Hydrometallurgy 97 (2009) 94–97

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Effect of CO_2 air enrichment in the biooxidation of a refractory gold concentrate by *Sulfolobus metallicus* adapted to high pulp densities

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ARTICLE INFO

Article history:
Received 22 August 2008
Received in revised form 24 January 2009
Accepted 24 January 2009
Available online 10 February 2009

Keywords:
Biooxidation
Cell adaptation
CO_2 transfer
CO_2 enrichment
High pulp density
Thermophile

ABSTRACT

The interest in bioleaching as an alternative to the traditional pyrometallurgical technologies is continuously increasing. In order to have an efficient biooxidation process some important limitations must be overcome, such as cell adaptation, gas transport phenomena, maximal allowable pulp density, metabolic stress and adverse hydrodynamic conditions. When air is supplied on the basis of the oxygen demand, the CO_2 demand may not be satisfied leading to carbon limited growth. The objective of this work was to study the influence of CO_2 air enrichment from 0 to 25% v/v on the biooxidation of a refractory gold concentrate of a population of *Sulfolobus* sp. cells previously adapted to high pulp densities.

Experiments were performed in a 3-liter stirred tank reactor at 15% w/v pulp density, 70 °C, 230 rpm, 1.0 vvm and initial pH of 1.8. The concentrate contained mainly pyrite, enargite, chalcopyrite and tenantite.

Results lead to the conclusion that the biooxidation was limited by the supply of carbon dioxide and that the limitation can be relieved by CO_2 enrichment of the bubbling gas up to 5% v/v. The higher productivities obtained after 15 days of culture were 920 mg Fe/l·d and 680 mg Cu/l·d with 5% enrichment, with extraction degrees of around 40%. Higher enrichments had positive effects on the gas transfer rates but not in the solubilization productivities and extraction degrees and seem to promote precipitation of copper and iron species.

1. Introduction

The interest in bioleaching as an alternative to the traditional pyrometallurgical technologies is continuously increasing (Olson et al., 2003, Crundwell, 2005). In order to have an efficient biooxidation process the participant microbial population should receive all the nutrients they need for performing their metabolic functions and generate the adequate conditions in the liquor to leach out the desired metals. Some important limitations should be overcome, as is the case of adaptation of the cell population to the mineral composition and environmental conditions, maximal pulp density and stress and hydrodynamic conditions (Acevedo et al., 2004; Harrison et al., 2007; Astudillo and Acevedo, 2008). Of special concern are the aeration and gas transport phenomena involved, as oxygen is the final electron acceptor of the oxidation process and carbon dioxide is the carbon source for cell growth. Gas transfer rate is dependent on their partial pressures, solubility in the leaching medium and hydrodynamic conditions (Boon and Heijnen, 1998). Because the low concentration of CO_2 in air (0.03% v/v) compared to O_2 content (21%), when air is supplied on the basis of coping with the O_2 demand the CO_2 demand may not be satisfied leading to carbon limited growth (Acevedo and Gentina, 2007). It must be noted that although carbon dioxide is more soluble in water than oxygen (lower Henry's constant), its equilibrium concentration is much lower.

It has been reported that a minimal concentration of dissolved oxygen of 1.5 ppm is required in order to avoid limitation (Dew and Miller, 1997; de Cock et al., 2003) although concentrations as low as 0.1 ppm have also been cited (Ritchie and Barter, 1997). In the other hand, Gericke et al. (2001) concluded that when the dissolved oxygen concentration is higher than 50% saturation the culture is not oxygen limited. It has also been reported that high oxygen concentrations may be inhibitory for the cells. De Cock et al. (2003) determined that dissolved oxygen concentrations in the range of 1.5 to 4.1 ppm ensure a cell activity over 90% of its maximal value in the case of *Sulfolobus*. Whatever is the case, bioleaching operations using regular air will be limited by either carbon dioxide or oxygen supply, a matter that can be adequately predicted comparing the carbon dioxide uptake rate and the carbon dioxide transfer rate as has been recently proposed (Boon and Heijnen, 1998; Acevedo and Gentina, 2007).

