



Chalcopyrite leaching and bioleaching: An X-ray photoelectron spectroscopic (XPS) investigation on the nature of hindered dissolution



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ABSTRACT

Chalcopyrite (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”. The nature of this layer is still under debate. In this work, the role of bacterial activity was examined on the leaching efficiency of chalcopyrite by mimicking the redox potential conditions during moderately thermophilic bioleaching of a pure chalcopyrite concentrate in an abiotic experiment using chemical/electrochemical methods. The results showed that the copper recoveries were equal in the presence and absence of the mixed culture. It was found that the presence of bulk jarosite and elemental sulphur in the abiotic experiment did not hamper the copper dissolution compared to the bioleaching experiment. The leaching curves had no sign of passivation, rather that they indicated a hindered dissolution. XPS measurements carried out on massive chalcopyrite samples leached in the bioleaching and abiotic experiments revealed that common phases on the surface of the samples leached for different durations of time were elemental sulphur and iron-oxyhydroxides. The elemental sulphur on the surface of the samples was rigidly bound in a way that it did not sublime in the ultra-high vacuum environment of the XPS spectrometer at room temperature. Jarosite was observed in only one sample from the abiotic experiment but no correlation between its presence and the hindered leaching behaviour could be made. In conclusion, a multi-component surface layer consisting of mainly elemental sulphur and iron-oxyhydroxides was considered to be responsible for the hindered dissolution.

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1. Introduction

Copper recovery via hydrometallurgy represented 22% of the 2012 worldwide copper production (ICSG, 2013). This mostly came from heap (bio)leaching of oxides and secondary sulphide minerals (covellite (CuS) and chalcocite (Cu_2S)). Bio-hydrometallurgical treatment of low-grade sulphide ores offers an attractive alternative to conventional pyrometallurgical routes in terms of both economy and environmental issues. However, bio-hydrometallurgical processes, such as heap bioleaching, are not a viable industrial option for the most economically important copper mineral, i.e. chalcopyrite (CuFeS_2). Chalcopyrite leaching in ferric sulphate medium has a low leaching yield and is usually very slow. Therefore, much research has been focused on

different aspects of chalcopyrite (bio)leaching including electrochemistry, dissolution mechanism, kinetics of dissolution, effect of leaching factors (pH, temperature, oxidant and redox potential), galvanic effect and leaching efficiency in the presence of different microbial cultures. Reviews on the available information regarding chalcopyrite leaching can be found elsewhere (Debernardi and Carlesi, 2013; Li et al., 2013).

The mechanism of bioleaching and the interaction between the microorganisms and sulphide minerals are among the hottest research subjects in the field (Olson et al., 2003; Rohwerder et al., 2003). A popular method to investigate the influence of bacterial activity on leaching of different sulphide minerals is the comparison of the leaching kinetics with and without bacteria (Crundwell, 2003). There is much contradictory data on chalcopyrite (bio)leaching with different investigations showing that the bacterial activity is either detrimental, has no effect or is beneficial to copper release (Third et al., 2000). In general, most of these studies suffer from a lack of accurate solution potential control in their abiotic experiments (Crundwell, 2003). Redox potential of a solution (E_h) is mainly determined by the ratio of the activities of

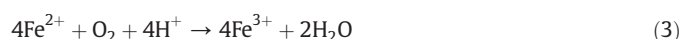
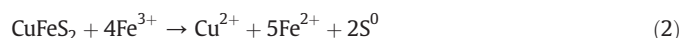
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ferric to ferrous ions in chalcopyrite leaching systems according to the Nernst equation (Eq. (1)) for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple:

$$E_h = E^\circ + \frac{R \cdot T}{n \cdot F} \cdot \ln \left\{ \frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \right\} \quad (1)$$

where E° is the standard electrode potential, R is the gas constant, $n = 1$ (number of transferred electrons) and F is the Faraday's constant. In bioleaching systems, chalcopyrite oxidation by ferric ions (Eq. (2)) results in ferric reduction and the redox potential decreases, while microbial activity oxidises ferrous ions back to ferric (Eq. (3)) and increases the solution potential. Thus, the redox potential is an outcome of the microbial activity as well as the mineral reactivity and depending on the leaching conditions, it considerably varies during bioleaching.



Solution redox potential is possibly the most important factor affecting chalcopyrite leaching (Hiroyoshi et al., 2000, 2001, 2004, 2008; Kametani and Aoki, 1985; Sandström et al., 2004) and it is vital to reproduce the redox potential conditions in abiotic and biotic leaching experiments. This can be achieved using an electrochemical cell equipped with an automatic redox potential controller (Harvey and Crundwell, 1997). When chalcopyrite is leached (Eq. (2)) in the cathode side of the vessel, the redox potential decreases while chemical or bacterial ferrous oxidation (Eq. (3)) raises the redox potential. Conversely, if the redox potential is higher than the set value, an electrical current is applied to reduce the ferric back to ferrous (Eq. (4)). Water decomposes on the anode electrode (Eq. (5)) and protons migrate to the working compartment through the cationic membrane to keep the charge balance in the cell.



