copper.

Thus, the results of the present work demonstrated that the moderately thermophilic consortium leached copper and zinc more actively; however, the biooxidation of the concentrate by the mesophilic microbial consortium provided higher selectivity of zinc leaching in comparison to copper.

Based on the data presented in Table, the rates of zinc and copper leaching at maximal solid phase content were calculated on the condition of complete removal of zinc from the concentrate. Complete leaching of zinc was reached after 9 days of the biooxidation by the mesophilic consortium, and the average rates of zinc and copper recovery were 206 and 38.2 mg/L day, respectively. At the same time, the zinc was completely recovered from the concentrate after 7 days of the bioleaching and the average rate of zinc and copper leaching was 257 and 72.8 mg/L day.

Thus, the possibility in principle of the complete removal of zinc from the collective copper-zinc sulfide concentrate during bioleaching by mesophilic and moderately thermophilic microbial consortia was demonstrated. The results on selective leaching of zinc made it possible to propose new approaches to the processing of refractory collective sulfide concentrates.

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