Minerals Engineering 92 (2016) 229–241

Contents lists available at ScienceDirect

Minerals Engineering

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

Simulating the main stages of chalcopyrite leaching and bioleaching in ferrous ions solution: An electrochemical impedance study with a modified carbon paste electrode

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ARTICLE INFO

Article history:
Received 17 June 2015
Revised 21 March 2016
Accepted 22 March 2016
Available online 29 March 2016

Keywords:
Carbon paste-chalcopyrite electrode
EIS
Ferrous ions effect
Acidithiobacillus ferrooxidans

ABSTRACT

In this work, we present an electrochemical study using a carbon paste electrode modified with chalcopyrite ($CuFeS_2$) in solution A of T&K medium with different ferrous ion concentrations, in the absence and presence of the bacterium *Acidithiobacillus ferrooxidans*. The aim was to evaluate the influence of ferrous ions and bacteria on the electrochemical behavior of chalcopyrite. Electrochemical impedance spectroscopy (EIS) was used to investigate the processes occurring at the electrode/solution interface in the different systems, considering the charge transfer reactions involving chalcopyrite and ferrous ions, the presence of a multicomponent layer, and diffusion. The main changes in the chalcopyrite response occurred before 67 h or 43 h of immersion, in the absence or presence of ferrous ions, respectively, indicating that the surface oxide layer present on chalcopyrite was dissolved faster in the presence of ferrous ions. The addition of bacteria decreased the charge transfer reaction resistance, especially when ferrous ions were present. In the presence of Fe^{2+}, sulfur and jarosite were detected in the solid residues after leaching, while only jarosite was detected in the bioleaching experiment. The results suggested that ferrous ions accelerated the dissolution of chalcopyrite, and that overlayers including biofilms did not halt chalcopyrite dissolution, indicating that there was no passivation.

1. Introduction

Copper is increasing in importance worldwide due to its use in the construction and appliance industries. Although the value of the metal varies according to market conditions, investment in exploration activities continues. China is the world's largest consumer of copper, and the largest producer of the metal is Chile. Copper and other metals can be recovered from byproducts of mining using conventional extraction or alternative processes such as biohydrometallurgy, which is mainly employed in metal recovery from low-grade ore and in adverse locations. Microorganisms are used in this process, with the most studied acidophilic bacterium being *Acidithiobacillus ferrooxidans*, which has been found to be capable of promoting oxidation of the mineral sulfide, hence facilitating metal recovery (Gahan et al., 2012).

The dissolution of several mineral sulfides has been studied, and the formation of new phases is widely reported in the literature (Bevilaqua et al., 2010; Monteiro et al., 1999; Sasaki et al., 1998). In the specific case of chalcopyrite ($CuFeS_2$), the most refractory and abundant copper source, it is understood that bacteria oxidize Fe^{2+} to Fe^{3+} ions, which attack the mineral sulfide (Bevilaqua et al., 2010). However, the refractory nature of this mineral sulfide prevents the achievement of high metal recoveries, and there is no agreement in the literature about the reasons for the slow dissolution rate of chalcopyrite (Crundwell, 2013; Holmes and Crundwell, 2013; Khoshkhoo et al., 2014a,b).

Recovery during the bioleaching process has been associated with the refractory properties of chalcopyrite and the formation of secondary surface species such as elemental sulfur, covellite (CuS), jarosites ($XFe(SO_4)_2(OH)_6$, where $X = K^+$, NH_4^+, Na^+, or H_3O^+), copper polysulfide (CuS_n), and non-stoichiometric copper compounds. These are detrimental to the oxidation of the surface by microorganisms and, consequently, to the extraction of copper (Córdoba et al., 2008; Hackl et al., 1995; Li et al., 2013; Sasaki et al., 2009).

Among the strategies that can be used to overcome this limitation can be highlighted the prevention and/or modification of the

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http://dx.doi.org/10.1016/j.mineng.2016.03.025
0892-6875/

surface layer formed during the oxidation process, by means of chemical or electrochemical control of the redox potential of the medium. Control of the redox potential of the Fe^{3+}/Fe^{2+} pair can minimize the formation of iron precipitates, mainly by keeping the Fe^{3+}/Fe^{2+} ratio low (Córdoba et al., 2008; Hiroyoshi et al., 2008a; Qin et al., 2013). There are many ways of controlling the potential, using the supply of oxygen (Third et al., 2002), addition of sodium sulfite (Sandström et al., 2005), use of chalcopyrite with a higher percentage of pyrite (FeS_2) (Hiroyoshi et al., 2008b), and imposition of potential by means of electrochemical techniques such as potentiostatic reduction (Nava et al., 2008), potential pulses (Lara et al., 2013), and cyclic voltammetry (Qin et al., 2013). Depending on the potential range imposed, different phases are formed on the surface, including bornite, covellite, elemental sulfur, non-stoichiometric copper compounds, and chalcocite (Ahmadi et al., 2011; Gu et al., 2013; Lara et al., 2013; Majuste et al., 2012; Nava et al., 2008). Generally, the imposed potential causes the reduction of chalcopyrite, which permits the extraction of iron from the crystalline structure, forming copper sulfides that are more susceptible to oxidative leaching (Gu et al., 2013). Additionally, the formation of jarosite under these conditions seems to be insufficient to block the surface, because these compounds are highly porous and are easily lost from the surface (Gu et al., 2013). Recently, Khoshkhoo et al. (2014a) studied a concentrated copper powder from the Boliden mine (Sweden), with application of a controlled redox potential, and concluded that a multi-component surface layer consisting mainly of elemental sulfur and iron oxyhydroxides was responsible for hindering dissolution. Jarosite was eliminated from the list of possible substances that might be responsible for hindering chalcopyrite dissolution, and elemental sulfur was considered the main component of the obstructive layer. In other work, the only confirmed products resulting from the mineral oxidation were sulfur and jarosites (Klauber, 2008). Polysulfides do not passivate the chalcopyrite surface and the solids formed during the oxidation do not need to be electrical conductors to dissolve according to the electrochemical mechanism (Crundwell, 2013). The methodologies employed to identify the chalcopyrite surface layers and their implications have been criticized because of the absence of kinetic parameters (Crundwell, 2013).