Using this method to control the solution potential at a constant set value is reported for bioleaching of pyrite (Fowler et al., 1999) and sphalerite (Fowler and Crundwell, 1999). A similar method was used to mimic the development of recorded redox potential data from the whole duration of a moderately thermophilic bioleaching experiment of a pyritic chalcopyrite concentrate (Khoshkhoo et al., 2014) and it was found that both recovery and rate of copper dissolution in the presence of microorganisms were the same as in their absence. Investigations of this kind have not been reported on pure chalcopyrite concentrates.

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). Several recent investigations have been directed towards employing surface analytical methods such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) for the identification of the passivating species. Unfortunately, there is not a clear consensus about the nature of the passivating layer with polysulphides, metal-deficient sulphides, jarosite and elemental sulphur being the main candidates (Debernardi and Carlesi, 2013). These candidates have been reviewed and polysulphides were rejected as candidates and the physical reality of the metal-deficient sulphides was also questioned (Klauber, 2008).

Besides potential problems with applying XPS and AES surface analysis techniques such as data interpretation, a source of uncertainty in the nature of the passivation layer is found in the diverse experimental

conditions employed. Many of the studies fail to correlate leaching kinetics with the observed surface species. It is well known that many surface compounds are found on chalcopyrite surface exposed to air (Brion, 1980). Samples treated even for a short time in an oxidising solution definitely show a greater extent of surface products. However, if the dissolution rate is not measured, it is impossible to correlate the observed surface species to its leaching behaviour. Another problem with XPS investigations is carrying out measurements on finely ground chalcopyrite concentrates that can be misleading due to the possible presence of bulk elemental sulphur and jarosite in the residue (Khoshkhoo et al., 2014). Elemental sulphur is a chalcopyrite dissolution product (Eq. (2)). Depending on the leaching conditions, jarosite formation is also a typical phenomenon during chalcopyrite leaching. The XPS data obtained on such residues also represent the surface of the bulk compounds. As a result, appropriate measures must be taken to produce a leached sample surface free of bulk elemental sulphur and other possible bulk precipitates.

In the present study, redox potential development during moderately thermophilic bioleaching of a chalcopyrite concentrate was reproduced via chemical/electrochemical methods. This reproduced the same leaching conditions in the absence of microorganisms and made it possible to investigate their role on chalcopyrite leaching efficiency. XPS measurements of massive chalcopyrite samples coupled with the chalcopyrite leaching behaviour correlated the chalcopyrite surface structure to its leaching behaviour.

2. Material and methods

2.1. Chalcopyrite concentrate

A high purity chalcopyrite concentrate from the Boliden owned Aitik mine in Sweden was used. Chemical analyses revealed that the concentrate contained 32.4% copper, 30.9% iron, 34.1% sulphur, 0.53% silica, 0.11% zinc and 0.05% lead. X-ray diffraction analysis only showed chalcopyrite in the concentrate. Chalcopyrite was also the only copper mineral that could be found in SEM photographs and EDS analyses. By assuming that all the copper content was present as chalcopyrite, it had a chalcopyrite grade of 94%. The concentrate was ground in a ring mill immediately before addition into the reactors to avoid extensive surface oxidation of the concentrate as well as producing comparatively similar initial surface characteristics in all experiments. Eighty percent of the ground concentrate was <45 µm and the mean diameter was 27 µm. In the abiotic experiment with controlled varying redox potentials, the concentrate was kept at 110 °C for 2 h prior to grinding in order to prohibit the activity of microorganisms.

2.2. Massive chalcopyrite samples

For XPS measurements, chalcopyrite pieces (from Aitik mine) with an approximate dimension of $3 \times 3 \times 3$ mm and an average weight of 60 mg were made. Each cube was produced such that it had at least two chalcopyrite faces verified by XPS measurements (see the Results and discussion section). The samples were polished and rinsed with ethanol immediately before being used in the experiments.

2.3. Microorganisms

Mineral salt medium (Dopson and Lindström, 2004) was used for growing a mixed culture of moderately thermophilic acidophiles at 45 °C. The culture contained strains related to *Acidithiobacillus ferrooxidans*, *Acidithiobacillus caldus* C-SH12, *Sulfobacillus thermosulfidooxidans* AT-1, “*Sulfobacillus montserratensis*” L15 and an uncultured thermal soil bacterium YNP (Dopson, 2004; Dopson and Lindström, 2004). The concentrate was gradually added to the adaptation bioreactor up to a solid content of 2.5% (wt/vol).

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