International Journal of Mineral Processing 134 (2015) 58–65

Contents lists available at ScienceDirect

International Journal of Mineral Processing

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

Isotopic signature of Cu and Fe during bioleaching and electrochemical leaching of a chalcopyrite concentrate

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ARTICLE INFO

Article history:
Received 10 April 2014
Received in revised form 1 September 2014
Accepted 25 November 2014
Available online 26 November 2014

Keywords:
Bioleaching
Electrochemical leaching
Chalcopyrite
Fe isotopes
Cu isotopes
Oxidative dissolution

ABSTRACT

Bioleaching is an important process in metallurgy and in environmental sciences, either for the acquisition of metals or for the formation of acid rock drainage. In this study the implications of the processes during bioleaching of a pyritic chalcopyrite concentrate were analysed regarding its Cu and Fe isotope fractionation. The development of the redox potential during the bioleaching experiment was then simulated in an electrochemical cell in the absence of microorganisms to investigate the effect of microbial activity on the Cu and Fe isotope fractionations. The leaching experiments were performed for 28 days at 45 °C with a solid content of 2.5% (w/v) at pH 1.5. It was found that Cu dissolution efficiency was similar in both experiments and the leaching curves were linear with no sign of passivation due to the presence of pyrite. The heavy Cu isotope (δ^{65}Cu) was leached more easily and as a result the leachate was enriched with the heavy Cu isotope at the beginning of both experiments and as the leaching progressed δ^{65}Cu values in the leachate became similar to the ones of the chalcopyrite concentrate, confirming an equilibrium fractionation happening in a closed system. There was no distinct difference in the Cu and Fe isotope fractionations in the absence and presence of microorganisms. Finally based on Cu and Fe isotope signatures, a simplified method is suggested for the estimation of the leaching extent during the oxidisation of sulphide materials in natural systems.

1. Introduction

Chalcopyrite ($CuFeS_2$) is the most abundant copper mineral in the world (Sandström et al., 2004). With an estimated global production of 17,000 ktons for the year 2012 which was 400 ktons less than the global demand for the same year (U.S. Geological Survey, 2013), the importance of Cu recovery from ores has increased. In addition to the increasing global demand, high-grade copper reserves are becoming more and more depleted. As a result, alternative methods for treatment of low-grade copper ores should be developed. For the treatment of low-grade sulphide ores, biohydrometallurgical processes are considered attractive due to a low capital investment as well as a straight forward technology.

Bioleaching is defined as the mobilization of metal cations from ores by biological oxidation and complexation processes. Heap bioleaching of secondary copper sulphide minerals including chalcocite (Cu_2S) and covellite (CuS) is a common practice around the world (Sandström et al., 2004). However, chalcopyrite is the most recalcitrant Cu ore to hydrometallurgical processing and presents a low dissolution rate compared to chalcocite and covellite. As a result, bioheapleaching of chalcopyrite currently cannot be accomplished economically (Debernardi and Carlesi, 2013). It is suggested that the main reason for the slow dissolution rate of chalcopyrite is the formation of a passive layer on the surface of the mineral which hinders further dissolution (Gómez et al., 1996). The nature of this layer is still under debate with elemental sulphur, jarosite, a metal deficient phase and polysulphides being the main candidates (Klauber, 2008).

The overall general reaction for chalcopyrite oxidation by ferric ion is presented in reaction [1]. It has been shown that by increasing the concentration ratio of ferric to ferrous ions (i.e. the redox potential of the system), the rate of dissolution increases to a limit and then it decreases (Kametani and Aoki, 1985). A two-step model was proposed by Hiroyoshi et al. (2000, 2001, 2004, 2008) to support this finding. The model suggests that chalcopyrite is reduced first to chalcocite (reaction [2]) and then in the second stage, chalcocite is oxidised (reaction [3]). This model describes why there is an optimum window of redox potential for dissolution of chalcopyrite.

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \quad (1)$$

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http://dx.doi.org/10.1016/j.minpro.2014.11.010
0301-7516/

$$CuFeS_2 + 3Cu^{2+} + 3Fe^{2+} \rightarrow 2Cu_2S + 4Fe^{3+} \quad (2)$$

$$2Cu_2S + 8Fe^{3+} \rightarrow 4Cu^{2+} + 2S^0 + 8Fe^{2+} \quad (3)$$

The dissolution mechanism of different sulphide minerals in the presence of acidophile microorganisms has been the subject of much research. The results of most of these works are summarised in a recent review (Li et al., 2013). A popular method to investigate the influence of microbial activity on leaching of sulphide minerals is the comparison of the leaching behaviour in the presence and absence of bacteria (Crundwell, 2003). Many of the performed studies have failed to maintain an accurate redox potential in their abiotic experiments similar to that in the biotic experiments (Crundwell, 2003). Since redox potential is an influential factor in the leaching behaviour of chalcopyrite, dissimilar redox potential conditions in abiotic and biotic experiments makes it impossible to reach to any conclusion regarding the role of microorganisms on the chalcopyrite leaching behaviour. Harvey and Crundwell (1997) solved this problem by using an electrochemical cell equipped with a redox potential controller. Using this method, bioleaching of pyrite (Fowler et al., 1999) and sphalerite (Fowler and Crundwell, 1999) at constant redox potentials was investigated. Chalcopyrite bioleaching was also studied under varying redox potential conditions by using a similar method (Khoshkoo et al., 2014).

