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Chalcopyrite leaching in alcoholic acid media

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ABSTRACT

In recent years, the kinetics and mechanism of chalcopyrite dissolution in different media have been the focus of much investigation since a fundamental understanding of the phenomena would help to resolve the problems that challenge the implementation of a hydrometallurgical processing alternative. The addition of polar organic solvents has been found to have a beneficial effect by depassivating the chalcopyrite surface. The present article describes chalcopyrite leaching in the presence of alcohols, such as 2-propanol and methanol, in an acid solution at different temperatures with distinct oxidants (H_2O_2, $CuSO_4$ and O_3). For both alcohols, the temperature was found to be a very important variable in the process. For 2-propanol, copper dissolution by hydrogen peroxide fits the shrinking core model controlled by chemical reaction in the temperature range up to 40 °C with an activation energy of 42 kJ mol^{-1}. At higher temperatures, the peroxide rapidly decomposed and the copper extraction ceased. In contrast to the straightforward kinetics in peroxide, the dissolution behavior using cupric ion and ozone as oxidants displayed a complex mechanism, initiating with the solid phase transformation upon reaction with the cupric ion to form an iron-free phase, which later was oxidized by the ozone. A reaction scheme is proposed according to the different phases formed during the leaching process, identified using ultraviolet and atomic absorption spectroscopies, as well as X-ray diffraction. Methanol was found to stabilize the cuprous ion and allow the formation of roxbyite (Cu_2S_2–$6Cu_2S$), which is essential to achieve high copper extractions.

1. Introduction

Chalcopyrite dissolution at moderate conditions has been a significant challenge, due to the passivation that occurs upon oxidation in acid solutions. In the majority of processes proposed, strong oxidants, frequently the ferric ion in chloride or sulfate media, and elevated temperatures are necessary to achieve high copper extractions (Córdoba et al., 2008). An alternative redox pair is Cu(II)/Cu(I), which is stable in the presence of various media, such as in chloride solutions (Lu and Dreisinger, 2013) and in polar organic solvents (Nelson et al., 1961). Recently, Solís-Marcíal and Lapidus (2013) found that both ethylene glycol and acetone in the oxidative acid leaching solutions yielded elevated copper extractions. The improvement was attributed to the greater stability of the cuprous ion in organic solvents. The role played by the cuprous ion in the leaching reaction could be the same as that observed in chloride media (Lu and Dreisinger, 2013), except that in organic solvents, the cuprous ion is not complexed and consequently, its activity is greater. Nelson et al. (1961) established that the Cu(I) ion is also stabilized by alcohols, such as 2-propanol, methanol, ethanol, etc. For that reason, this research studied the chalcopyrite leaching mechanism in alcoholic acid media, using 2-propanol or methanol.

2. Experimental material and methods

The −149 + 177 μm fraction of a relatively pure chalcopyrite from Kidd Creek mine (Excalibur Mineral Corporation, Inc.) was used for the leaching experiments.

The leaching experiments were performed in a 1 L Pyrex® reactor, equipped with a condenser. The solutions were prepared with reagent grade chemicals and deionized water. Heating tape was used to sustain the temperature in the reactor, which was regulated with a thermocouple connected to an on–off controller.

All leaching tests employed 140 mL of 1 M sulfuric acid and 60 mL of alcohol (70/30% v/v), with the desired volume of reagent grade hydrogen peroxide (30% v/v) to reach the required concentration. The total volume was then completed to 280 mL with distilled water. Consequently, the final sulfuric acid concentration was 0.5 M and those of 2-propanol and methanol were 3.7 and 6.9 M, respectively. In other experiments, cupric sulfate pentahydrate and ozone were used as the oxidants. When ozone was employed as an oxidant, once the desired temperature was reached, it was continuously bubbled into the solution. The ozone [0.0349 g min^{-1} O_3] was produced by supplying medicinal grade oxygen into the Biozon ozonizer (Basktek, S.A. de C.V.). Subsequently, 3 g of chalcopyrite was introduced into the solution and suspended by constant agitation. Samples of the solution were taken to determine the iron and copper concentrations by atomic absorption spectrometry (AAS, Varian SpectrAA 220FS). The cuprous

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ion determinations were carried out in a Varian CARY5000 spectrophotometer. Diluted samples (1:100) of the leaching solution were analyzed in a quartz cell in the 200 to 800 nm range. Once the test was finalized, the residue was filtered and allowed to air-dry. The resultant phases were determined by X-ray diffraction analysis of the solid residues (D8 Advanced), using a velocity of 0.1° per second.

3. Results and discussion

3.1. 2-Propanol

Chalcopyrite leaching with polar organic solvents requires the use of an oxidant to reach the necessary solution potential (Solís-Marcíal and Lapidus, 2013). Hydrogen peroxide is one of the frequently used clean oxidants due to its high redox potential (1.77 V versus SHE) in acid media (Adebayo et al., 2003).

The initial peroxide concentration is a sensitive variable in mineral dissolution processes. For this reason, leaching tests were carried out on the chalcopyrite with 2-propanol/sulfuric acid solutions, varying the hydrogen peroxide concentration at 50 °C (1, 2 and 3 M). Copper extractions for these experiments are reported in Fig. 1, where initial dissolution rates coincide with the peroxide concentration. However, after a short time, the extraction ceases for all concentrations probably due to the decomposition of the peroxide at the system temperature (associated with the solution potential) (Solís-Marcíal and Lapidus, 2013). The concentration at which the greatest dissolution was achieved was 2 M, although the combined effect of high temperature with large concentration accelerated the peroxide degradation, confirming the observations of other authors (Adebayo et al., 2003; Antonijevic et al., 2004; Dimitrijevic et al., 1996).

