Photocorrosion of copper sulfides: Toward a solar mining industry

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ABSTRACT

Copper sulfides such as chalcopyrite ($CuFeS_2$), covellite (CuS) and chalcocite (Cu_2S) are the most abundant, and thus mainly used, minerals in the copper mining industry worldwide. These metallic sulfides have semiconductor properties and they can be activated by sunlight. Some of them have been used as photocatalysts for water purification. However, photocorrosion phenomena decrease the photocatalytic activity and cause the leaching of metal ions into the solution. This phenomenon is undesirable for photocatalytic purposes, however, it could be used as a complementary method for sulfide minerals leaching. In this work, we studied photocorrosion assisted by solar light to evaluate the photoleaching of copper and iron from $CuFeS_2$, CuS and Cu_2S. In addition, heterogeneous photocatalysis using TiO_2 was also evaluated. Copper and iron leaching was determined in sulfide mineral suspensions under visible light irradiation. For the first time, it is demonstrated that the photocorrosion of copper sulfides occurs under controlled conditions. This proof of concept demonstrates that photocorrosion and photocatalysis could be considered for copper leaching from copper sulfide minerals. This novel study could generate a new route for copper leaching using solar light under mild conditions with less environmental impacts.
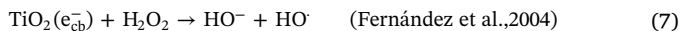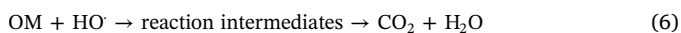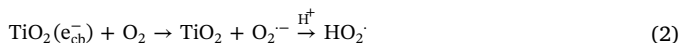
1. Introduction

Copper is found in nature mainly as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S) and covellite (CuS) and bornite (Cu_5FeS_4). It is well known that copper sulfide mineral species are refractory to leach even using concentrated sulfuric acid. These minerals have low solubility in acidic medium and their processing involves three successive stages: grinding, flotation and melting/oxidation. Nowadays, oxidation of sulfide minerals is performed by pyrometallurgical processes, which involve high investment in foundry infrastructure, intensive use of heat, elevated operational cost and hazardous emissions such as SO_2, arsenic and CO_2 (Dimitrijevic et al., 2009). The main copper deposits in the world are located in the Atacama desert (north of Chile) where the highest solar irradiance on earth has been reported (Ferrada et al., 2015; Cornejo et al., 2017). This high solar irradiation is currently used for photovoltaic and thermo solar harvesting (Fuentealba et al., 2015). However, this abundant photochemical energy resource has been scarcely used in copper mining processes (Grágeda et al., 2016).

In this work, chalcopyrite, chalcocite and covellite were utilized to study visible light driven photocorrosion and photocatalytic leaching of copper. It is well known that heterogeneous photocatalysis is an advanced oxidation process (AOP) which uses a catalyst with semiconductor properties. The most used catalysts are TiO_2 or ZnO,
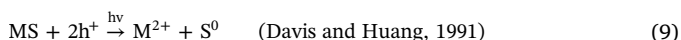
however, chalcogenides such as CdS, ZnS, MoS_2, WS_2, have also been used due to their low band gap allowing the absorption in the visible spectrum (Garg et al., 2016; Huo et al., 2017; Joy et al., 2017; Cao, 2016; Raubach et al., 2013). Copper sulfides have also been employed as photocatalyst (Luminita et al, 2011; An et al., 2015; Wang et al., 2009), The photocatalytic process is initiated when the catalyst is irradiated with energy greater than or equal to its band gap (E_g), promoting charge carriers separation (Wenderich and Mul, 2016; Balzani et al., 2017). Photo-generated electrons and holes can migrate to the surface of the solid (Eq. (1)) (Herrmann, 1999). Then, electrons and holes can initiate redox reactions as shown in Eqs. (2)–(7), using TiO_2 as model photocatalyst. The photo-electrons from the conduction band (cb) can reduce oxygen and subsequently generate radicals such as superoxide anion and hydroperoxide radicals (Eq. (2)). Moreover, the absorbed water can be oxidized by the hole of the valence band (vb) and form protons (H^+) and hydroxyl radicals ($HO^.$) (Eq. (3)). Also, the holes can directly oxidize organic matter (OM) or hydroxide anions adsorbed on the catalyst surface to produce additional hydroxyl radicals (Eqs. (4) and (5). Furthermore, the radical species can react with the organic matter adsorbed on the catalyst surface to achieve partial or complete mineralization (Eq. (6)). Additionally, H_2O_2 has been used, instead of oxygen, as electron acceptor to improve the photocatalytic performance (Eq. (7)) (Fernández et al., 2004; Litter, 1999, 2017).

