



# Electrochemical simulation of redox potential development in bioleaching of a pyritic chalcopyrite concentrate



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## ABSTRACT

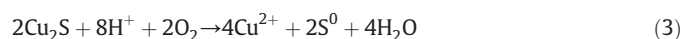
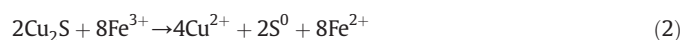
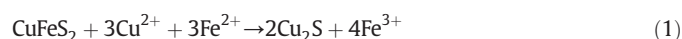
The majority of the world's copper reserves are bound in the sulphide mineral chalcopyrite ( $\text{CuFeS}_2$ ), but supply of the copper is hindered by the recalcitrance of chalcopyrite to (bio)leaching. The main reason for the slow rate of chalcopyrite dissolution is the formation of a layer on the surface of the mineral that hinders dissolution, termed "passivation". The nature of this layer and the role of microorganisms in chalcopyrite leaching behaviour are still under debate. Moderately thermophilic bioleaching of a pyritic chalcopyrite concentrate was mimicked in an electrochemical vessel to investigate the effect of the absence and presence of microorganisms in copper dissolution efficiency. Data from the redox potential development during bioleaching was used to program a redox potential controller in an electrochemical vessel to accurately reproduce the same leaching conditions in the absence of microorganisms. Two electrochemical experiments were carried out with slightly different methods of redox potential control. Despite massive precipitation of iron as jarosite in one of the electrochemically controlled experiments and formation of elemental sulphur in both electrochemical experiments, the efficiencies of copper dissolution were similar in the electrochemical tests as well as in the bioleaching experiment. No passivation was observed and copper recoveries exhibited a linear behaviour versus the leaching time possibly due to the galvanic effect between chalcopyrite and pyrite. The data suggest that the main role of microorganisms in bioleaching of a pyritic chalcopyrite concentrate was regeneration of ferric iron. It was also shown that the X-ray photoelectron spectroscopy measurements on the residues containing bulk precipitates cannot be employed for a successful surface characterisation.

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## 1. Introduction

Chalcopyrite ( $\text{CuFeS}_2$ ) is both the most economically important and the most difficult copper mineral to (bio)leach. The main reason for the slow rate of chalcopyrite dissolution is the formation of a layer on the surface of the mineral that hinders dissolution, termed "passivation" (Gómez et al., 1996). This has directed several recent investigations towards employing surface analytical methods such as X-ray photoelectron spectroscopy (XPS) for identification of the species that might be responsible for passivation. XPS is a powerful tool for surface analysis to a depth of a few nanometres but data analysis for chalcopyrite is difficult and its interpretation varies widely amongst different authors. Therefore, there is not a clear consensus about the nature of the passivating layer and it is still under debate with jarosite, elemental sulphur, polysulphides and metal-deficient sulphides being the main candidates (Klauber, 2008). Reviews on the available information regarding the chalcopyrite surface oxidation products and its passivation have recently been published (Debernardi and Carlesi, 2013; Li et al., 2013).

There are many factors involved in chalcopyrite passivation such as temperature, acidity, type and concentration of the oxidant and the redox potential of the solution. Redox potential has a prominent effect on the rate and extent of chalcopyrite passivation and is one of the most researched factors (Córdoba et al., 2008; Sandström et al., 2004; Third et al., 2002). It has been proposed that the rate of chalcopyrite dissolution increases with increasing redox potential and then decreases after a critical potential is reached (Kametani and Aoki, 1985). A two-step model was proposed to support faster chalcopyrite leaching rates at lower oxidation potentials (Hiroyoshi et al., 2000, 2001, 2004, 2008). The model suggests that in the first step chalcopyrite is reduced by ferrous ions in the presence of cupric ions to form chalcocite (Eq. (1)). In the second step, chalcocite which is more amenable to leaching than chalcopyrite is oxidised by ferric ions or oxygen according to Eqs. (2) and (3).

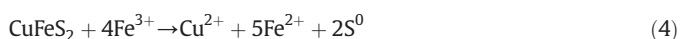


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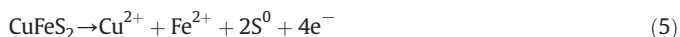
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This model suggests that the redox potential has to be low enough for reduction of chalcopyrite in the first step and high enough for oxidation of chalcocite in the second step. Consequently, there is a range of oxidation potential in which the chalcopyrite dissolution rate is optimum (Sandström et al., 2004). Reported ranges vary widely but many studies place the optimum bioleaching between 610 and 690 mV vs SHE (Koleini et al., 2011) although critical points as high as 690 to 730 mV vs SHE have been reported (Dixon et al., 2008). The wide variation in the optimum redox potential window is dependent on the copper concentrate and arises due to differences in crystal orientation, impurity content and mineral stoichiometry (Tshilombo, 2004).

One successful method to overcome the slow rate of chalcopyrite leaching is the Galvanox™ process (Dixon et al., 2008) that is based on the galvanic effect between contacting minerals with different rest potentials. The mineral with higher rest potential, in this case pyrite, acts as cathode and the mineral of interest (chalcopyrite) with a lower rest potential serves as anode and is oxidised. The overall reaction for oxidation of chalcopyrite via ferric ion is given as:



This reaction can be written as two half-cell reactions; an anodic half-cell reaction (Eq. 5) and a cathodic half-cell reaction (Eq. (6)).



