Effect of pH and Fe(III) ions on chalcopyrite bioleaching by an adapted consortium from biogas sweetening

A.D. Dorado*, M. Solé, C. Lao, P. Alonso, X. Gamisans
Department of Mining Engineering and Natural Resources, Universitat Politècnica de Catalunya, Av. Bases de Manresa, 61-73, 08242, Manresa, Spain
**Corresponding author. Tel. +34 93 8777236. E-mail address: dorado@emrn.upc.edu (A.D. Dorado)*

ABSTRACT

Particle size, pH and Fe(III) ions affect the process of bioleaching of copper from chalcopyrite ores. In the study presented herein a copper sulfide ore was subjected to bioleaching process using a mixed microbial consortium obtained from a biotrickling filter treating high loads of H_2S at different mineral particle size, distinct medium pH and various additional Fe(III) ion concentrations as leaching agent. After 1300 hours of operation, the total copper recovery achieved a value of 50 % in the most acidic conditions. A decrease of 2.5 units of pH implied an increase in the efficiency of 35%. It was also observed an optimal particle size (between 2 and 3 mm), considerably higher than previous reported studies, meaning a decrease in operational cost to mill material. Finally, results indicate that there is a threshold concentration of ferric ion from which the system is not sensitive (500 ppm).

Keywords: bioleaching; sulphide ores; particle size; bacteria

1. Introduction

In the context of metal sulfides bioleaching, most research is conducted using known iron and sulfur oxidizing bacterial consortia (Rawlings 2002). Recently, a few studies have reported the use of mixed cultures. Qiu et al. (2005) reported that a mixed culture of *Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans* was better in leaching chalcopyrite than the two pure cultures separately. The same behavior was observed by Zhang et al (2008). Moreover, particle size, which influences the specific surface area, is an important factor in determining the kinetics of the leaching reactions (Ahonen and Tuovinen, 1995). In most chalcopyrite bioleaching works, the authors used very low particle size: 25-35 µm (Vilcáez et al., 2009), 45 µm (Third et al., 2000) or 75 µm (Zhou et al. 2009). However, little is known about the behavior at higher particles sizes which means less energy to treat the original sample and represent a more actual situation to those found in heaps at industrial scale.

Another parameter influencing the bioleaching process is the pH of the medium where the process takes place. It has been reported that most of iron and sulfur-oxidizers microorganisms responsible of bioleaching processes grow or oxidize energy sources at pH range 1.5–2.0. However, this interval could be modified in the case of using a consortium. In addition, chemical processes taking place at low pH could overestimate the bioleaching capacity of the system.

In the present study, a series of bacterial and chemical leaching experiments were conducted to clarify contradictory reports in the literature. A copper-sulfide ore was subjected to bioleaching process using a mixed microbial consortium which was obtained from a lab-scale biotrickling filter treating high loads of H_2S. In order to know which conditions influence more significantly the process, a systematic comparative study has been carried out considering biological, physical and chemical characteristics of the process together with the operational conditions. Experiments were compared at different mineral particle size, medium pH and additional Fe(III) ion concentrations as leaching agent.

2. Materials and methods

2.1. Mineral

A characterization of mineral samples, from Rio Tinto's Mines (Spain), was performed by X-ray diffraction analysis with a Panalytical X'Pert PRO MPD X-ray diffractometer. Quantitative mineral phase analyses of the samples showed the following composition: chalcopyrite 37.2 wt.%, SiO_2 53.4 wt.% and FeO(OH) 9,3 wt.%.

2.2. Microorganisms

A mixed microbial consortium (hereinafter named SOX), obtained from a lab-scale gas-phase biotrickling filter treating high loads of H_2S was used as inoculum. Sulfur-oxidizing bacteria existing in the biotrickling filter biofilm were previously characterized (Maestre et al., 2010). In this study the presence of *Thiothrix spp., Sulfurimonas denitrificans, Halothiobacillus neapolitanus, Thiobacillus denitrificans, and Thiomonas intermedia* was detected by cloning and sequencing 16S rRNA fragments.

2.3. Bioleaching experiments

Bioleaching experiments were carried out in 250 mL Erlenmeyer flasks containing 100 mL of mineral medium, 5 g of chalcopyrite ore and 10% (V/V) of the mixed microbial consortiums described above. The mineral medium composition was (in $g\,l^{-1}$): $(NH_4)_2SO_4$, 0.4; KCl, 0.1; KH_2PO_4, 0.2; and $MgSO_4{\cdot}7H_2O$, 0.4. The same mineral medium buffered at pH 6 (NaH_2PO_4/Na_2HPO_4 0.2M) or pH 1,5 (KCl/HCl 0.2 M) was used to test the pH effect on bioleaching experiments. $Fe_2(SO_4)_3{\cdot}7H_2O$ was added into the medium in the experiments performed to study the effect of additional Fe(III) ion.

Particle size influence was tested at 0.4-2 mm, 2-3 mm and 3-5 mm of particle size. Subsequently, the effect of pH and the additional Fe(III) ion presence was studied at pH=1.5, 4 and 6, and finally with additional solutions of 100, 500 and 1000 ppm of Fe(III) ion concentrations. Control experiments were carried out without inoculum.