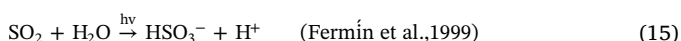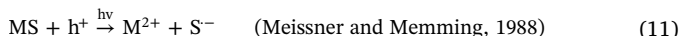$$TiO_2 + h\nu \rightarrow TiO_2(e_{cb}^- + h_{vb}^+) \tag{1}$$

$$TiO_2(e_{cb}^-) + O_2 \rightarrow TiO_2 + O_2^{\cdot-} \xrightarrow{H^+} HO_2^{\cdot} \tag{2}$$

$$TiO_2(h_{vb}^+) + H_2O \rightarrow TiO_2 + H^+ + HO^{\cdot} \tag{3}$$

$$TiO_2(h_{vb}^+) + HO^- \rightarrow TiO_2 + HO^{\cdot} \tag{4}$$

$$TiO_2(h_{vb}^+) + OM \rightarrow TiO_2 + OM^{+\cdot} \tag{5}$$

$$OM + HO^{\cdot} \rightarrow \text{reaction intermediates} \rightarrow CO_2 + H_2O \tag{6}$$

$$TiO_2(e_{cb}^-) + H_2O_2 \rightarrow HO^- + HO^{\cdot} \quad \text{(Fernández et al.,2004)} \tag{7}$$

TiO_2, a typical semiconductor, has been used for photocatalytic studies due to its great stability against photocorrosion, despite its high band gap. On the contrary, copper sulfides ($CuFeS_2$, CuS, Cu_2S) present semiconductor properties with lower band gap absorbing radiation in the visible region. However, in the last case, photocorrosion takes place under irradiation promoting the leaching of the metal to the solution, decreasing the photocatalytic efficiency (Weide et al., 2016; Matsumoto et al., 1996; Luminita et al., 2011). This effect is unfavorable for the use of copper sulfide as photocatalyst, while it could favor the leaching of metal from sulfide copper minerals. Photoleaching of metal sulfides begins with the creation of charge-carrier's pairs (h^+ and e^-) on the surface of the solid in presence of radiation (Eq. (8)) (Janackovi et al., 2015). In absence of oxygen, the metallic sulfide (MS) could photocorrode in aqueous media and producing sulfur (Eq. (9)) (Davis and Huang, 1991). On the other hand, in the presence of oxygen, the reaction proceeds with the oxidation of sulfide to sulfate (Eq. (10)) (Meissner and Memming, 1988).

$$MS \xrightarrow{h\nu} h^+ + e^- \quad \text{(Janackovi et al.,2015)} \tag{8}$$

$$MS + 2h^+ \xrightarrow{h\nu} M^{2+} + S^0 \quad \text{(Davis and Huang, 1991)} \tag{9}$$

$$MS + 2O_2 \xrightarrow{h\nu} M^{2+} + SO_4^{2-} \quad \text{(Meissner and Memming, 1988)} \tag{10}$$

Meissner et al. have reported formation of several intermediates during sulfide photocorrosion (Meissner and Memming, 1988). For instance, radical intermediates, such as $S^{\cdot-}$, can be formed by direct oxidation through holes (Eq. (11)) or by sulfur reduction via conduction band electrons (Eq. (12)). On the other hand, the radical $SO_2^{\cdot-}$ can be formed by direct oxidation of $S^{\cdot-}$ (Eq. (13)) which in turn is oxidized to SO_2 (Eq. (14)). Other identified intermediates are SO_3^{2-} and SO_4^{2-} as shown in Eqs. (15) and (16). Fermín et al. proposed a detailed pathway of (the following) photocorrosion considering the participation of holes and supporting the role of oxygen in the general mechanism (Fermín et al., 1999).

