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Hydrometallurgy



Two-stage bacterial-chemical oxidation of refractory gold-bearing sulfidic concentrates

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ABSTRACT

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produced Fe³⁺ solution was investigated. During the chemical stage, the most easily oxidized sulfidic elements were shown to be removed from the concentrates. After chemical leaching of the arsenopyrite concentrate, the oxidation levels for sulfidic iron and arsenic were 64.3% and 31.1%, respectively; for the pyrite concentrate, the oxidation levels of sulfidic iron and sulfur were 21.2 and 25.8%, respectively. Biooxidation of the arsenopyrite and pyrite gold-bearing concentrates has been carried out in the onestage (control) and two-stage (experimental) variants in reactors in feed batch mode. An activity of biooxidation of sulphidic concentrates without preliminary oxidation by Fe³⁺ solution (one-stage process) during the control experiments and after preliminary oxidation of Fe³⁺ solution (two-stage process) in experimental variants was studied. At 4 days residence time, the oxidation level for sulfidic arsenic from the arsenopyrite concentrate was 38.4% in the control process and 92.8% in the experimental one; gold recovery by cyanidation was 67.76% and 92.95%, respectively. At 8 days residence time, the results of the control process were lower, than of experimental process after 4 days of oxidation: the oxidation level of sulfidic arsenic was 59.7%; gold recovery was 82.38%. In the control variant, the time of biooxidation of the pyrite concentrate was 36 days; in the experimental variant, it was 5 days. The oxidation levels for sulfidic iron and sulfur were 40.3 and 55.7%, respectively; gold recovery by cyanidation was 76.9%. The results obtained demonstrate that two-stage bacterial-chemical processes are promising for intensification of the biohydrometallurgical processing of refractory sulfidic concentrates containing not only nonferrous metals, but noble metals as well.

The chemical oxidation of the arsenopyrite and pyrite gold-bearing concentrates with the microbially-

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1. Introduction

Intensification of biological oxidation of sulfidic minerals is essential for development of hydrometallurgy. To achieve this goal, both search for new promising microbial communities (Yahya and Johnson, 2002), and development of new technological approaches are required.

One of approaches to intensified leaching of non-ferrous metals involves oxidation of sulfidic minerals (MS) by Fe^{3+} ions under acidic conditions with iron reduction to Fe^{2+} according to reaction (1). Microorganisms carry out Fe^{2+} oxidation to Fe^{3+} according to reaction (2) in a separate stage.

$$MS + 2Fe^{3+} = M^{2+} + S^0 + 2Fe^{2+}$$
(1)

$$4Fe^{2+} + 4H^{+} + O_2 = 4Fe^{3+} + 2H_2O$$
(2)

The BRISA technology was proposed for copper recovery from sulfides (Carranza et al., 1997). The BRISA technology is based two-stage treatment of copper concentrates including (a) chemical leaching at elevated temperature according to reaction (1) and (b) regeneration of the oxidizer by a bacterial culture (*Acidithiobacillus ferrooxidans*) according to reaction (2). The technology has been tested on the concentrates of secondary copper sulfides (covellite and chalcocite) (Palencia et al., 2002), as well as for chalcopyrite (Romero et al., 2003). After 8–10 h, over 90% copper recovery was achieved.

The Rio Tinto Research and Technology development company has carried out trials on leaching of copper ores in Australia (Smalley and Davis, 2000). The plant for high-temperature (85 °C) leaching at atmospheric pressure with ferric iron sulfate (at 20 g/L Fe³⁺) was developed for the ores containing mostly chalcocite (73.4%) and bornite (15.6%). Copper content in the ore varied from 5.9 to 7.4%, the average pulp density was maintained at 30%. The plant produced about 40 kg of cathode copper per day. After 24 h, 93% of copper was recovered, with 86% leached during the first 6 h. The leaching solution was regenerated in a specialized block; the mixed bacterial culture used for the purpose was adapted to acidic conditions and high levels of copper (up to 10 g/L) and iron ions (up to 20 g/L). The rate of iron oxidation was 0.55 g Fe²⁺/L h.





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This technology, however, did not involve the capacity of bacteria used to oxidize, apart from iron (reaction (2)), also elemental sulfur according to the following reaction:

$$2S^{0} + 3O_{2} + 2H_{2}O = 2H_{2}SO_{4}$$
(3)

Consumption of sulfuric acid was therefore high, 40 kg per ton of processed ore.

We proposed a new variant of two-stage bacterial leaching of copper-zinc concentrate containing 15.25% zinc as sphalerite and 1.5% copper as chalcopyrite (Fomchenko et al., 2006; Fomchenko and Biryukov, 2009).

The leaching was carried out in a continuous mode. At the first stage, the solid phase was chemically leached with the ferric iron solution ($\sim 10 \text{ g/L}$) at 70 °C and pulp density of 33%. The suspension was then transferred to the sludge thickener where the solid phase was separated into the coarse and fine fractions. The former was returned for chemical leaching, while the latter was used in the second stage of oxidation by a mesophilic or thermophilic microbial association. In this technological setup, reaction (1) was carried out in a chemical reactor, while reactions (2) and (3) occurred in a bioreactor. Both chemical oxidation (at the first stage) and microbiological oxidation (at the second stage) occurred therefore under the optimal conditions. The process involved continuous liquid recirculation between the first and second stages. After 24 h of leaching, 91.5 and 77.3% recovery levels were achieved for zinc and copper, respectively. The traditional one-stage process on the same raw material took 120 h.

