



The effect of redox control on the continuous bioleaching of chalcopyrite concentrate



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ARTICLE INFO

Article history:

Received 9 March 2015

Revised 4 July 2015

Accepted 14 July 2015

Available online 29 July 2015

Keywords:

Continuous bioleaching

Redox control

Chalcopyrite

Moderate thermophiles

ABSTRACT

A continuous bioleaching process was developed for the dissolution of chalcopyrite concentrate with electrochemically redox control. Therefore, using a flotation concentrate containing 46% chalcopyrite and 23% pyrite, bioleaching tests were carried out at 47 °C with 15% pulp density under controlled and uncontrolled redox conditions. To increase the copper recovery in contrast to the conventional bioleaching (~39.62%), the effect of redox potential on the chalcopyrite bioleaching was investigated by electrochemically controlled bioleaching. The results showed that by controlling the redox potential, faster copper leach kinetics could be achieved. At last, reducing the redox potential from high levels to optimum window (420–440 mV SCE) caused an increase in copper recovery from around 39% to higher than 69% (over 25 g/L Cu²⁺).

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1. Introduction

Many studies have been dealt with the issue of slow kinetics of chalcopyrite bioleaching and finding out the dominant mechanisms which are responsible for the passivation of chalcopyrite in leaching environment. Various theories have been proposed to account for this phenomenon, mostly involving passivation of the mineral by ferric precipitates and/or sulfur, though there is no agreement on the exact mechanistic reason for the recalcitrance of chalcopyrite to leaching (Gericke et al., 2010; Sandstrom et al., 2005). Based on the results of leaching experiments, it has been reported that the leaching rate of chalcopyrite depends on a redox potential of leaching solution. Kametani and Aoki (1985) was the first who established the effect of suspension potential on the leaching of chalcopyrite and reported that the mixed solutions of ferrous and ferric sulfate had a critical potential at which the leaching rate is maximum.

The imperfect dissolution of copper from chalcopyrite can be overcome by operating at controlled redox levels (Ahmadi et al., 2011; Ahmadi et al., 2010; Córdoba et al., 2008; Third et al., 2002). Pulp potential can be controlled in two ways, electrochemically by applying a potential from an external source through a

working electrode or chemically by the addition of reducing and oxidizing agents. However, the addition of an oxidizing or reducing agent to the bacterial leaching vessel may be detrimental for bacterial activity. In this context, some researchers used controlling the oxygen mass transfer for maintaining the redox potential at the low levels (Gericke et al., 2010; Gericke et al., 2008). Another option could be oxidizing or reducing the ferrous and ferric ions directly by electrolysis during the course of bacterial leaching experiments (Harvey and Crundwell, 1997). In addition, preventing undesirable reactions in the solutions containing many kinds of electrochemically active species, appropriateness of the reaction extents to the concentration of the reactants, and the leading high efficiency of the electrolysis are other benefits of the controlled-potential electrolysis (Matsumoto et al., 1999a).

Gericke et al. (2010) implemented bioleaching tests in bench-scale pilot facilities using moderate thermophile consortia under controlled redox potential conditions to assess the effect of redox control on chalcopyrite leach kinetics. Their results showed that a significant increase in the copper leaching kinetics and copper extractions was achieved by controlling the redox potential of the system around 420 mV at 45 °C. Ahmadi et al. (2010) compared the results of bioleaching and electrochemical bioleaching of high grade chalcopyrite flotation concentrates in a stirred bioreactor. They concluded that copper recovery could be increased to more than 35% by the use of electrochemical bioleaching. The results of the optimized-leaching process at 20% pulp density in 10 days

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showed that, by using bioleaching in 400–430 mV ORP range, copper recovery reaches about 80% which is 3.9 times higher than abiotic electrochemical leaching, 1.5 times higher than conventional bioleaching, and 1.17 times higher than electrochemical bioleaching at 440–480 mV ORP. The control of ORP by electrochemical method has some advantages over other methods applied by some researchers (Gericke et al., 2010; Pinches et al., 2001; Third et al., 2002) which improve dissolution rate of copper from chalcopyrite during the bioleaching process. The benefits include: chalcopyrite conversion to less refractory phase, chalcocite and covellite minerals, by direct electron transfer to the mineral (Ahmadi et al., 2011; Fuentes-Aceituno et al., 2008) and the use of electrochemical control of redox potential which improves bacterial subsystem (Ahmadi et al., 2010; Harvey and Crundwell, 1997; Matsumoto et al., 1999b) and promotes the chalcopyrite dissolution.

Given the promising results obtained in bioleaching with electrochemically controlled redox potential, the purpose of this research was to develop a continuous bioleaching process with electrochemically ORP control to assess the impact of redox controlling on copper extraction from chalcopyrite flotation concentrate.

