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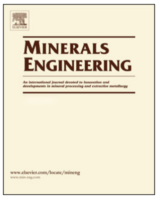

Kinetic study of chalcopyrite dissolution with iron(III) chloride in methanesulfonic acid

Tania Hidalgo[a,b,*], Laura Kuhar[b], Andreas Beinlich[a], Andrew Putnis[a]

[a] The Institute for Geoscience Research (TIGeR), Curtin University, Perth 6845, Australia
[b] CSIRO Mineral Resources, P.O. Box 7229, Karawara, W.A. 6152, Australia

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ABSTRACT

The suitability of methanesulfonic acid as a copper lixiviant with ferric chloride as an oxidant was studied by analysing the leaching kinetics and by characterising solid residues from leach tests on a chalcopyrite-rich ore sample. The effects of temperature, initial acidity, ferric-ion concentration and particle size were determined. The leach kinetics were dependent on the temperature and particle size, whereas the acid and ferric concentrations had a minimal impact on the leaching rate within the ranges studied. Although a sulfur layer formed on the solid residue, the reaction mechanism could be modeled with the shrinking-core model with surface chemical-reaction control, which implies that lixiviant flow through the sulfur layer did not control the reaction rate. The apparent activation energy was 101 kJ mol^{-1} as calculated by the Arrhenius and 'time-to-a-given-fraction' methods. The activation parameters of the reaction were an enthalpy (ΔH^{++}) of 99.4 kJ mol^{-1}, and an entropy (ΔS^{++}) of −197 J mol^{-1} K^{-1} as calculated by using transition state theory and the Eyring equation.

1. Introduction

Pure or alloyed copper is used extensively in society in agriculture, construction, electric appliances and equipment, transport, machinery and medicine (Barceloux, 1999). The increasing demand for this metal and the imbalance between its extraction and the discoveries of copper deposits require the exploitation of refractory and low-grade ores that have previously been regarded as uneconomical (Northey et al., 2014; Tilton and Lagos, 2007). Hydrometallurgical methods have become a feasible approach for copper production, with heap leaching being a common hydrometallurgical technique for low-grade metal extraction (Bartlett, 1997). In-situ recovery (ISR) has been suggested as a profitable alternative to recover copper from inaccessible, deep ore bodies (Northey et al., 2013). Refractory chalcopyrite ($CuFeS_2$) is the most common copper-bearing mineral and represents more than half of global copper mineral reserves (Wang, 2005). Copper extraction from chalcopyrite requires the addition of an oxidant and lixiviant. Several lixiviant–oxidant systems have been tested to provide rapid copper extraction without iron-hydroxy-product-precipitate and passivation-layer formation (Córdoba et al., 2009). Ferric oxidant has proven to be a viable oxidant for chalcopyrite leaching, particularly in bioleaching systems, and has already been implemented in industrial copper-extraction processes, such as the BioCop, Sepon and Geocoat™ applications (Kowalczuk and Chmielewski, 2008).

Eqs. (1)–(3) present the reactions between chalcopyrite and ferric chloride in an acid environment. Chalcopyrite oxidation results in sulfur-layer formation, which could result in a coating of the chalcopyrite surface. This sulfur may be oxidised by excess ferric oxidant to form sulfate at a significantly slower rate than the chalcopyrite dissolution. Complete sulfur oxidation within a limited experimental time scale occurs only if the temperature is sufficiently high and if sufficient oxidant is present in the system.

$$CuFeS_2 + 4FeCl_3 \rightarrow CuCl_2 + 5FeCl_2 + 2S^0 \quad (1)$$

$$S^0 + 6FeCl_3 + 4H_2O \rightarrow SO_4^{2-} + 6Fe^{2+} + 8H^+ + 18Cl^- \quad (2)$$

$$CuFeS_2 + 16FeCl_3 + 8H_2O \rightarrow CuCl_2 + 2H_2SO_4 + 17FeCl_2 + 12HCl \quad (3)$$

