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Two-step oxidation of a refractory gold-bearing sulfidic concentrate and the effect of organic nutrients on its biooxidation

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ABSTRACT

Methods for improving the treatment efficiency of a refractory gold-bearing sulfidic concentrate are proposed. These methods consist of the oxidation of the concentrate during a two-step process, which includes a high temperature ferric leaching step and a subsequent biooxidation step, and the use of organic nutrients during the biooxidation step. The concentrate contained 34.7% pyrite and 7.9% arsenopyrite. The biooxidation of the concentrate (for a one-step process) was conducted at 45 °C in two bioreactors that were connected in series under continuous conditions. The pyrite and arsenopyrite oxidation levels after 240 h were 60.2% and 92.0%, and the gold recovery level by carbon-in-pulp cyanidation was 65.7%. The two-step process included the leaching of the concentrate by a biologically generated Fe^{3+}-containing solution and the subsequent biooxidation of the leach residue. In this case, the pyrite and arsenopyrite oxidation levels after 240 h of biooxidation were 65.7% and 94.1%, and the gold recovery level was 71.7%.

The effect of an organic nutrient (yeast extract) on biooxidation during the two-step process was studied. The pyrite and arsenopyrite oxidation levels after 240 h of biooxidation under mixotrophic conditions were 73.5% and 95.1%, and the gold recovery level was 77.9%. The effect of the organic nutrient on the microbial population was determined. *Sulfobacillus thermosulfidooxidans* and *Acidithiobacillus caldus* were the predominant microorganisms studied under both autotrophic and mixotrophic conditions. Archaeon *Acidiplasma* sp. MBA-1 was a minor component of the microbial community under autotrophic conditions but was one of the predominant microorganisms studied under mixotrophic conditions. These results suggest that the organic nutrient changed the composition and increased the activity of the microbial population.

Thus, a two-step process with organic nutrients added during biooxidation may be considered as an effective strategy for treating refractory pyrite–arsenopyrite concentrates.

1. Introduction

Enhanced biooxidation of sulfidic minerals is essential for the development of biohydrometallurgy. To achieve this intensification, a two-step process for treating gold-bearing sulfidic concentrates was proposed by Fomchenko et al. (2010). During the first step, metals are leached by a microbially produced ferric sulfate. The solid phase content may be significantly higher than that in traditional biohydrometallurgical technology, and the process temperature may be as high as 80 °C, which would significantly increase the process rate. During the second step, ferric iron is regenerated, elemental sulfur is oxidized, and sulfides are terminally oxidized. Depending on the temperature of the first step, regeneration is conducted by different communities of acidophilic, chemolithotrophic microorganisms. The separation of the chemical and biological steps of the process enables the creation of favorable conditions for mineral oxidation chemical processes and microbial activity.

The solubilization of metals by acidophilic, chemolithotrophic microorganisms is widely and successfully used in the industrial process of bioleaching or biomining to extract noble and nonferrous metals. Acidophilic microorganisms that are able to oxidize sulfidic minerals are phylogenetically heterogeneous and include representatives of several bacterial and archaeal phyla, such as mesophilic (*Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans*), thermotolerant (*Leptospirillum ferriphilum*, *Ferroplasma acidiphilum*, *Acidiferrobacter thiooxydans*), and moderately thermophilic species (*At. caldus*, *Sulfobacillus* spp., *Acidimicrobium* spp., and *Acidiplasma* spp.). Because the oxidation reactions of sulfidic minerals are exothermic, the most promising technological process temperature is 40–55 °C (Rawlings, 2011). Moderate thermophiles predominate under these conditions (Okibe et al., 2003; Dopson and Lindstrom, 2004; Hawkes et al., 2006; Cleaver et al., 2007; Bryan

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et al., 2011; Spolaore et al., 2011; Bulaev et al., 2011, 2012; van Hille et al., 2011). It is known that most moderately thermophilic acidophilic microorganisms that oxidize metal sulfide (*Sulfobacillus* spp., *Acidimicrobium* spp., and *Acidiplasma* spp.) are mixotrophic, i.e., they use both organic nutrients and CO_2 as carbon sources (Johnson and Hallberg, 2009). The enzyme systems that are used for CO_2 fixation cannot satisfy the metabolic requirements of these microorganisms under normal conditions; thus, aeration using CO_2-enriched air or the addition of organic compounds is necessary for the stable growth of these microorganisms.

Dissolved organic carbon (DOC) was shown to accumulate at high concentrations (100 mg/L) in cultures of autotrophic, acidophilic microorganisms (Okibe et al., 2003). These exometabolites could stimulate the growth of heterotrophic and mixotrophic acidophiles (Norris et al., 1980). For instance, archaea *Fp. acidiphilum* were able to grow in spent *At. caldus* cell-free media (Nancucheo and Johnson, 2010).

Okibe et al. (2003) investigated the numerical abundance of microorganisms in three inline stirred tanks, in which a polymetallic sulfidic concentrate was subjected to biooxidation at 45 °C. It was shown that the relative numbers of mixotrophic prokaryotes in the pulps of the reactors varied as a function of the DOC concentration. Autotrophic microorganisms (*At. caldus*, *L. ferriphilum*) were predominant in the first of the three inline reactors, while mixotrophic microorganisms (*Sb. acidophilus*, *Fp. acidiphilum*) were dominant in the third reactor because the DOC concentration was higher in the pulp of the last reactor.