2. Materials and methods

2.1. Materials

For all experiments a representative sample of flotation concentrate obtained from Sarcheshmeh Copper Mine (Kerman, Iran) was used. Chemical analysis of the concentrate is presented in Table 1. The mineralogical composition of the concentrate was determined using X-ray diffraction (XRD) analysis and the results showed chalcopyrite (CuFeS_2) and pyrite (FeS_2) as the main phase, and Covellite (CuS), Chalcocite (Cu_2S), sphalerite (ZnS) and silica (SiO_2) as minor phases. Particle size analysis of flotation concentrate revealed that 80% of concentrate particles was smaller than 45 μm .

A mixed culture of moderately thermophile bacteria consisted of acidophilic iron and sulfur oxidizing bacteria isolated from the Sarcheshmeh Copper Mine was used during experiments. The culture was initially grown in shake flasks using a temperature-controlled shaker at 45 °C, pH 1.6 and 150 rpm in 9 K medium comprising of 3 g/L $(\text{NH}_4)_2\text{SO}_4$, 0.5 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 g/L KCl, 0.014 g/L $\text{Ca}(\text{NO}_3)_2$ and 0.63 g/L K_2HPO_4 with the addition of 45 g/L ferrous sulfate and 5% elemental sulfur as energy sources. Involved microorganisms were adopted with the copper concentrate at pulp densities from 2% to 15% (w/v) by replacing the energy substrate.

2.2. Apparatus

Bioleaching was performed in three continuous stirred tank reactors (CSTRs). Volume of the first reactor was 12 L and the second and third reactors had 5 L volumes. The system consisted of a feed pulp tank at the beginning, and a container at the end for effluent collection. Nutrients were added to the feed tank, and feed slurry was supplied to the first reactor from the feed tank by a peristaltic pump. Pulp transfer between the reactors was done by means of gravity overflow.

The fully baffled reactors with dual-impeller agitation system were provided with 2% CO_2 -enriched air by using a sparger situated below the impeller with the speed of 450 rpm. Temperature

of each reactor was controlled in the range suitable for the moderately thermophile bacteria. Two-electrode method was used to electrochemically control the pulp potential. Anode compartment (lead–antimony alloy) was separated from the main chamber by a ceramic membrane for controlling electrochemical reactions. Also, a stainless steel mesh, acting as the cathode electrode, was placed into the reactor solution. A redox-potential controller which its output was adjusting DC current between anode and cathode was used in order to reduce the redox potential to the set point (Fig. 1).

2.3. Procedures

Continuous-bioleaching experiments were carried out at these conditions: 15% (w/v) pulp density, an acid concentration of 55 kg/ton, a temperature of 47 °C, aeration rate of 0.5 vvm (volume of air/volume of slurry/min), and an overall 7-day residence time. pH and oxidation reduction potential (ORP) of the pregnant leach solution (PLS) were measured using a pH probe (826 pH-meter Metrohm model) and an Ag/AgCl reference redox probe (Mettler Toledo, MP120 model), respectively. The concentration of copper and iron in solution were determined by an atomic absorption spectrophotometer (Varian 220).

Once a steady state condition was achieved, a set of pulp samples was collected from each reactor and the residues analyzed for copper, iron and sulfur. The composition of solid residue was determined after filtration, acid washing and drying using X-ray fluorescence. Bioleach residues were analyzed using scanning electron microscope (SEM) based image and XRD.

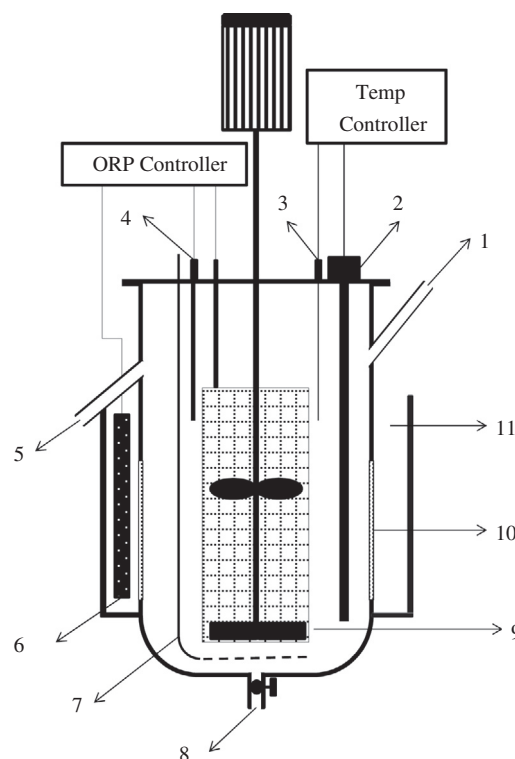


Fig. 1. Schematic illustration of the applied reactors: 1 – Inlet of feed, 2 – thermal element, 3 – thermometer, 4 – ORP electrode, 5 – Outlet of feed, 6 – Anode electrode, 7 – air sparger, 8 – Reactor drain, 9 – Cathode electrode, 10 – Ceramic membrane and 11 – Anode compartment.

Table 1
Chemical composition of flotation concentrate.

Elements	Si	Al	K	Cu	Ca	Fe	S	Zn
Wt.%	8.09	2.11	0.66	24.3	0.29	28.08	33.29	0.87

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