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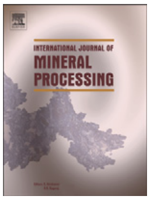

Kinetics of chalcopyrite leaching in either ferric sulphate or cupric sulphate media in the presence of NaCl

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ABSTRACT

The shrinking core model (SCM) has been extensively applied in the kinetics analysis of particulate systems. This is because in its classical form it is one of the simplest models developed for fluid–solid reactions. However, it requires single-sized solid grains failing to describe the leaching kinetics for broad particle size distributions (PSDs). The current investigation successfully applied an extension of the SCM to the leaching of chalcopyrite with a broad PSD in a mixed chloride–sulphate solution. Such a medium was selected because there is renewed attention to leaching in mixed systems due to the increasing utilization of saline waters in both leaching and bioleaching of sulphide ores. Moreover, chloride is a catalyst of chalcopyrite leaching. Specifically, the effects of temperature (70 °C to 90 °C) and reagent (Fe^{3+}, Cu^{2+} and Cl^-) concentrations on the leaching kinetics were determined. The results showed that chalcopyrite leaching was faster with Cu^{2+} (larger rate constant) than with Fe^{3+}, but the activation energy was similar in both cases with 66.6 kJ/mol for 0.5 mol/L of Cu^{2+} and 66.8 kJ/mol with 1.0 mol/L Fe^{3+}.

1. Introduction

Chalcopyrite ($CuFeS_2$) is the most abundant copper mineral, comprising roughly 70% of the world reserves, therefore its relevance to the copper industry is evident (Kaplun et al., 2011). Such a mineral is also a very stable copper sulphide, and is refractory with regards to hydrometallurgical processing. For this reason, chalcopyrite leaching is slower as compared to that of other copper sulphides such as chalcocite (Cu_2S) and bornite (Cu_5FeS_4). Thus, numerous studies have been carried out seeking to determine the various parameters that influence its leaching kinetics, such as temperature, particle size, stirring rate, and solution type (Yévenes et al., 2010b).

Hydrometallurgical processes developed to treat chalcopyrite ores and/or concentrates can be classified as nitrate, chloride, sulphate or ammonia leaching with respect to the applied leaching solution. Regardless of the selected leaching agent the presence of an oxidant such as ferric iron, cupric ions or oxygen is always required to oxide the sulphide and release copper. Notwithstanding, sulphate-based leaching has some advantages over other leaching media because sulphate leaching is generally simpler and better understood and the recovery of copper by solvent extraction–electrolysis is relatively straightforward. However, there is a critical shortcoming: the leaching kinetics of chalcopyrite is slow in ferric sulphate systems (Hackl et al., 1995). One way of circumventing this problem, which has been extensively investigated, is the addition of chloride ions to the sulphate medium (Ruiz et al., 2011). This is because the presence of chloride ions reduces chalcopyrite passivation and stabilizes Cu(I) ion in solution, adding a second redox couple to the system, thus facilitating copper extraction (Carneiro and Leão, 2007; Watling, 2013).

The mechanisms proposed for the dissolution of chalcopyrite in both sulphate and chloride media are still very controversial and several alternative mechanisms have been suggested. The oxidative dissolution of chalcopyrite in acid ferric or cupric solutions can be described by the mixed-potential electrochemical model and the following anodic reaction is proposed ((1)) (Nicol et al., 2010):

$$CuFeS_2(s) = Cu^{2+}(aq) + Fe^{2+}(aq) + S^0(s) + 4e \quad E^\circ = 0.425V\,(vs\ \ SHE) \tag{1}$$

Eq. 1 is coupled to the cathodic reactions (2 or 3) (Yoo et al., 2010):

$$4Fe^{3+}(aq) + 4e = 4Fe^{2+}(aq) \quad E^\circ = 0.77V \quad (vs\ \ SHE) \tag{2}$$

and/or

$$4CuCl_2{}^0(aq) + 4Cl^-(aq) + 4e = 4CuCl_3{}^{2-}(aq) \quad E^\circ = 0.54V \quad (vs\ \ SHE) \tag{3}$$

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Elemental sulphur has been commonly detected as a product of chalcopyrite dissolution, but the formation of metal-deficient sulphides in acidic media has also been suggested. The formation of intermediate non-stoichiometric phases is represented by (4), where y is larger than x (Warren et al., 1982; Majuste et al., 2012):

$$CuFeS_2(s) = Cu_{(1-x)}Fe_{(1-y)}S_{(2-z)}(s) + xCu^{2+}(aq) + yFe^{2+}(aq) + zS^0(s) + 2(x+y)e \quad (4)$$

The non-stoichiometric phase presented in (4) would be oxidized to covellite (CuS) and, subsequently, to elemental sulphur (S), through consecutive reactions ((5) and (6)) or, then, directly ((7)) (Warren et al., 1982; Majuste et al., 2012).

$$Cu_{(1-x)}Fe_{(1-y)}S_{(2-z)}(s) = (2-z)CuS(s) + (-1-x+z)Cu^{2+}(aq) + (1-y)Fe^{2+}(aq) + 2(-x-y+z)e \quad (5)$$

$$CuS(s) = Cu^{2+}S^0(s) + 2e \quad (6)$$

$$Cu_{(1-x)}Fe_{(1-y)}S_{(2-z)}(s) = (1+x)Cu^{2+}(aq) + (1-y)Fe^{2+}(aq) + (2-z)S^0(s) + 2(2-x-y)e \quad (7)$$

Covellite (CuS) was positively detected on mineral particles after leaching in chloride (Yévenes et al., 2010b) and sulphate (Córdoba et al., 2008b) solutions whereas bornite (Cu_5FeS_4) has been cited as an intermediate phase (Majuste et al., 2012).