$$MS + h^+ \xrightarrow{h\nu} M^{2+} + S^- \quad \text{(Meissner and Memming, 1988)} \tag{11}$$

$$S^0 + e^- \xrightarrow{h\nu} S^{\cdot-} \quad \text{(Meissner and Memming, 1988)} \tag{12}$$

$$S^{\cdot-} + O_2 \xrightarrow{h\nu} SO_2^{\cdot-} \quad \text{(Meissner and Memming, 1988)} \tag{13}$$

$$SO_2^{\cdot-} + h^+ \xrightarrow{h\nu} SO_2 \quad \text{(Meissner and Memming, 1988)} \tag{14}$$

$$SO_2 + H_2O \xrightarrow{h\nu} HSO_3^- + H^+ \quad \text{(Fermín et al.,1999)} \tag{15}$$

$$HSO_3^- + H_2O + 2h^+ \xrightarrow{h\nu} SO_4^{2-} + 3H^+ \quad \text{(Fermín et al.,1999)} \tag{16}$$

In the present work, the photocorrosion of $CuFeS_2$, Cu_2S, CuS is presented as a proof of concept for the solar photocorrosion and leaching of copper sulfide minerals. Furthermore, the effect of TiO_2 and H_2O_2 addition were evaluated.

2. Experimental

2.1. Reagents and chemicals

Natural chalcopyrite was provided by the Institute of Economic Geology at the University of Concepción, Chile. Additionally, synthetic CuS and Cu_2S were purchased from Sigma-Aldrich (US). Copper sulfides concentrates were obtained from mining companies. Ultrapure water (18.2 M Ohm cm^{-1}) used in all experiments was obtained using Merck Millipore system. All reagents were analytical grade and purchased from Sigma-Aldrich (US). Hydrogen peroxide 30% Perhydrol® was purchased from Merck Millipore (US). TiO_2 P-25 used as a catalyst was provided by Degussa Company (Germany).

2.2. Photocorrosion assays

Photocorrosion experiments were performed using a 400 mL borosilicate reactor transparent to sunlight and UV-A radiation (Yepsen et al., 2015). A suspension of 200 mL containing 0.1 g L^{-1} of sample (copper sulfides or mineral concentrate) was irradiated with a 400 W mercury vapor lamp Powerstar HQI-E Daylight OSRAM (Germany) that simulates the solar spectrum. The experimental set-up is shown in Fig. 1. The lamp irradiance was 22.3 W m^{-2} at 360 nm measured with a UVP model UVX radiometer (Jena, Germany). During reaction, temperature was maintained at 25 °C and samples were taken at different time intervals. The sampling volume was 1 mL in each sample and the remaining volume in the reactor was 195 mL. The calculated concentration was corrected considering the final volume after sampling. Samples were filtered using nitrocellulose membrane with 0.2 μm porosity (Millipore, US), acidified until pH 1 using nitric acid and stored until determination of dissolved metals. All experiments were performed in triplicate.

2.3. Analytical methods

To determine the effectiveness of artificial or solar light assisted photocorrosion processes, the amount of released metal ions into solution was measured and reported as percentage of the total amount of Cu and Fe contained in the original sample. The maximum amount of metal present in the original sample was determined by acid digestion followed by FAAS analysis (Aanalyst 200, Perkin Elmer, US). The wavelength used for FAAS measurements were 324.8 nm and 248.5 nm for copper and iron, respectively.

Hydrolysis reactions were performed at pH below 3 and 25 °C. Heterogeneous photocatalysis runs were done in presence of TiO_2 (0.001 g L^{-1}) at pH 3 and 25 °C in order to evaluate the photocatalytic
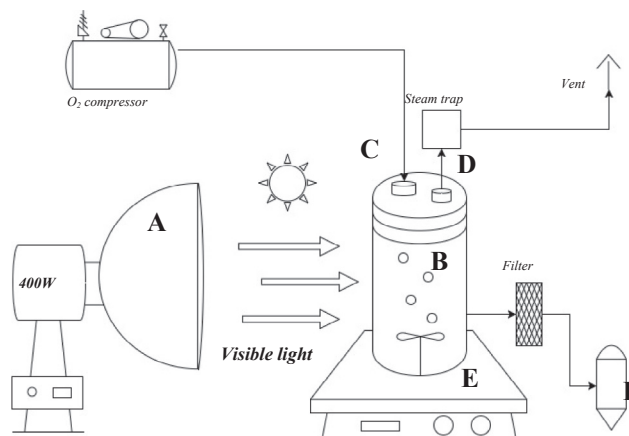

Fig. 1. Experimental set-up to follow the photocorrosion of copper sulfides. (A) solar lamp simulator 400 W, (B) 400 mL borosilicate photoreactor, (C) O_2 inlet, (D) O_2 outlet, (E) magnetic stirrer, (F) samples collected.