Cu has two stable isotopes ^{63}Cu and ^{65}Cu with natural abundances of 69.15% and 30.85%, respectively while Fe has four stable isotopes: ^{54}Fe (natural abundance 5.84%), ^{56}Fe (91.75%), ^{57}Fe (2.12%) and ^{58}Fe (0.28%) (De Laeter et al., 2003). Changes in chemical conditions, such as redox potential or bacterial uptake can lead to the favouring of one isotope either in the product or in the reactant of a given process (Pérez Rodríguez et al., 2013; Navarrete et al., 2011). Applications of the use of Cu isotope signatures in metallurgy have been proposed to quantify the fractionation factors related to the Cu minerals involved during the dissolution process. With this, it could be possible to determine the minerals undergoing the most extensive leaching extraction (Mathur and Schlitt, 2010). Environmental applications in the use of isotopic signatures of Cu and Fe during (bio)leaching experiments include the understanding of the behaviour of those metals during weathering reactions, which could cause environmental impact such as acid mine drainage (AMD) (Kimball et al., 2009; Wiederhold et al., 2006).

Most of the studies related to Cu and Fe isotope fractionation during (bio)leaching are performed using mono-mineral solids or sulphide rich rocks, taking into account factors such as pH, mineral recovery and microbial activity among others (Fernandez and Borrok, 2009; Kimball et al., 2009). However, the redox potential in those investigations has not been well controlled. In the present study, a bioleaching experiment was performed and later its redox potential conditions were mimicked by using an electrochemical cell equipped with a redox potential controller. As a result, the same leaching conditions as in the bioleaching experiment were reproduced in the absence of bacteria. This study aims to establish the effect of microbial activity in the isotope fractionation of Cu and Fe during chalcopyrite bioleaching and to analyse the implications of the obtained results in natural systems.

2. Materials and methods

2.1. Leaching material

The material used in the leaching experiments was a Cu concentrate from the Kristineberg mine in northern Sweden (Boliden Mineral AB). The chemical analysis of the concentrate was 23.6% Cu, 34.7% Fe, 37.5% S, 2.1% Zn and 0.7% Pb. XRD analysis confirmed only the presence of chalcopyrite and pyrite in the concentrate. Before the addition to the leaching reactors, the concentrate was ground to a particle size with d_{80} of less than 45 μm. In the electrochemical experiment, the concentrate was kept at 110 °C for 2 h prior to grinding in order to inhibit microbial activity.

2.2. Microorganisms

In the bioleaching experiment, a mixed culture of moderately thermophilic acidophiles was used. The culture contained clones related to *Acidithiobacillus caldus* C-SH12, *Sulfobacillus thermosulfidooxidans* AT-1, *Sulfobacillus montserratensi* L15, and an uncultured thermal soil bacterium YNP (Dopson and Lindström, 2004). The mineral salt medium (MSM) with the following composition: (in g/L) 3 $(NH_4)SO_4$, 0.1 KCl. 0.01 $CaNO_3 \cdot 4H_2O$, 0.5$MgSO_4 \cdot 7H_2O$, 0.05 K_2HPO_4 and 3.3 Na_2SO_4 was used as the nutrient medium and pH was adjusted to 1.5 with 5 M H_2SO_4. The bacterial culture was activated in an adaptation bioreactor where Cu concentrate was gradually added up to a content of 2.5% (w/v).

2.3. Bioleaching experiment

In the bioleaching experiment, 2.5% (w/v) of the concentrate was added to a 2 L baffled reactor at 45 °C containing 0.9 L of MSM. Air was blown into the reactor at a rate of 1 L/min. pH was adjusted to 1.5 with 5 M H_2SO_4 or 5 M NaOH solutions. Redox potential was measured using a platinum electrode with a Ag/AgCl reference electrode (Metrohm). All the reported redox potential values in this paper are versus the Ag/AgCl reference electrode, unless otherwise specified. The bioleaching reactor was inoculated with 10% (v/v) of the solution from the active microbial culture giving a total leaching volume of 1 L. For confirmation of the microbial culture activity, a control experiment with the same conditions was carried out where 0.8 g/L of thymol was added to inhibit the bacterial activity. The tests continued 28 days for the bioleaching experiment and 19 days for the abiotic experiment. Samples were taken for isotope analysis at different levels of redox potential.

2.4. Electrochemical leaching experiment

An electrochemical cell was used to carry out a controlled redox potential leaching experiment (Harvey and Crundwell, 1997). The recorded redox potential values during the bioleaching experiment were modelled versus the leaching time and the model was used to automatically control the redox potential in the electrochemical vessel. Leaching was carried out in the cathode side of the cell under exactly similar conditions as in the bioleaching experiment. O_2 or H_2O_2 was used as the oxidising agent to increase the redox potential. At any given time, if the redox potential was higher than the set value defined by the model, automatically a current was applied to reduce the iron from ferric to ferrous, and consequently decreasing the redox potential back to the set value. Samples were taken at the same intervals as in the bioleaching experiment. No bacterial cells in the pulp were visible under optical microscopy inspection after the experiment.

2.5. Chemical analysis

Solution samples were analysed for dissolved Cu and Fe by Atomic Absorption Spectroscopy (AAS; Perkin Elmer, Analyst 100). Total iron concentration was determined by AAS after dissolution of iron precipitates in 6 M HCl. Residue samples were digested by alkali fusion or microwave-assisted acid digestion in closed vessels and analysed for Cu and Fe by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) according to US-EPA methods 200.8 (modified) and 200.7 (modified). The instrumental precision was better than 5% based on long-term variations.

2.6. Isotope analysis

Samples for isotope analyses were taken from the bioleaching experiment at different stages of microbial activity: at redox potential 395 mV (day 5.2) when the culture started to become active, at redox potential