In the absence of oxidant, chalcopyrite may react with acid to yield soluble copper as shown in Eq. (4), this reaction is not spontaneous but has been observed experimentally (Lu et al., 2016).

$$CuFeS_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2H_2S \quad (4)$$

Previous studies with hydrochloric acid and ferric chloride have shown that the main reaction product is elemental sulfur, which forms rapidly during the leaching reaction. Minimal further oxidation of S^0 to sulfate results, despite extended leaching times (Dutrizac, 1990; Jones and Peters, 1976). Eq. (1) is believed to be the dominant reaction,

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[*] Corresponding author.
E-mail address: tania.hidalgo@csiro.au (T. Hidalgo).

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Nomenclature

A	pre-exponential factor
b	stoichiometric coefficient
Ea	activation energy
ΔG^{++}	Gibbs energy of activation
h	Planck's constant
ΔH^{++}	enthalpy of activation
k_B	Boltzmann's constant
k_c	apparent reaction rate constant
r	radius of unreacted particle at time t
r_0	initial particle radius
R	ideal gas constant
ΔS^{++}	entropy of activation
t	time
t_x	time to transform a given fraction
T	recorded temperature
τ	time to consume the entire particle
x	fraction reacted

follow by a slow conversion of some of the elemental sulfur to sulfate as was identified by Dutrizac (1990), where more than 95% of the sulfur in sulfide converted to elemental sulfur, and less than 5% sulfate formed. This result was found to be independent of oxidant and acid concentrations.

Several kinetic studies have been conducted over a range of temperatures and pH conditions below 2.5 in the presence of hydrochloric and sulfuric acids to evaluate copper extraction (Table 1). Chalcopyrite leaching with ferric chloride is reported to be controlled by an electrochemical reaction at the surface of the mineral. This reaction requires a high energy input because strong chemical bonds in the crystalline structure of the chalcopyrite result in a significant energy consumption by the displacement of ions from bulk of the particle to the surface (Córdoba et al., 2008). The formation of a sulfur surface coating could result in a diffusion-controlled reaction. However, as shown in Table 1, most researchers have reported a chemical-reaction-control mechanism rather than diffusion control. Therefore, this sulfur layer appears to allow for continued lixiviant access to the reaction interface, which may indicate that the coating has an elevated porosity (Havlík et al., 1995; Hirato et al., 1986; Rath et al., 1988). Activation energies that have been calculated for chalcopyrite dissolution with ferric chloride vary from 15 kJ mol^{-1} to 93 kJ mol^{-1}, and the reaction kinetics are dependent on the material type (natural or synthetic), particle size and gangue content (Dutrizac, 1981).

There has been an increasing interest in hydrometallurgical applications, such as ISR and heap leaching, because of more stringent environmental controls for copper-ore/concentrate processing by conventional pyrometallurgical techniques, which are associated with hydrogen-sulfide and sulfur-dioxide production, and because of the prospect of an increased exploitation of otherwise non-profitable ores (Feng et al., 2015a; U.S Congress, 1988). A major concern related to ISR and heap leaching is the risk of water and soil contamination from the lixiviant and pregnant leach solution (Seredkin et al., 2016), and therefore, the selection of a lixiviant of low toxicity for subterranean use is desired.