Carbon limitation can be relieved increasing the gas flow rate or increasing CO_2 concentration in the gas. Very diverse results have been reported by different authors for CO_2 enrichment. Torma et al. (1972) working with a zinc concentrate determined that when using regular air the productivity was proportional to pulp density up to 12% w/v while using carbon dioxide enriched air increased the proportionality range up to pulp densities of 24%. Working with a pulp density of 8% d'Hugues et al. (2001) find out that increasing CO_2 in the

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doi:10.1016/j.hydromet.2009.01.010

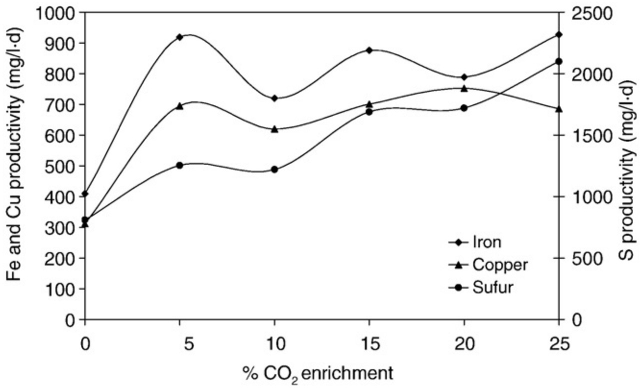

Fig. 1. Effect of CO_2 enrichment on iron, copper and sulfur solubilization productivity in batch operation in a 3-liter stirred tank reactor after 15 days of culture at 15% w/v pulp density, 70 °C, 230 rpm, 1.0 vvm (no enrichment run) and initial pH of 1.8.

gas from 1 to 2% did not produce any effect, while Petersen et al. (2001) determined a similar situation occurred working with air-lift reactors. In contrast Acevedo et al. (1998) found that enrichments up to 4% have a positive effect in specific growth rate, and Fe, Cu and As solubilization rates from an enargite–pyrite gold concentrate by *A. ferrooxidans*. While de Cock et al. (2003) reported a positive effect of CO_2 enrichment in the range of 7 to 17% in the cultivation of *Sulfolobus* sp. in 9 K medium with 3 g/l of sodium tetrathionate as energy source. Furthermore, Gericke et al. (2001) observed that only a low CO_2 enrichment of 0.25% was enough to obtain high solubilization rates in the continuous bioleaching of a high chalcopyrite content concentrate by a thermophilic bacterial culture.

Considering that the main limitations of bioleaching processes in stirred tanks are the negative effect of high pulp densities on unadapted cell populations and the limited supply of carbon dioxide, the objective of this work was to study the influence of CO_2 enrichment on the biooxidation of a refractory gold concentrate of a population of *Sulfolobus* cells adapted to a pulp density of 15% w/v.

2. Materials and methods

2.1. Microorganism and culture conditions

A *Sulfolobus metallicus* strain adapted to 15% w/v pulp density was used. It was cultured in Norris medium (Norris, 1989) with the 38 to 75 µm particle size fraction of a flotation gold concentrate (Minera El Indio, IV Region, Chile) containing 42 g Au/tonne, 38.4% pyrite (FeS_2), 16.4% enargite (Cu_3AsS_4), 10.6% chalcopyrite ($CuFeS_2$), 10.7% tenantite ($Cu_{12}As_4S_{13}$) and 23.9% gangue.

Experiments were run in a 5-liter stirred tank bioreactor operated with 3 l of pulp. A 7 cm diameter and 0.7 cm height flat blade turbine and a Heidolph model R2R-1 variable speed agitator were used. Agitation rate was 230 rpm in all runs. Air was supplied at 1.0 vvm by a Gast MFG Corp. compressor model DDA-V174-ED. CO_2 from AGA-Chile was used for 5, 10, 15, 20 and 25% v/v enrichment. Gas rotameters were used for flow measurement. Initial pH was adjusted to 1.8 with sulfuric acid and was not controlled during the cultures. The temperature was kept constant at 70 °C by circulating thermostatically controlled water through a submerged coil. Water loss due to evaporation was periodically compensated by the automatic addition of distilled water. Samples taken periodically were centrifuged for 15 min at 15,000 rpm (Biofuge 15, Heraeus Sepatech, Midland, ON, Canada). Clear liquid was used to determine pH, Eh, ferrous ion, total iron, copper and sulfate.

