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Mesophilic and thermophilic bioleaching of copper from a chalcopyrite-containing molybdenite concentrate

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ABSTRACT

The purpose of this study was to evaluate the bioleaching of copper from a chalcopyrite-bearing molybdenite flotation concentrate using a shake flask technique and mesophilic and thermophilic microorganisms. The premise of the study was that Cu-bearing phases may be selectively solubilized through bioleaching from the bulk molybdenite for subsequent recovery from the leach solution. The composition of mineral salts in bioleach solutions was evaluated, but it did not have significant effects on the bioleaching. The addition of pyrite or a combination of sulfur and ferrous sulfate increased the redox potential and acid formation but did not have a major effect on the bioleaching of Cu. Statistical analysis indicated no significant differences in the bioleaching of copper between eight different mineral salt formulations amended with sulfur and ferrous iron. Silver at 69 mg/l (added as Ag_2SO_4) enhanced the dissolution of chalcopyrite. The bioleaching of the molybdenite concentrate at 3% (w/v) pulp density yielded 97% dissolution of Cu in the presence and 55% in the absence of added Ag. Bioleaching at thermophilic temperatures (70 °C) yielded up to 75% Cu dissolution from the concentrate at 6% (w/v) pulp density, whereas the yields were about 27% at mesophilic temperatures. On a mass basis, molybdenum dissolution exceeded copper leaching but the relative yields were <9%. If the molybdenite concentrate is upgraded by removing Cu through bioleaching, molybdenum loss into solution may be offset by recovering it from leach solutions.

1. Introduction

Molybdenite (MoS_2) ores are the major sources of molybdenum and rhenium on a global scale. Molybdenite is frequently associated with copper sulfides and is often a by-product in copper mining. The bioleaching of molybdenite has generally proven to be relatively slow and with low yields (Tributsch and Bennett, 1981; Kelley, 1986; Askari Zamani et al., 2005, 2006). The rates of molybdenite bioleaching are highly dependent on the experimental conditions such as the inoculum, pH, temperature, aeration, bioreactor design, pulp density, Mo content, and particle size, to mention a few examples. The oxidative dissolution of molybdenite is accelerated by ferric iron and yields intermediate thiosulfate (Schippers and Sand, 1999). The bioleaching of molybdenite concentrates is challenging because of the potential toxicity of molybdenum to the microorganisms that are active in the process. The resistance to molybdenum in acidithiobacilli has not been elucidated. While there is a wealth of molecular biochemical information of Mo in enzymes and cofactors in prokaryotes (Schwarz et al., 2007), the genetic and physiological basis of resistance is not well understood. Chalcopyrite ($CuFeS_2$) is common in molybdenite concentrates because their separation by flotation is not complete. Removal of chalcopyrite through bioleaching would not only yield dissolved Cu for subsequent recovery from the solution but it could also upgrade molybdenum concentrate if the process is selective for copper. Romano et al. (2001a,b) reported that bioleaching with mesophilic and thermophilic cultures could be used to partially dissolve chalcopyrite from a molybdenite concentrate. The relative dissolution of molybdenum from the concentrate remained <0.5%. These experiments were preceded by adaptation of the cultures to the Cu-containing molybdenite concentrate. Chalcopyrite is a relatively recalcitrant mineral in the bioleaching process due to surface passivation, a result of the precipitation of jarosites, elemental S and secondary Cu-sulfides on chalcopyrite surface (Watling, 2006; Klauber, 2008; Akcil and Deveci, 2010; Debernardi and Carlesi, 2013; Li et al., 2013). Because of the relatively low yields and kinetics, several studies have experimented with bioprocess conditions in attempts to delay the onset of the passivation and to increase the rate of copper dissolution from chalcopyrite. For example, the bioleaching of chalcopyrite can be enhanced with the use of thermophiles at elevated

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temperatures and with silver ion catalysis. Elevated temperatures in the bioleaching increase the yields and rates of copper dissolution from chalcopyrite concentrates (Plumb et al., 2008; Norris et al., 2013). The enhancement may be due to a combination of inverse temperature-dependence of the passivation and faster and more efficient oxidation of chalcopyrite by thermophiles as opposed to mesophilic acidophiles. The effect of the temperature on the rate of mineral bioleaching is not chalcopyrite-specific. In contrast, the catalytic effect of silver ion in the bioleaching process is most specific for chalcopyrite, demonstrated with multiple samples and acidophilic microorganisms including mixed cultures (Ahonen and Tuovinen, 1990a,b; Gómez et al., 1999; Muñoz et al., 2007a,b,c; Córdoba et al., 2009; Feng et al., 2013). For chalcopyrite-containing molybdenite concentrates, the rates of copper bioleaching vary with specific experimental conditions, and it is unclear how the molybdenite matrix affects the bioleaching of copper from the chalcopyrite phase.

For upgrading molybdenite concentrates for further processing, it may be feasible to minimize the Cu content of molybdenite through bioleaching. For the present study, the feasibility of the bioleaching of copper was assessed with a molybdenite flotation concentrate which contained chalcopyrite as well as pyrite (FeS_2) as the minor phases. The premise of the work was based on available literature, which indicated that copper dissolution from chalcopyrite could be enhanced by increasing the temperature of the bioprocess. Mineral salts in the leach solutions were varied along with additional Fe^{2+} and elemental S, and the effect of silver ion on the bioleaching of chalcopyrite was also tested. Mesophilic, moderately thermophilic and thermophilic acidophiles were used in this study. Chemical leaching tests were performed as abiotic controls at the same temperatures using ferric iron as a leaching agent.