The use of lixiviants with a lower environmental impact is attractive in copper hydrometallurgical applications, such as heap leaching and in-situ recovery, especially if these circumvent potential toxic gas production and surface and groundwater contamination. Hydrochloric or sulfuric acid lixiviants have been used in the ferric-ion system, because the presence of a strong acid accelerates chalcopyrite dissolution (Lu et al., 2000; Lundstrom et al., 2008; Wang, 2005). Despite the potential for use of these acids in heap-leaching and ISR applications, an alternative environmentally friendly lixiviant that is less corrosive than hydrochloric acid would be useful for heap leaching and would facilitate the application of the ISR technology (Noor and Al-Moubaraki, 2008). Methanesulfonic acid (MSA) is an organic acid that is formed by the atmospheric oxidation of dimethyldisulfide. The environmental advantages of MSA include an elevated degradability, a low corrosivity and a lack of hazardous volatile products generation, which make it more 'green' compared with hydrochloric, sulfuric, fluoroboric and nitric acids. Its increasing importance as an electrolyte system (Gernon et al., 1999; Florence et al., 2011) has improved MSA's commercial availability for bulk industrial applications. The average cost of one metric ton of MSA (70% purity) is more than 50% of the cost of sulfuric acid (98% purity) and hydrochloric acid (32% purity). MSA may be perceived to be an expensive reactant and as such, has not been used extensively in metal-extraction applications. Nonetheless, its strong acidity, potential for recycling and its environmental advantages make it a viable alternative for applications such as heap leaching and ISR.

In the presence of MSA, ferric methanesulfonate may form by Eq. (5) with subsequent proposed reactions as shown in Eqs. (6)–(8).

$$FeCl_3 + 3CH_3SO_3H \rightarrow Fe(CH_3SO_3)_3 + 3HCl \tag{5}$$

$$CuFeS_2 + 4Fe(CH_3SO_3)_3 \rightarrow Cu(CH_3SO_3)_2 + 5Fe(CH_3SO_3)_2 + 2S^0 \tag{6}$$

$$S^0 + 6Fe(CH_3SO_3)_3 + 4H_2O \rightarrow SO_4{}^{2-} + 6Fe^{2+} + 8H^+ + 18CH_3SO_3{}^- \tag{7}$$

$$CuFeS_2 + 16Fe(CH_3SO_3)_3 + 8H_2O \rightarrow Cu(CH_3SO_3)_2 + 2H_2SO_4 + 17Fe(CH_3SO_3)_2 + 12CH_3SO_3H \tag{8}$$

Organic acids are a possible alternative for less harmful lixiviants, but requirements for a strong acid have limited their applicability (Feng et al., 2015a). MSA's high dissolving strength and acid strength compared with other organic acids make it suitable for the extraction of heavy metals such as lead and copper. MSA's acid dissociation constant is −1.92, which is higher than that of nitric acid (−1.3) and close to that of sulfuric acid (−2). This strong organic acid is almost 99.8% ionized in a 0.1 mol L^{-1} solution (BASF, 2012; D. Gernon et al., 1999; Feng et al., 2015a; Patai and Rappoport, 2006; Wu et al., 2014). MSA is readily biodegradable, with sulfate, water, biomass and carbon dioxide being generated as a product of biological activity. MSA's lack of odour, its low toxicity and corrosiveness and the fact that it is unlikely to generate harmful gases during its use make it a 'greener' alternative to the sulfuric- and hydrochloric-acid leaching of chalcopyrite and potentially attractive for use in heap-leaching or ISR applications (Hasan and Rohan, 2010). Despite the environmental benefits of this acid having been analysed for other applications, such as electrowinning, catalysts and polymer solvents (Commarieu et al., 2002; D. Gernon et al., 1999; Florence et al., 2011; Hasan and Rohan, 2010), limited studies have been conducted on the effectivity of MSA as a lixiviant in hydrometallurgical processes. Studies have focused primarily on carbonate dissolution (Feng et al., 2015a; Feng et al., 2015b; Wu et al., 2014), and its applicability to the leaching of refractory copper minerals such as chalcopyrite has not yet been evaluated. This study is aimed at understanding the reaction kinetics of the ferric-chloride/MSA system in the dissolution of a natural chalcopyrite sample with gangue inclusions at low to moderate temperatures (< 90 °C) to elucidate its possible application in hydrometallurgical processing.

2. Experimental

2.1. Materials

A chalcopyrite-bearing sample was ball milled and dry sieved. Sized samples were blended with a ball mill and riffle split into representative