In conclusion, electrochemical tests are important as alternatives for the study of bioleaching systems, because they enable assessment of the influence of ferric/ferrous ions on chalcopyrite, as well as evaluation of the possible influence of the redox potential in a medium that simulates the leaching conditions. These assays have the advantages of speed, convenience, relatively low cost, high sensitivity, low power consumption, and the use of small amounts of samples and reagents. In the specific case of electrochemical impedance spectroscopy, there is the additional advantage of being a transient technique in which the AC signal is applied to the system for only a short period, avoiding any detrimental effects on microorganisms. The oxidation of chalcopyrite by *At. ferrooxidans* has been studied using EIS techniques, including analysis of the correlation between changes in the mineral surface and bacterial adhesion (Bevilaqua et al., 2004), and the bioleaching of residues (Bevilaqua et al., 2013).

Considering that iron ions are ubiquitous in copper-based minerals such as chalcopyrite, the oxidant activity in bioleaching processes always leads to the formation of ferric ions and sulfuric acid (Bevilaqua et al., 2002). It was therefore decided to use EIS to compare the influence of redox potential on chalcopyrite dissolution, using different concentrations of ferrous ions and in the presence and absence of bacteria. A carbon paste electrode modified with chalcopyrite was utilized as the working electrode because of its advantages compared to massive electrodes. The latter tend to fracture during the polishing procedure and the resulting irregular and heterogeneous surface can affect the reliability of data recorded over the course of an experiment (Horta et al., 2009). The repeatability of this carbon paste electrode has already been proved in a previous study (Horta et al., 2009). The present work concerns the use of electrochemistry to study a system that simulates the main stages of chalcopyrite leaching and bioleaching in the presence of ferrous ions. The goal was to evaluate the ways in which the chemical potential imparted to the system by controlling the Fe^{2+} ions concentration could influence the electrochemical response.

2. Electrochemical impedance spectroscopy

When the applied perturbation is an AC potential and the response is an AC current, and vice versa, the transfer function is the impedance. Electrochemical impedance spectroscopy (EIS) is a method in which the impedance of an electrochemical system is measured as a function of the frequency of an applied AC wave. In this process, after the system has attained equilibrium or steady state, it is perturbed by applying an AC signal, so a new equilibrium or steady state is reached. The time (in seconds) taken for this relaxation is known as the time constant, τ, which is given by:

$$\tau = RC,$$

where R is the resistance (in ohms) and C is the capacitance (in farads). The time constant is characteristic of each event occurring in the system.

To simplify calculations, the perturbation and response are transformed from the time domain to the frequency domain using a Laplace transformation. In the frequency domain, fast processes (low τ values) occur at high frequencies, while slow processes (high τ values) occur at low frequencies. The frequency around which a process occurs may be ascertained using:

$$F = 1/2\pi\tau$$

A great advantage of EIS is the wide frequency window normally employed (10^{-3} to 10^{5} Hz), which enables investigation of all the processes occurring in this time domain. As a consequence, several time constants can be identified in the frequency range studied. Hence, solution resistance, porous layers, and barrier layers can be studied at high frequencies; intermediate frequencies can be used in the case of bulk properties, fast charge transfer processes, and oxide layer properties; and surface properties, slow charge transfer processes, and diffusion phenomena can be investigated at low frequencies. In simple terms, impedance may be considered as the 'resistance' to the flow of alternating current:

$$\widetilde{E} = \widetilde{I}Z,$$

where E and I are the waveform amplitudes for potential and current, respectively, and Z is the impedance. Two different components contribute to impedance: a real component due to the resistive response associated with resistors, generally represented by Z_{real} or Z'; and an imaginary component related to the capacitive or inductive response associated with capacitors, inducers, etc., represented by $-Z_{imag}$ or $-Z''$.

The impedance Z is a complex quantity that depends on the frequency ($\omega = 2\pi f$, where ω is given in radians and f in Hz), and for each frequency it is only possible to measure one impedance value, except in the case of a pure resistor where $Z(\omega) = R$, a point on the Z_{real} axis of the Nyquist plot. The impedance in Cartesian coordinates is given by:

$$Z(\omega) = Z_{real}(\omega) - jZ_{imag}(\omega),$$

where j is a complex number and $j^2 = -1$.