Mass dissolution ratios, pH and Eh are reported as final values for each run. Volumetric productivities and degrees of extraction of iron, copper and sulfur were calculated after 15 days of culture.

2.2. Analytical methods

Ferrous and ferric ions, total soluble iron, copper and sulfate ions were determined as reported elsewhere (Astudillo and Acevedo, 2008).

Eh and pH were measured with PtAg/AgCl and Ag/AgCl electrodes, respectively. Dissolved oxygen was continuously monitored with a Mettler Toledo Impro 6000 polarographic electrode.

The volumetric oxygen transfer coefficient, k_La_o, was determined from the slope of the dissolved oxygen concentration vs time curve obtained by turning off the air for a short period (Humphrey, 1998; Acevedo 2004). k_La_c for CO_2 was estimated by multiplying de oxygen k_La_o values by 0.89 as proposed by Boogerd et al. (1990).

3. Results and discussion

3.1. Volumetric productivity and extraction degree

Fig. 1 shows the volumetric productivities (rates of solubilization per unit of pulp volume) of iron, copper and sulfur solubilization as a function of air enrichment with CO_2. It can be observed that enrichment is beneficial in all cases, supporting the hypothesis of CO_2 limitation when bubbling regular air.

For iron and copper solubilization a significant increase in productivities can be noted for 5% CO_2 after which the effect levels off. In the case of sulfur a more sustained increase in productivity can be appreciated. It must be kept in mind that it was the sulfate ion that actually was analyzed and that the leached sulfur was calculated from those analyses assuming that sulfate was the only sulfur species in solution. Nevertheless, evidence exists that low proportions (1–2%) of other sulfur species result from the oxidation of pyrite by ferric iron (Schippers et al., 1999). Moreover, the relation between solubilized copper and iron and sulfur was very near what expected from stoichiometry.

The degree of extraction of iron and copper presents a similar behavior with respect to CO_2 enrichment as can be seen in Fig. 2. Going from regular air to 5% CO_2 gas doubles the solubilized metal after 15 days of culture. No significant effect of further enrichment is appreciated. As in the case of productivity, the effect of CO_2 on sulfur extraction differs from its effect on copper and iron in that a sustained positive effect is apparent up to 25% CO_2. This difference in behavior could be due to copper and iron precipitation at high CO_2 concentrations in air. If that is the case then high CO_2 enrichments would be deleterious for an actual process since it could lead to passivation and additional resistances over the mineral particle surface. A 5% CO_2 gas would give the best performance with the lower enrichment cost.

In order to support the above interpretation of the results the ratios between the three elements (Fe/Cu, Cu/S and Fe/S) of the main species present in the concentrate and the overall mean values of the

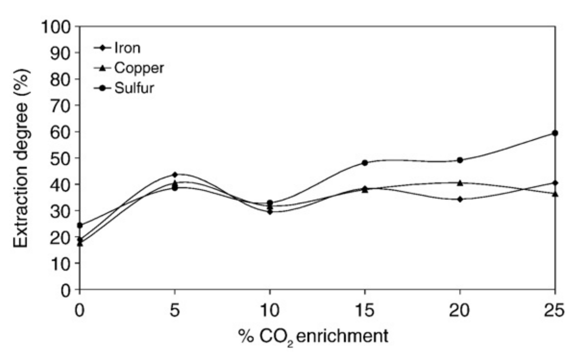

Fig. 2. Effect of CO_2 enrichment on the degree of extraction of iron, copper and sulfur in batch operation in a 3-liter stirred tank reactor after 15 days of culture at 15% w/v pulp density, 70 °C, 230 rpm, 1.0 vvm (no enrichment run) and initial pH of 1.8.