The effects of organic nutrients on chalcopyrite bioleaching for different temperatures were investigated by Li et al. (2011). The addition of yeast extract (YE) to the nutrient media enhanced the bioleaching rate and the proportion of mixotrophic microorganisms for temperatures from 40 to 60 °C, which are optimal for moderate thermophiles.

The goals of this work were to study approaches for improving the biooxidation process of a refractory gold-bearing sulfidic concentrate (including preliminary high-temperature ferric leaching and the addition of organic nutrients to the media) and to determine the change in the composition of the microbial population due to organic nutrients during a two-step process.

2. Materials and methods

2.1. Concentrate

A pyrite–arsenopyrite flotation concentrate was used in this work as the gold-bearing sulfidic concentrate. The chemical and mineralogical compositions of the concentrate are presented in Tables 1 and 2, respectively. It can be observed that over 90% of the iron was present as sulfides. Quartz and silica–alumina minerals were the main nonmetallic minerals, and the organic carbon content was insignificant. The P_{80} was −0.074 mm, and the total sulfidic mineral content was up to 43%.

2.2. Generation of ferric iron and the ferric leaching of the concentrate

A mesophilic microbial consortium containing *At. ferrooxidans*, *L. ferrooxidans, Sb. thermotolerans*, and the enrichment culture obtained from the copper–zinc flotation waste of the Uchalinskoe deposit were used as an inoculum to obtain a ferric iron-containing culture liquid for the subsequent ferric leaching of the concentrate. The biooxidation of ferrous iron ($FeSO_4{\cdot}7H_2O$) was conducted in a 5.0 L vessel that contained 4.0 L of the liquid held at 30 °C with an aeration rate of 4 min^{-1}. The liquid phase consisted of a 9 K media (Silverman and Lundgren, 1959) and 10% (v/v) inoculum. The final Fe^{3+} concentration was 34.2 g/L with pH 1.5. This liquid (the microbial cells were not separated) was used as a lixiviant for the ferric leaching.

Ferric leaching was conducted in a 2.0 L reactor that contained1.0 L of pulp. The stirring rate was 760 rpm, and the temperature was maintained at 80 °C by heat exchangers connected to a thermostat. The leaching was conducted under batch conditions. The solid phase was loaded and mixed with the biologically generated Fe^{3+}-containing solution; tests were conducted at a pulp density of 20% (w/w). The liquid was preheated to the desired temperature with an initial pH 1.15. The solid phase that was obtained after 7 h of ferric leaching was used for subsequent biooxidation experiments.

2.3. Biooxidation experiments

The investigation of the biooxidation of the concentrate was conducted using three series of experiments: (a) a one-step process that had no source of additional organic nutrients in the media, (b) a two-step process that had no source of additional organic matter in the media and (c) a two-step process that included the addition of yeast extract (0.02%). Experiments on the biooxidation of the concentrate were conducted in two reactors that were connected in series under continuous conditions with periodic feeding and with effluent removal. Biooxidation was conducted in 2.0 L reactors that contained 1 L of pulp. A salt solution of the 9 K media without Fe^{2+} was used as the liquid phase. A moderately thermophilic microbial consortium containing *At. caldus* INMI-10, *Sb. thermosulfidooxidans* strains HT-4 and HT-1, and the indigenous culture obtained from the concentrate were used as an inoculum for the biooxidation experiments. The pulp density was maintained at 20% (w/v). The total residence time of the pulp in the two reactors was 10 days. The experiments were conducted at 45 °C with an aeration of 4 min^{-1} and a stirring speed of 520 rpm. The pH of the pulp was continuously monitored, and $Ca(OH)_2$ was added when necessary to maintain the pH value in the range from 1.3 to 1.6.

2.4. Characterization of the microbial consortium

2.4.1. Isolation of pure microbial cultures and cultivation conditions

Pure cultures of autotrophic and mixotrophic microorganisms were obtained by inoculating selective media with terminal 10-fold dilutions of the pulp liquid phase at 45 °C. The modified media 9 K with ferrous sulfate (Melamud and Pivovarova, 1998) and the same media supplemented with 0.02% YE were used to isolate the autotrophic and mixotrophic ferrous iron-oxidizing microorganisms, respectively. The media with the same mineral composition that had elemental sulfur (10 g/L) as an energy source and this same media supplemented with 0.02% YE were used to isolate the autotrophic and mixotrophic sulfur-oxidizing microorganisms, respectively. Cultivation was conducted in 250 mL Erlenmeyer flasks that contained 100 mL of the media and 10 mL of the inoculums using a rotary shaker (170 rpm).

Table 1
Chemical composition of the concentrate.

Element	Fe_{tot}	Fe_s	As	S_{tot}	S^0	S_s	Ca	Mg	Sb	C_{tot}	C_{org}	Cu	Zn	Ni	Au	Ag
Content (wt.%)	20.7	18.9	3.63	21.8	0	21.1	1.42	1.58	0.56	2.29	1.37	0.038	0.041	0.027	23.8 g/t	26.0 g/t

The index S indicates the content of the element in sulfidic minerals.