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# New insights into the influence of redox potential on chalcopyrite leaching behaviour



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#### ABSTRACT

Chalcopyrite (CuFeS<sub>2</sub>) is the most economically important and most refractory copper mineral when treated in conventional sulphate media leaching systems. In this study, the effect of solution redox potential on leaching of a pure and a pyritic chalcopyrite concentrate was investigated using concentrates with fresh and aged surfaces. In experiments using concentrates with fresh surfaces, the response to redox potential depended on the presence of pyrite: fresh pyritic concentrate leached more effectively at low redox potential (in agreement with reductive leaching mechanisms), while the leaching efficiencies from fresh pure concentrate were similar at high and low redox potentials. The data suggested that the reductive leaching mechanism does not necessarily result in higher and faster recoveries in the absence of the galvanic interaction induced by the presence of pyrite. It was also found that exposure of chalcopyrite to atmospheric oxidation prior to leaching (ageing) had an effect on leaching behaviour in response to redox potential: copper recoveries in leaching of aged concentrates were higher at high redox potentials. This behaviour was attributed to the presence of iron–oxyhydroxides on the surface of aged concentrates. Based on the data from this investigation and previous surface studies, it is proposed that iron– oxyhydroxides play an important role in triggering the hindered dissolution of chalcopyrite.

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#### 1. Introduction

As the most abundant copper mineral, chalcopyrite (CuFeS<sub>2</sub>) is the most economically important copper resource. Leaching of chalcopyrite in sulphate media is mainly preferred for its easy handling and compatibility with established chalcocite (Cu<sub>2</sub>S) and covellite (CuS) heap leaching/bioleaching processes as well as with conventional solvent extraction and electrowinning technologies (Marsden, 2007). However, the slow dissolution of chalcopyrite at ambient pressure in sulphate media has hindered its industrial application. Nevertheless, due to the continuous depletion of high grade ores, future hydrometallurgical alternatives for chalcopyrite treatment will increase in importance and applications. As a result, different aspects of chalcopyrite leaching have been extensively researched in recent decades. A summary of these studies can be found in Debernardi and Carlesi (2013) and Li et al. (2013). A review of hydrometallurgical options for chalcopyrite treatment is available in Dreisinger (2006) amongst others.

The slow dissolution of chalcopyrite is termed 'passivation' or 'hindered dissolution' and is believed to be due to formation of

\* Corresponding author. *E-mail address:* mohammad.khoshkhoo@ltu.se (M. Khoshkhoo). compounds on the mineral surface during leaching. The most frequently suggested candidates to form the passivating layers are metal-deficient phases, elemental sulphur and jarosite (Klauber, 2008). Recently iron–oxyhydroxides have also been proposed to cause passivation (Khoshkhoo et al., 2014a). Similarly, other aspects of chalcopyrite (bio)leaching, such as the mechanism, kinetics, role of microorganisms and effect of different leaching parameters are still under debate. A short review of the concepts that are central to the discussions presented in this investigation is given in the following sections.

#### 1.1. Galvanic dissolution of chalcopyrite

The effect of impurities on the dissolution of chalcopyrite is a relatively old observation (Dutrizac and MacDonald, 1973). For sulphide minerals that are in contact with each other, the mineral with higher rest potential acts as a cathode and is preserved, while the mineral with lower rest potential acts as an anode and is oxidised (Mehta and Murr, 1983). For chalcopyrite, pyrite gives rise to increased copper release as it acts as the cathode and chalcopyrite serves as the anode and is oxidised. The main reaction for chalcopyrite dissolution in ferric/ferrous sulphate systems is the oxidation of chalcopyrite by ferric ions:



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

Being electrochemical in nature, this reaction can be expressed as an anodic half-cell reaction (Eq. (2)) and a cathodic half-cell reaction (Eq. (3)):

$$CuFeS_2 \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 4e^-$$
 (2)

$$4Fe^{3+} + 4e^{-} \to 4Fe^{2+}$$
(3)

The limiting step is reported to be the reduction of ferric iron which is slow on the surface of chalcopyrite due to presence of hindering layers (Dixon et al., 2008). When pyrite and chalcopyrite are in contact, the iron reduction takes place on the pyrite surface, which is much faster. As a result, the total dissolution rate is increased.

#### 1.2. Reductive leaching mechanism

Reductive leaching of chalcopyrite generally refers to dissolution of chalcopyrite at low redox potential. The redox potential of a system containing ferric and ferrous ions is mainly determined by the ratio of free ferric to ferrous ions, according to the Nernst equation (Eq. (4)):

$$E_h = E^\circ + \frac{R \cdot T}{n \cdot F} ln \frac{\{\mathrm{Fe}^{3+}\}}{\{\mathrm{Fe}^{2+}\}}$$

$$\tag{4}$$

where  $E^{\circ}$  is the standard electrode potential, *R* is the gas constant, *n* is the charge number, *F* is Faraday's constant, and {Fe<sup>3+</sup>} and {Fe<sup>2+</sup>} are activities of ferric and ferrous ions, respectively. From chalcopyrite oxidation by ferric ions (Eq. (1)), it seems that higher redox potentials, i.e. higher ferric to ferrous ions concentrations, should favour its dissolution. This is not what is usually observed and instead, dissolution increases with increasing redox potential and then decreases after a critical potential is reached (Kametani and Aoki, 1985). A two-step model based on thermodynamic calculations was proposed to support this observation (Hiroyoshi et al., 2000). The model suggests that in the first step chalcopyrite is reduced by ferrous ions in the presence of cupric ions to form chalcocite (Eq. (5)). In the second step, chalcocite which is more amenable to leaching than chalcopyrite is oxidised by ferric ions or oxygen according to Eqs. (6) and (7).

