



Probing the effect of aqueous impurities on the leaching of chalcopyrite under controlled conditions



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ABSTRACT

Chalcopyrite-containing deposits frequently comprise other sulfide and various silicate and carbonate minerals. Under acidic leaching conditions, as encountered in acid mine drainage or during industrial hydrometallurgical processing, these minerals can dissolve and release various impurities that may subsequently impact the leach behaviour of chalcopyrite. To gain further insight into these effects, batch leaching of chalcopyrite under controlled conditions of 75 °C, pH 1 and E_h 750 mV SHE in the presence of selected cationic impurities, that are common components of these associated minerals, has been examined.

The addition of pre-equilibrated Fe^{2+} in the range of 20–50 mM gave rise to a negative reaction order using the initial rate method (IRM). In contrast, the IRM analysis indicated a positive reaction order for added Fe^{2+} over the range 5–20 mM; however, the overall leach processes generally slowed compared to leaching in the absence of added cations. This may be due to increasing iron concentrations, due to chalcopyrite dissolution, as leaching progressed. Results from the IRM analysis also indicated that Al^{3+} (5–50 mM) and K^+ (5–150 mM) both resulted in positive reaction orders and accelerated chalcopyrite leaching, while Ca^{2+} (5–20 mM), Si oxyanions (5–50 mM), Na^+ (5–50 mM) and Mg^{2+} (5–50 mM) all slowed the leach process.

Porous sulfur layers, observed by scanning electron microscopy, do not appear responsible for these trends as their morphologies appear almost the same for leaching with and without added impurities. Time-of-flight secondary ion mass spectroscopic analyses showed no significant differences between samples collected from leaching in the absence and presence of impurities indicating that surface species within the top one to two monolayers do not contribute to the reduced leach efficiency. X-ray photoelectron spectroscopic analyses suggested that Fe(III)–O/–OH surface speciation may be associated with the reduced leach efficiency observed in the presence of some of the impurities.

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1. Introduction

Chalcopyrite ($CuFeS_2$) is the Earth's most abundant copper-bearing mineral and the source of most copper (Habashi, 1978; Ness, 2000). It commonly co-exists with other sulfide e.g. pyrite, silicate e.g. feldspar and carbonate e.g. dolomite minerals that are present in a large number of natural environmental and mining settings. Aqueous oxidation of chalcopyrite results in adverse environmental impacts, associated with acid and metalliferous drainage (AMD), resulting in release of toxic metals, including copper, to groundwaters, with a pH of less than 1 in extreme cases (Acero et al., 2009; Kimball et al., 2009; Williams and Smith, 2000). In contrast, the aqueous oxidation of chalcopyrite is viewed as a potentially industrially advantageous process for copper extraction as compared to pyrometallurgical processes (Dutrizac, 1978, 1991; Ghahremaninezhad et al., 2010; Hirato et al., 1987; Hiroyoshi et al., 1997, 2008; Kaplun et al., 2011; Li et al., 2010; Parker et al., 2003).

Many lixivants have been applied to the leaching of chalcopyrite, including chloride, sulfate, nitrate, amines, etc. (Hackl et al., 1995). Acidic ferric sulfate has been the most widely applied facilitative oxidant (Nazari et al., 2011). The actions of other chemical oxidants such as $K_2Cr_2O_7$ and $NaNO_3$ (Antonijević et al., 1994; Aydogan, 2006; Sokić et al., 2009) have also been examined. While it has been found that $K_2Cr_2O_7$ and $NaNO_3$ enhance the copper extraction rate from chalcopyrite, the specific effects of K^+ and Na^+ on chalcopyrite leaching were not discussed. In many earlier published works, the leaching behaviour of chalcopyrite was studied in the presence of NaCl (Carneiro and Leão, 2007; Dutrizac, 1992; Li et al., 2010; Lu et al., 2000; Padilla et al., 2003; Velásquez-Yévenes et al., 2010). However, no discussion on the effect of Na^+ was made. Indeed, there are no relevant studies regarding the influence of either K^+ or Na^+ and other cations (except Fe^{3+}) such as Mg^{2+} , Ca^{2+} and Al^{3+} on the leaching of chalcopyrite.