Copper leaching in chloride systems has been investigated for quite some time (Watling, 2014). However, no industrial process has been implemented, mostly likely because of the corrosion problems related to chloride leaching. The CESL process utilizes chloride ions to catalyse chalcopyrite oxidation (by oxygen) to copper sulphate, but it did not result in a commercial process so far despite being already trialled in a demonstration scale (Sahu and Asselin, 2011). Nevertheless, the major mining companies have patents covering chloride leaching (Nicol et al., 2012; Ohtsuka and Mitarai, 2008; Rautenbach et al., 2011) and with the increasingly stringent regulations on water usage in many countries, saline water and seawater are becoming a real option for hydrometallurgical operations as for example, in BatuHijau (Indonesia), BHP Nickel (Australia), Lipesed, Michilla, Esperanza, Algorta Norte, Mantos de la Luna and Las Luces (Chile), which are using raw seawater in their processes (Torres et al., 2015). That explains the renewed interest in chloride leaching. Notwithstanding, many scientific aspects of the combined sulphate–chloride leaching are still not well understood despite its technological importance.

The shrinking core model (SCM) (Levenspiel, 1999) is one of the simplest models developed for fluid–solid reactions and has been extensively applied in the kinetics analysis of particulate systems. Its traditional form assumes an isothermal *nth*-order irreversible kinetics and a pseudo-steady state (PSS) approximation, which implies in a constant concentration of the dissolved reagent. Moreover, the model was developed for particles the same size (single-sized particles) in its classical form. There were many attempts of extending the SCM to conditions more complex than those originally described by Levenspiel (1999), but the classical form remains largely used in hydrometallurgy. Nevertheless, many leaching kinetics studies are performed with broad particle size distributions (PSDs), particularly when ultrafine milling is applied, which violates the assumptions of the classical SCM. Incorporating the effect of PSD in the kinetics analysis of fluid–solid reaction systems was proposed subsequently to the original development of the SCM (Murhammer et al., 1986) and one of the simplest mathematical models incorporating such effects was proposed by Gbor and Jia (2004).

Examples of the SCM application to model chalcopyrite leaching comprise the following systems: (i) hydrogen peroxide (Antonijević et al., 2004), (ii) chloride media (Baba et al., 2013) and (iii) the leaching kinetics of covellite produced from the reaction between chalcopyrite and gaseous sulphur (Padilla et al., 2013). Nevertheless, some inconsistencies can be found in the scientific literature, particularly in terms of the rate-determining step (Nicol et al., 2010). Some researchers proposed that chalcopyrite leaching is a chemical controlled process (Córdoba et al., 2008b; Hirato et al., 1987; Kaplun et al., 2011; Ruiz et al., 2011); whereas others reported a diffusion-controlled mechanism (Bonan et al., 1981; Carneiro and Leão, 2007; Córdoba et al., 2008c). Therefore, the activation energy vary broadly with values between 38 kJ/mol and 130 kJ/mol proposed for ferric sulphate leaching in the 35 °C–100 °C temperature range (Dutrizac, 1981). Another source of inconsistencies is the type of experiment selected. Some works were performed with particulate systems (Al-Harahsheh et al., 2008; Bonan et al., 1981; Córdoba et al., 2008b; Dutrizac, 1981; Havlík and Kammel, 1995; Lu et al., 2000; Yoo et al., 2010) whereas other investigated the leaching kinetics of massive chalcopyrite samples (Cai et al., 2012; Palmer et al., 1981) or applied rotating disc techniques to synthetic and natural chalcopyrite (Dutrizac, 1978; Hirato et al., 1987). Also, kinetics analysis using electrochemical data can be usually found (Lundström et al., 2005; Majima et al., 1985; Majuste et al., 2012). In addition, some works did not have a detailed description of the mineral features (Watling, 2013).

Therefore, the current work investigated the leaching kinetics of a chalcopyrite sample, taking into account the effect of the particle size distribution (PSD) through the Gbor and Jia (2004) approach to the SCM. Particularly, the effects of temperature and type of oxidant (either ferric or cupric ions) on the dissolution rate of chalcopyrite in combined sulphate chloride media were investigated.

2. The effect of PSD on the SCM

Gbor and Jia (2004) incorporated the effect of PSD into the SCM for each of the possible kinetic controls developed for shrinking core particles of constant size: (i) chemical reaction-control; (ii) ash layer diffusion-control and (iii) film-diffusion control. According to the authors, for mono-sized particles of diameter *D*, undergoing a shrinking core form of dissolution, the fraction unconverted is a function of particle size and time ((8)).

$$1-X_B = f(D,t) \quad (8)$$

where X_B = fraction of B in solid that is converted to products.

For a chemically-controlled process, the fraction unconverted (1-X_B) as function of diameter (D) and time (t) is represented by (9).

$$f(D,t) = 1-X_B = \left(1-\frac{k_{rn}t}{D}\right)^3 \quad (9)$$

where $k_{rn} = k_rD$, and is independent of particle size since k_r (rate constant for chemical control) is inversely proportional to D (or R).

For an ash/inert layer diffusion-controlled process, no algebraic expression can be obtained for f(D,t). The value of f(D,t) has to be determined for each D, using (10).

$$1-3(1-X_B)^{\frac{2}{3}} + 2(1-X_B) = k_{dn}t/D^2 \quad (10)$$

where $k_{dn} = k_dD^2$, and is independent of particle size since k_d (rate constant for ash layer diffusion control) is inversely proportional to D^2 (or R^2).

Finally, for a liquid film-diffusion controlled process:

$$f(D,t) = 1-X_B = \left(\frac{k_{mn}t}{D}\right) \quad (11)$$

where $k_{mn} = k_mD$, and is independent of particle size since k_m (rate constant film diffusion control) is inversely proportional to D (or R).