$$CuFeS_2 + 3Cu^{2+} + 3Fe^{2+} \rightarrow 2Cu_2S + 4Fe^{3+}$$
(5)

$$2Cu_2S + 8Fe^{3+} \rightarrow 4Cu^{2+} + 2S^0 + 8Fe^{2+} \eqno(6)$$

$$2Cu_2S + 8H^+ + 2O_2 \rightarrow 4Cu^{2+} + 2S^0 + 4H_2O \tag{7}$$

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. Consequently, there is a window of oxidation potential in which the chalcopyrite dissolution rate is optimal. This range is reported to be around 600–680 mV vs SHE (Koleini et al., 2011) which is considered as a low redox potential level in chalcopyrite leaching systems.

The reductive leaching mechanism has also been described by another model based on evolution of surface layers measured by X-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (ToF-SIMS) and scanning electron microscopy (SEM) (Harmer et al., 2006). In this model, it is suggested that chalcopyrite is partially oxidised by ferric ions in the first step, resulting in a polysulphide phase and release of cupric and ferrous ions (Eq. (8)). The second step consists of reduction of the polysulphide intermediate by ferrous ions to sulphide (Eq. (9)) and finally, the sulphide is oxidised with ferric ions forming elemental sulphur accompanied by additional release of cupric and ferrous ions into the solution (Eq. (10)). This model also requires a relatively low redox potential to satisfy the conditions for oxidation and reduction reactions.

$$3n\text{CuFeS}_{2(\text{solid})} + (12n - 12)\text{Fe}_{(\text{aq})}^{3+} \rightarrow \left[4(\text{CuFe})^{4+} \cdot 6\left(\text{S}_{n}^{2-}\right)\right]_{(\text{solid})} + (3n - 4)\text{Cu}_{(\text{aq})}^{2+} + (15n - 16)\text{Fe}_{(\text{aq})}^{2+} \quad \text{where } n \ge 2$$
(8)

$$\begin{split} & \left[ 4(\text{CuFe})^{4+} \cdot 6\left(\text{S}_{n}^{2-}\right) \right]_{(\text{solid})} + (12n-12)\text{Fe}_{(\text{aq})}^{2+} + (12n-12)\text{H}_{(\text{aq})}^{+} \\ & \rightarrow \left[ 4(\text{CuFe})^{4+} \cdot (12n-12)\text{H}^{+} \cdot 6n(\text{S}^{2-}) \right]_{(\text{solid})} + (12n-12)\text{Fe}_{(\text{aq})}^{3+} \\ & \text{where } n \ge 2 \end{split}$$

$$\begin{split} & [4(\text{CuFe})^{4+} \cdot (12n-12)\text{H}^+ \cdot 6n(\text{S}^{2-})]_{(\text{solid})} + (12n)\text{Fe}^{3+}_{(\text{aq})} \to 6n\text{S}^0_{(\text{solid})} \\ & + 4\text{Cu}^{2+}_{(\text{aq})} + (12n+4)\text{Fe}^{2+}_{(\text{aq})} + (12n-12)\text{H}^+_{(\text{aq})} \quad \text{where } n \geqslant 2 \end{split}$$

In the present investigation, results from leaching of a pure concentrate as well as a pyritic concentrate performed under strictly controlled redox potential conditions are presented and the interaction of galvanic dissolution with reductive leaching mechanism is discussed.

#### 2. Materials and methods

#### 2.1. Aitik chalcopyrite concentrate (high purity concentrate)

A high purity chalcopyrite concentrate from the Boliden Mineral AB owned Aitik mine in Sweden was used. The concentrate was washed with ethanol and water, dried by acetone rinsing at room temperature, divided into 15 g lots, sealed in plastic containers flushed with nitrogen and kept at 4 °C. The concentrate was ground in a ring mill for 15 s immediately before addition to the leaching reactors. This procedure was carried out to assure presence of fresh chalcopyrite surfaces and comparatively similar initial surface characteristics in all the experiments. The reproducibility of the grinding procedure was tested in triplicates giving a  $d_{50}$  of  $18 \pm 1 \mu$ m, a  $d_{80}$  of  $42 \pm 3 \mu$ m and a specific surface area of

Table 1
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Chemical and mineralogical composition of the concentrate used in leaching experiments.

	Chemical composition (%)						Calculated mineralogy (%)			
	Cu	Fe	S	Zn	Pb	SiO <sub>2</sub>	CuFeS <sub>2</sub>	FeS <sub>2</sub>	ZnS	PbS
Aitik (ground)	32.4	30.9	34.1	0.11	0.05	0.53	94.0	4.00	0.16	0.06
Aitik (38–53 μm)	31.8	30.2	35.2	0.05	0.01	0.45	92.0	6.00	0.07	0.01
Kristineberg (ground)	23.6	34.7	37.5	2.10	0.70	1.10	68.0	26	3.20	0.80
Kristineberg (38–53 µm)	21.6	33.8	39.9	1.7	0.58	0.68	62.4	32.4	2.53	0.67
Aitik Pyrite Conc.	0.04	36.4	39.6	< 0.01	<0.01	23.0 <sup>a</sup>	0.12	76.0	0.01	< 0.01

<sup>a</sup> Total gangue including aluminosilicate minerals (mostly kyanite) for pyrite concentrate.

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