These cations can be released from gangue minerals e.g. carbonate minerals such as calcite and dolomite, and silicate minerals such as talc, chlorite and feldspar (Duan et al., 2003; Garlick, 1964; Mathur et al., 2000; Yoon, 1981), associated with chalcopyrite (and other

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copper) ores and may affect the leaching conditions and chalcopyrite leaching behaviour (Dopson et al., 2008, 2009). These species, besides affecting activities of, and complexing with, other aqueous ions, may also be involved in surface speciation possibly resulting in passivation via precipitation, or specific adsorption thus affecting the total reactive chalcopyrite surface area. For example, metal ions (e.g. Na^+ , K^+ , Fe^{3+}) and sulfate are precursors for precipitation of jarosite minerals (Córdoba et al., 2008).

Although a large number of studies have been conducted on the leaching of chalcopyrite with addition of Fe^{3+} (Carneiro and Leão, 2007; Córdoba et al., 2009; Dutrizac, 1978, 1989, 1990; Havlík et al., 1995; Maurice and Hawk, 1998; Munoz et al., 1979), none of these was undertaken under strictly controlled E_h conditions, which affects the leaching kinetics and mechanisms (Nicol et al., 2010; Sandström et al., 2005; Viramontes-Gamboa et al., 2007). Varying E_h throughout the leach process introduces the additional variable of varying ratios of the activities of Fe^{3+} to Fe^{2+} thus introducing increased complexity to any mechanistic analysis of chalcopyrite leaching.

Our previous study (Li et al., 2010) has shown that relative surface area normalised chalcopyrite leach rates, derived from experiments conducted at pH 1 and 2 and at 750 mV (SHE), are proportional to the activity of free Fe^{3+} in the absence of addition of iron into the leach media, and that there is no correlation between the presence of specific surface species and the leach rate. Our subsequent work (Kaplun et al., 2011) confirmed this finding. A similar positive kinetic relationship between the chalcopyrite leach rate and the activity of free Fe^{3+} was also found by Kaplun et al. (2011) for leaching with 4 mM iron addition (as ferric sulfate) in the slow copper leach rate regime from 10 h leaching until completion. However, compared to the experiments with no iron addition, leaching experiments with iron addition gave rise to slower leach rates. Kaplun et al. (2011) attempted to understand this by examining surface species using X-ray photoelectron spectroscopy. Some differences were found for Fe 2p and S 2p spectra collected on leach samples from experiments with and without iron addition, but no conclusions were made in regards to whether surface species or solution species contributed to the decrease in the chalcopyrite leach efficiency (i.e. percentage of copper extraction within a certain time) when iron was added. Therefore, it remains unclear as to whether surface components or solution species contribute to the different leach rates observed for leaching with or without iron addition. Similarly, the role of other impurities (Na^+ , K^+ , Ca^{2+} , Al^{3+} , etc.) in determining surface and solution speciation is yet to be understood.

Hence, the overall aim of this study was to understand the effects of common associated cationic impurities such as Mg^{2+} , Na^+ , Ca^{2+} , Fe^{2+} and Si oxyanions on the leaching of chalcopyrite. In addition, we aim to elucidate and, if possible, separate the roles of surface and solution species on the leaching of chalcopyrite in the presence of aqueous impurities.

2. Materials and methodology

2.1. Chalcopyrite

The chalcopyrite used was originally sourced from Sonora, Mexico. A piece of chalcopyrite was first crushed and then further ground in a rod mill, followed by wet sieving to obtain material with a size range of 38 to 75 μm . The chalcopyrite grains were then sonicated to remove clinging fines. Finally, the chalcopyrite particles were dried in an oven at 60 °C and purged with N_2 to prevent surface oxidation. The removal of clinging fines (confirmed by SEM; inset in Fig. 1a) is required to keep the particle size distribution narrow and to avoid rapid initial dissolution rates due to high surface area fines. The specific surface area of the chalcopyrite particles determined by BET was $0.24 \pm 0.04 \text{ m}^2/\text{g}$.