The limiting step is reported to be the reduction of iron (Eq. (6)) which is slow on the surface of chalcopyrite (Dixon et al., 2008; Tshilombo, 2004). When pyrite and chalcopyrite are in contact, the iron reduction takes place on the pyrite surface, thus improving the dissolution rate.

Bioleaching is considered to be an attractive process for extraction of copper from low grade copper sources. Bacterial heap leaching of secondary copper minerals (covellite and chalcocite) is currently practiced on an industrial scale, while its use for chalcopyrite is limited, mostly due to the passivation problem (Sandström et al., 2004). A popular method to investigate the influence of bacterial activity on leaching of different sulphide minerals is comparison of the leaching kinetics with and without bacteria (Crundwell, 2003). For chalcopyrite, there are already contradictory results with different investigations showing that the bacterial activity is either detrimental, has no effect or is beneficial to chalcopyrite leaching (Third et al., 2000). The results of most of these works are summarised in a recent review (Li et al., 2013). In general, most of these studies suffer from a lack of accurate redox potential control in their abiotic experiments. As a result, data comparing biotic and abiotic systems does not conclusively support a clear answer to the question of bacterial role on leaching efficiency (Crundwell, 2003). By using an electrochemical cell equipped with a redox potential controller, this problem was overcome (Harvey and Crundwell, 1997). Using this method, bioleaching of pyrite with a pure culture of *Acidithiobacillus ferrooxidans* at constant redox potentials was investigated (Fowler et al., 1999). In another investigation, similar experiments on sphalerite were performed (Fowler and Crundwell, 1999). Investigations of this kind have not been reported on chalcopyrite.

In the present study, redox potential data from moderately thermophilic batch bioleaching of a pyritic chalcopyrite concentrate was used to mimic the redox potential development using an electrochemical cell equipped with an automatic redox potential controller. This reproduced the same leaching conditions in the absence of microorganisms and made it possible to investigate the role of microorganisms on chalcopyrite leaching efficiency. This is the first study of its kind to investigate chalcopyrite leaching under controlled, variable redox potentials.

## 2. Material and methods

### 2.1. Material

A copper concentrate from the Boliden owned Kristineberg mine in Sweden was used. The concentrate contained 23.6% copper, 34.7% iron, 37.5% sulphur, 2.1% zinc, 0.7% lead and 1.1% silica. X-ray diffraction analysis could only reveal the presence of chalcopyrite and pyrite in the concentrate since other species were too low in concentration. SEM photographs showed that the pyrite and chalcopyrite grains mostly exist as separate grains. Calculated mineralogy gave the approximate composition as: 68% chalcopyrite, 26% pyrite, 3.2% sphalerite and 0.8% galena.

In the bioleaching and electrochemically controlled varying redox potential experiments, the concentrate was ground in a ring mill to a particle size with  $d_{80}$  of minus 45  $\mu\text{m}$  and a mean diameter of 27  $\mu\text{m}$  before it was added into the reactors. The grinding was carried out immediately before addition of the concentrate into the reactors to avoid surface oxidation by air and to provide more or less the same initial surface characteristics of the concentrate in all the experiments. In the electrochemically controlled experiments with varying redox potentials, the concentrate was kept at 110 °C for two hours prior to grinding in order to prohibit the activity of microorganisms. In the electrochemically controlled experiments with constant redox potential, the concentrate was used as received from Boliden Mineral AB with a particle size of  $d_{80}$  minus 80  $\mu\text{m}$  and a mean diameter of 45  $\mu\text{m}$ .

### 2.2. Microorganisms

A mixed culture of moderately thermophilic acidophiles was grown in mineral salt medium (MSM) (Dopson and Lindström, 2004) containing, per litre, 3 g  $(\text{NH}_4)_2\text{SO}_4$ , 0.1 g KCl, 0.01 g  $\text{CaNO}_3 \cdot 4\text{H}_2\text{O}$ , 0.5 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.05 g  $\text{K}_2\text{HPO}_4$  and 3.3 g  $\text{Na}_2\text{SO}_4$  at 45 °C. The moderately thermophilic culture contains strains related to *A. ferrooxidans*, *Acidithiobacillus caldus* C-SH12, *Sulfobacillus thermosulfidooxidans* AT-1, "*Sulfobacillus montserratensis*" L15 and an uncultured thermal soil bacterium YNP ((Dopson and Lindström, 2004) and unpublished data). The copper concentrate was gradually added to the adaptation bioreactor up to a solid content of 2.5% (wt/vol).

### 2.3. Bioleaching

A batch bioleaching experiment was performed in a 2 L baffled reactor at 45 °C. Air at a rate of 1 L/min was blown into the reactor. The reactor was inoculated with 10% (vol/vol) of the active microbial culture giving a total initial concentration of 140 mg Fe/L, 90 mg Cu/L and 21 mg Zn/L. In order to avoid excessive precipitation during the experiment and to facilitate subsequent surface analysis, a solid content of 2.5% (wt/vol) was used. The redox potential was regularly recorded 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 pH was frequently checked and adjusted to 1.5 by addition of 5 M sulphuric acid or 5 M sodium hydroxide solution. Samples were taken at regular intervals for analysis of dissolved copper and iron as well as the iron which has been leached and subsequently precipitated. At day 28, the experiment was terminated and the pulp filtered. The residue was washed and then dried overnight and saved for further analysis. In order to validate the activity of the culture, an abiotic experiment under the same leaching conditions and sampling procedure was performed, where 0.8 g/L (wt/vol) of thymol was used for prohibition of bacterial activity.

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