2. Materials and methods

2.1. Molybdenite concentrate

The MoS_2-containing ore at the Sarcheshmeh Copper Complex also contains Cu-bearing minerals. The MoS_2-containing fraction is separated from Cu-sulfides with a rougher and seven sequential flotation cells in a four series bank. In this process, the molybdenite concentrate is moved to the next stage and the Cu-bearing tailing is diverted to the previous stage. The process has an open milling circuit after the second cleaner stage, and a closed milling circuit after the fourth cleaner stage, in which 90% of the concentrate is reduced to 38 μm. The grade of molybdenite is increased from the fifth stage to the seventh stage of the flotation. The final concentrate has the lowest amount of copper (0.44% Cu). In the course of process monitoring, it was discovered that the sample from the fifth cleaner contained 0.98% Cu, the highest grade of Cu in the last three cleaners. Elevated Cu content in excess of 0.5% in the molybdenite concentrate poses multiple problems in the process as well as in product quality. Therefore, the representative sample from the fifth cleaner stage was used in the bioleaching and chemical leaching experiments. Samples were retrieved from the circuit over a two month period followed by drying and blending, and the subsample (90% −38 μm) for bioleaching and chemical leaching tests in this study was obtained with the coning and quartering method. The concentrate output used in this study contained 0.98% Cu, 1.56% Fe, 53.84% Mo, and 0.055% Re. The d_{80} of the sample was 33 μm, determined gravimetrically after size fractionation with a cyclosizer (Sepor, Inc., Wilmington, CA) according to the Stokesian settling characteristics of the particles.

2.2. Bacterial cultures and media

Three mixed cultures (mesophilic, moderately thermophilic, and thermophilic) of acidophilic microorganisms were used in this study. The mesophilic (32 °C) mixed culture comprised iron and sulfur oxidizing bacteria (*Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, and *Leptospirillum ferrooxidans*) that were originally enriched from mine drainage of the Sarcheshmeh copper mine, Kerman (Bakhtiari et al., 2008; Ahmadi et al., 2010). The moderately thermophilic (45 °C) mixed culture was obtained from Mintek SA, Johannesburg (Ahmadi et al., 2010; Vakylabad et al., 2012). This culture comprised a known mixture of *Acidithiobacillus caldus*, *Leptospirillum ferriphilum*, *Sulfobacillus* spp. and *Ferroplasma* spp. The thermophilic culture (70 °C) was comprised of *Acidianus brierleyi* and *Sulfolobus acidocaldarius*, originally enriched from the Sarcheshmeh copper mine site (van Staden et al., 2005). All three mixed cultures oxidized elemental sulfur and ferrous iron.

The cultures were originally grown with a chalcopyrite concentrate as an energy source in shake flasks (150 rev/min). The 9K mineral salt medium (3.0 g $(NH_4)_2SO_4$, 0.5 g $MgSO_4 \cdot 7H_2O$, 0.1 g KCl, 0.5 g K_2HPO_4, and 0.01 g $Ca(NO_3)_2$ per liter, pH 1.8) was used for the mesophilic chalcopyrite culture. The thermophilic mixed cultures were grown with chalcopyrite in media that contained (per liter) 0.2 g $(NH4)_2SO_4$, 0.2 g $MgSO_4 \cdot 7H_2O$, and 0.2 g K_2HPO_4, at pH 1.5. Due to the potential toxicity of molybdenum, the cultures were gradually adapted to grow with molybdenite as the sole source of energy. This involved a successive enrichment by stepwise increases in the molybdenite concentration (up to 10% w/v) while decreasing the concentration of chalcopyrite over a period of 3 months. The cultures were transferred several times in molybdenite concentrate medium to adapt the cultures to the experimental conditions. The media were adjusted with sulfuric acid to pH 1.8 for the mesophiles and pH 1.5 for the thermophiles, and growth was monitored by measuring the redox potential and pH.

2.3. Leaching experiments

The experiments were designed to address the amenability of the Cu-bearing molybdenite to the bioleaching to minimize the Cu-content of the molybdenite concentrate. Specific formulations of nutrient solutions, silver catalytic effect, and the use of thermophiles at elevated temperatures were tested in the study. Two different leaching experiments were carried out. In the first experiment, 13 leach solution formulations (Table 1) were tested with the mesophilic culture at 32 °C using 15% (v/v) inoculation and 3% (w/v) pulp density of the molybdenite concentrate. The cultures were supplied with pyrite, elemental S, or Fe^{2+} (as $FeSO_4 \cdot 7H_2O$) as additional energy sources for the bacteria and were incubated in shake flasks at 150 rpm. Formaldehyde instead of the inoculum was used for the abiotic control, added in three aliquots over the first 2 days to a final concentration of 20 ml/100 ml culture. In the second experiment, the mesophilic, moderately thermophilic and thermophilic cultures were grown at 6% (w/v) pulp density in shake flasks at 150 rpm. The cultures received 15% (v/v) inocula of previously adapted cultures. Chemical leaching tests with 20 g Fe^{3+}/l (added as ferric sulfate) were carried out under otherwise similar conditions. A chemical control without Fe^{3+} was also prepared, with formaldehyde substituting for the inoculum. Water lost by evaporation was determined gravimetrically and was compensated for by adding distilled water.

2.4. Analytical methods

At intervals, redox potential and pH were measured directly in the culture flasks and the suspensions were sampled for microscopic cell counts after ~1 min of settling. Microscopic cell counts were determined using a Neubauer chamber with a depth of 1/50 mm and area of 1/400 mm^2. For analysis of metals, the suspended solids were allowed to settle for 30 min before sampling of the solution phase. Samples were filtered (0.45 μm) for analysis of dissolved copper, molybdenum and total dissolved iron (total Fe_d). Sample volumes were replaced with sterile mineral salt solution. The final results have been corrected for the dilution effect caused by partial replacement of the nutrient