Scanning electron microscopic (SEM) analysis found a small portion of gangue minerals in the chalcopyrite (Fig. 1a). Quantitative X-ray powder diffraction (XRD) analysis of the chalcopyrite sample (Fig. 1b),

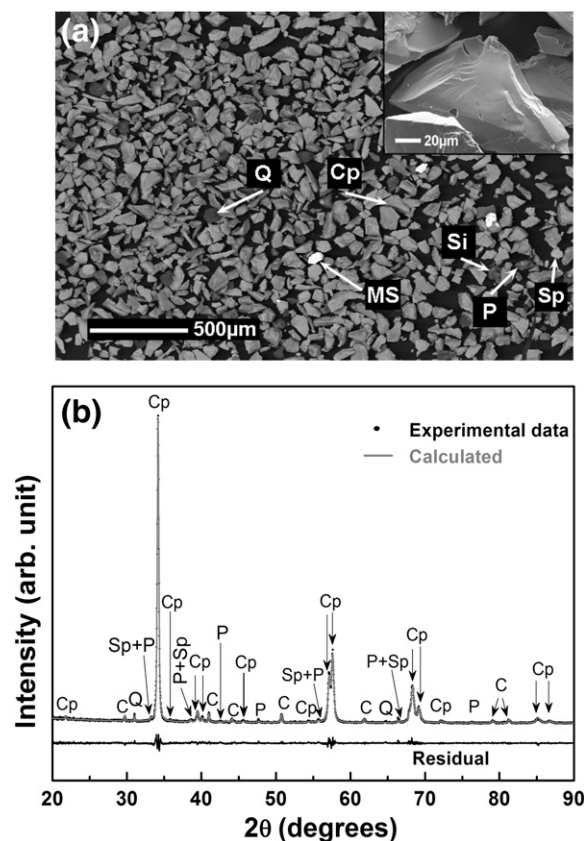


Fig. 1. (a) A backscattered SEM image of chalcopyrite before leaching. Inset shows an enlargement of the chalcopyrite surface (a secondary electron SEM image). (b) A quantitative XRD analysis of chalcopyrite using TOPAS. Note that sphalerite and pyrite are labelled in the order of their abundances when their diffraction peaks overlap. Diffractions due to $\text{Co K}\alpha_2$ were removed. Cp – chalcopyrite; C – corundum; Q – quartz; P – Pyrite; Sp – sphalerite; MS – metal (lead and bismuth) sulfides; Si – (calcium and iron) silicate.

with corundum added as an internal standard, resulted in the following composition (in wt.%): 93% chalcopyrite, 2% pyrite, 1% quartz, 0.3% sphalerite, and 4% amorphous phase(s), generally consistent with the SEM results. A complete acid digestion was also performed using 4 g of the chalcopyrite (38–75 μm) to determine its elemental composition by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Table 1).

2.2. Leaching experiments

Each batch reactor leaching experiment was conducted in a 1.2 L glass reaction vessel with a five port lid. The ports were used to house a thermometer, Teflon impeller, high temperature E_h probe, H_2O_2 (for redox control) inlet and a reflux condenser. Heating was provided by a thermostatically controlled silicone oil bath and the slurry was stirred using a digital overhead stirrer attached to the Teflon impeller. Leaching experiments were all conducted in pH 1 H_2SO_4 at 750 mV and 75 °C (Table 2). E_h values throughout this paper are referenced to standard hydrogen electrode (SHE). Each leaching experiment used 1 L of pH 1 H_2SO_4 , which had been equilibrated with any added impurities in the batch reactor for at least 24 h prior to the addition of chalcopyrite. All impurities including Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} and Fe^{2+} were added as their sulfate form, while Si was introduced as H_2SiO_3 . For leaching in the presence of aqueous Fe^{2+} , 30 wt.% H_2O_2 was added slowly into the lixiviant to adjust the E_h to 750 mV prior to chalcopyrite leaching. Fe^{2+} , rather than Fe^{3+} , was used for iron addition, as addition of the latter does not enable equilibration to 750 mV within 12 h as was suggested to be the case in Li et al. (2010). Chalcopyrite (4 g at 38–75 μm) was then fed into the reaction vessel. The solution E_h was

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