2.4. Analytical methods

pH was measured with a Crison basic 25 pH-meter. Copper and total iron concentrations in the bioleached solutions were determined by an atomic absorption spectrophotometer (*Thermo* Corporation) after the filtration of the suspension through a 0.22 μm membrane filter. Fe(II) determination was carried out by 1,10-phenanthroline method *(*APHA, 1998*)* with a Lambda 25 UV/VIS spectrophotometer.

3. Results and discussion

3.1. Influence of the particle size

The leaching rate of SOX is around 0.36% d^{-1} (36 times higher than the leaching of copper without biomass). Present results detected that after 600 hours of operation the copper recovery showed an upward trend indicating that higher recovery can be obtained after longer periods of time. Experiments, which were carried out at different mineral particle size, from 0.4 mm to 5 mm, provided some unexpected results. An optimal particle size where efficiency is enhanced was observed (particles between 2 and 3 mm). Very low particle size negatively affected the process. It has been described that bacterial activity decreased in the presence of fine particles which apparently could cause damage to the bacterial cells (Nemati et al., 2000). Deveci (2003) concluded that the rate and extent of loss in viability of a bacterial population increased when decreasing the particle size below to a critical fineness, since the adverse effect tends to decrease. In this sense, it should be considered that while grinding ore to a smaller particle size often increases copper recovery, the benefit conferred by the treatment would be offset due to the increased cost of material milling. In addition, fine particles in a heap decrease the permeability for aqueous solution and air circulation.

3.2. Influence of pH

Figure 1A shows the evolution of pH for the performance at neutral (close to 6), acidic (close to 4) or highly acidic conditions (close to 1.5). The abiotic experiment was carried out at pH conditions of the mineral medium which was 6. An increase in pH was observed initially for all biotic experiments. This could be due to the protonic attack during acidic dissolution of the chalcopyrite. Rodríguez et al (2003) observed that the H^+ concentration decreased initially due to the consumption of acid during the protonic attack of the chalcopyrite. Later on, acidity increased, because of the oxidation of elemental sulfur by sulfur-oxidizing microorganisms. The same pH evolution was observed by Zhou et al (2007). In the present study, from day 12 copper concentrations in the leachate increased simultaneously to pH decrease. The most relevant observation in Figure 1A is that copper recovery efficiency is enhanced at low pH. Exactly, after 1300 hours of contact time between mineral medium, biomass and chalcopyrite ore, the total copper recovery achieves a value up to 50 % in the most acid conditions, 15% in the slightly acid conditions and practically negligible at neutral conditions (similar values to those for the abiotic system). This means that a decrease of 2.5 pH units implies an increase in the efficiency of 35%. Chemical copper leaching was reproduced at a pH of 1.5 with a value of 7.6 %.

3.3. Ferric ion addition influence

Results obtained for the experiments conducted at Fe(III) initial concentrations of 100, 500 and 1000 ppm, are shown in Figure 1B. Some studies reported that additional Fe(III) ions only enhance the initial leaching rates but not the final leaching yields (Vilcáez et al., 2009). However, in the present study, it was observed that the maximum copper recovery was obtained when the biological process was doped with Fe(III) concentrations of 500 and 1000 ppm (0.01M and 0.02M, respectively). Results indicate that iron added participate in the bioleaching process since less iron is leached from the mineral. Studies found in literature concluded that Fe(III) concentrations above 0.01M does not affect the chalcopyrite bioleaching kinetics (Dutrizac, 1981; Konishi et al., 2001). Results presented herein indicate that the presence of additional Fe(III) ions improve the bioleaching performance, despite there is a boundary concentration from which the system is not sensitive (500 ppm). Considering indirect bioleaching mechanism is occurring (Rodríguez et al. 2003), the biological process is the limiting step. Therefore, when enough Fe(III) concentrations are added, the limiting step is the sulfur oxidation rate. In the case of strong acid conditions (pH=1.5), during the whole experimental period the Fe(III) ion concentration was higher than in the case of Fe(II). After the adaptation period, accumulation of Fe(III) ions occurred fast. The accumulation of Fe(III) indicates that the rate of iron reoxidation performed by microorganisms is higher than the sulfur oxidation rate performed by Fe(III) ions. Thus, the biological process of Fe(III) ion regeneration is not the limiting step.

4. Conclusions

An unspecific consortium from the biological oxidation of gaseous H_2S has been tested as inoculum for the bioleaching of chalcopyrite ores. The optimal particle size found was between 2 and 3 mm. The medium pH revealed as a critical parameter on the bioprocess performance. Experiments set at an initial pH of 1.5 showed the most positive result: a copper dissolution of 50%. Process is enhanced due to the sum of both effects, chemical and biological leaching, being more important the biological contribution. A boundary condition was found for the positive effect of the Fe(III) ions addition (500 ppm). The beneficial effect was observed mainly during the startup phase. Present conditions less strict than conventional works in bioleaching of chalcopyrite (larger particle size (2-3 mm), mixed consortium and low temperatures (30ºC)) decrease potential economic costs of the technology with promising results.

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CAPTIONS

Fig. 1: Copper recovery (filled symbols) and pH (non-filled symbols) evolution along operating time in the study of the pH effect (A) and additions of ferric ions (B). The nomenclature A-pH is for acid experiments (~4), HA-pH for high acid (~1.5) N-pH for neutral conditions (~6). The nomenclature L-Fe is for experiments at low ferric ion concentration (100 ppm), M-Fe for middle ferric ion concentration (500ppm) and H-Fe for high concentration (1000 ppm).