For a two-stage process, a moderately thermophilic microbial association may be used. We have previously proposed a two-stage bacterial-chemical technology for leaching copper from copper concentrates involving moderately thermophilic chemolithotrophic microorganisms (Fomchenko et al., 2007). Leaching of the rich copper concentrate containing 27.0% copper, mainly as covellite and chalcocite, 91% of copper was dissolved after 20 h. The residue obtained after the chemical stage contained 7.7% copper, while copper content in the residue of the second stage (from the bioreactor) was only 2.1%. These results demonstrated that the concentrate obtained after chemical leaching was efficiently leached at the following, biological stage.

Thus, the separation of the chemical and biological stages resulted in significantly intensified leaching of nonferrous metal from sulfidic raw material. However, two-stage bacterial–chemical oxidation has not been used for gold recovery from sulfidic raw materials.

Presently, biotechnologies for gold recovery from sulfidic refractory ores attract much attention (Brierley, 2007). Biotechnologies may be applied even to high-arsenic gold-bearing concentrates. High levels of oxidation and recovery of sulfidic minerals is achieved; the subsequent sorption cyanidation results in recovery of up to 98% of fine-dispersed gold, much higher than the levels of recovery by direct cyanidation or pyrometallurgical mode (Abbruzzese et al., 1994).

BIOX[®] (Dew et al., 1997) is the most widespread technology for biological oxidation in the reactors of arsenopyrite-pyrite goldbearing concentrates. Intensification of the processes of biological oxidation of sulfidic concentrates is an important issue, since the average duration of the oxidation process under industrial conditions is 4 to 6 days (Rawlings et al., 2003).

There were attempts to replace biooxidation of refractory sulphidic gold-bearing concentrates with chemical oxidation by ozone and Fe^{3+} solution in sulfuric medium (Li et al., 2009). Despite good results on gold extraction by cyanidation (96.5%), the given way is very complicated and expensive.

The goal of the present work was to investigate the processes of chemical oxidation of arsenopyrite and pyrite concentrates and biological oxidation with and without preliminary oxidation by Fe^{3+}

ions, as well as to develop the approaches to intensification of biooxidation technologies and enhanced gold recovery.

2. Materials and methods

2.1. Sulfidic concentrates

Two types of gold-bearing sulfidic concentrates were used in the present work. The first one was the industrial arsenopyrite flotation concentrate obtained from the ore of the Olympiadinskoe deposit (Russia). The 80% class fineness was 0.044 mm, the total content of iron sulfide (pyrrhotite) and arsenic sulfide (arsenopyrite) was up to 75%. Quartz and carbonate were the major nonmetallic minerals. The second type was the pyrite concentrate obtained under laboratory conditions from the ore of the Samolazovskoe deposit (Russia). The content of iron sulfide (pyrite) was about 30%; gold content was 22.77 g/t. The chemical composition of the concentrates is presented in Table 1. Only main elements are presented as compounds of the concentrates.

2.2. Microbial cultures

The microbial association predominant in the process of biological oxidation in the industrial bioreactors of the Polyus Gold factory was used for biooxidation experiments and for generation of ferric iron for subsequent chemical leaching experiments. The association included strains of various *Sulfobacillus* species, bacteria of the genus *Leptospirillum*, and archaeal strains of *Ferroplasma acidiphilum* (Sovmen et al., 2008).

2.3. Generation of the ferric iron

Ferrous iron biooxidation was carried out in 5.0-L vessel with 4 L of the liquid at temperature of 39 °C and aeration 4 min^{-1} . Liquid contained 9 K medium (Silverman and Lundgren, 1959) supplemented with 0.02% (w/v) of yeast extract and 10% (v/v) inoculum. The initial pH of the medium was adjusted to 1.5 with 98.5% H₂SO₄. The pH and concentration of ferrous and ferric iron were monitored twice a day. The pH values were maintained in the range from 1.5 to 1.8 with addition of sulfuric acid (98.5%) when necessary. FeSO₄·7H₂O was added in liquid when ferrous iron was oxidized. The final Fe³⁺ concentration was 20–30 g/L. This liquid was used for lixiviation during chemical leaching experiments.

2.4. Chemical leaching experiments

Before chemical oxidation or biooxidation the concentrates were treated with diluted sulfuric acid in 2-L reactor (440 rpm) during 20 h and dried overnight at 60 °C. The pH of the pulp was monitored continuously and 98.5% H_2SO_4 was added when necessary to maintain its values in the range from 1.5 to 1.6. The pulp density was 17% (w/v). This operation was used to remove carbonates from the concentrates.

Chemical leaching was carried out in a 2.0-L reactor containing 1 L of the pulp. The stirring speed was 440 rpm. The temperature was maintained by means of heat exchangers connected to a thermostat. Experiments were carried out at 50, 65 and 80 $^{\circ}$ C.

Table 1					
Analytical	data	for	the	concentrates.	

Element	Arsenopyrite concentrate	Pyrite concentrate
Fe (wt.%)	27.0	15.06
As (wt.%)	8.21	-
Sb (wt.%)	5.59	-
S _s (wt.%)	20.32	14.89
S ⁰ (wt.%)	n.d.	0.25
Au (g/t)	108	22.77

n.d.-not detected.

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