To confirm that the low extraction was due to peroxide decomposition, the same experiments were performed at a lower temperature (40 °C). Fig. 2 shows the same initial tendency, but copper extraction continues to rise throughout the experiments until passivation or oxidant depletion sets in after ~240 min. Adebayo et al. (2003) experimented at similar conditions, without the organic solvent, achieving significantly lower extractions (~20%). This confirms that alcohol additions diminish chalcopyrite passivation, although the kinetics is slower.

Experiments were performed in the limited temperature range between 25 and 50 °C with an initial peroxide concentration of 3 M. As may be perceived in Fig. 3, the initial kinetics increase with the temperature. However, as noted previously, at 50 °C peroxide rapidly decomposes, ending copper extraction. As a reference, Adebayo et al. (2003) and Antonijevic et al. (2004) only dissolved 30% and 45%, respectively, under similar conditions.

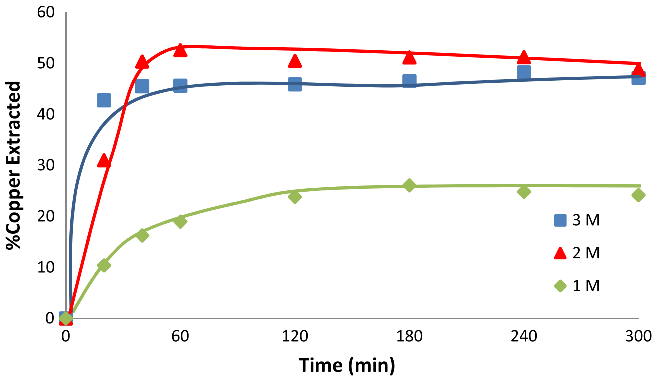

Fig. 1. Copper extraction from chalcopyrite versus time for solutions of 0.5 M H_2SO_4 with 3.7 M 2-propanol (70–30% v/v), varying the H_2O_2 concentration at 50 °C.

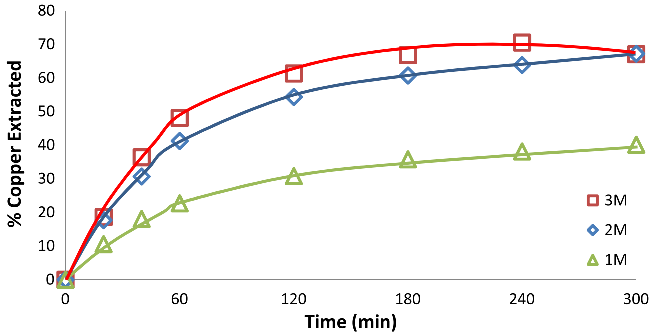

Fig. 2. Copper extraction from chalcopyrite versus time for solutions of 0.5 M H_2SO_4 with 3.7 M 2-propanol (70–30% v/v), with different H_2O_2 concentration at 40 °C.

Since chalcopyritic iron is simultaneously removed in this leaching process (data not shown here), the chalcopyrite is expected to react leaving only a very porous layer of elemental sulfur in its wake.

$$CuFeS_2(s) + 1\frac{1}{2}H_2O_2(aq) + 3H^+ + R \rightarrow Cu^+R\,(aq) + Fe^{2+} + 2S^0 + 3H_2O \qquad (1)$$

where R is the polar organic solvent.

For that reason, the shrinking core model with chemical reaction control was used to analyze the experimental data (Levenspiel, 1972). The integrated expression is the following:

$$1-(1-x)^{1/3} = \frac{bkC_{H_2O_2}t}{\hat{C}_{Cu}d} \qquad (2)$$

where x is the fractional conversion of the chalcopyrite, t is the leaching time, $\hat{C}_{Cu}$ is the molar copper concentration in the mineral, kC_{H_2O2} is the first order kinetic constant, d is the chalcopyrite particle diameter and b is the stoichiometric coefficient.

The experimental results are plotted as a function of Eq. (2) in Fig. 4, where a reasonable agreement was achieved for the initial extractions at the lower temperatures.

An Arrhenius plot of the slope values (ln [slope] versus 1/T) is shown in Fig. 5, where an activation energy of 42 kJ mol^{-1} was calculated. This value coincides with those found by Adebayo et al. (2003) and Antonijevic et al. (2004), using peroxide.

3.2. $CuSO_4$ and O_3 as oxidants

The principal disadvantages of using hydrogen peroxide are its elevated cost and its instability at high temperatures. For this reason,

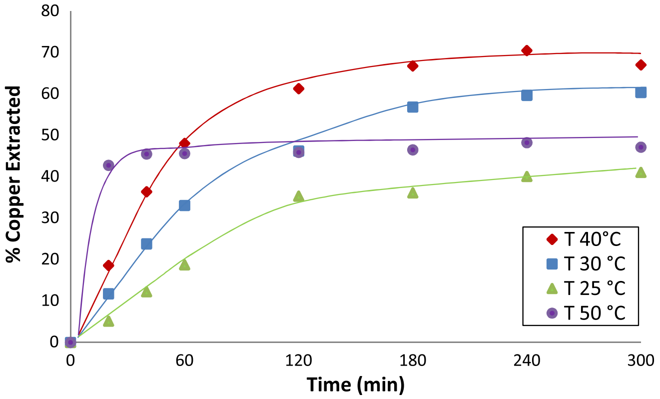

Fig. 3. Copper extraction from chalcopyrite versus time for solutions of 0.5 M H_2SO_4 with 3.7 M 2-propanol (70–30% v/v) and 3 M of H_2O_2, at different temperatures.