



# The effect of silver on the acidic ferric sulfate leaching of primary copper sulfides under recycle solution conditions observed in heap leaching. Part 2: Synergistic additives



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## ABSTRACT

The leaching of a chalcopyrite-bearing ore in sulfate solutions typical of heap leaching systems with various additives present was investigated. The catalytic effects of Ag ions and other additives, which included ethylene glycol, chloride ions and a wetting agent, were investigated experimentally for potential synergistic effects. It was established that the benefit of low Ag ion concentrations on Cu extraction can be enhanced significantly by the presence of additional components in the leach solution. The presence of Ag ions and ethylene glycol resulted in increased Cu extraction compared to just Ag ions. It was observed that in the presence of both chloride ions and Ag ions, the Cu extraction was significantly higher at high chloride concentrations than at lower concentrations. A strong synergistic effect on Cu extraction was observed also between Ag ions and a wetting agent. Cu extractions exceeding 80% after 10 days were observed when Ag ions and the wetting agent were both present. Only a small amount of the wetting agent was required to produce this result.

## 1. Introduction

The most abundant copper bearing mineral is chalcopyrite (Koleini et al., 2011), which accounts for about 70% of all known copper deposits (Martínez-Gómez et al., 2016). Chalcopyrite is also the most refractory of all copper sulfides (Parker et al., 2003). The refractory nature is responsible for the slow dissolution of chalcopyrite. As a result of the slow dissolution, the commercial application of hydrometallurgical processes such as heap leaching for copper extraction from chalcopyrite becomes uneconomic, even though copper oxides and secondary sulfides can be economically processed by heap leaching (Hiroyoshi et al., 1997). It is essential to develop a heap leaching process that can be economically applied to chalcopyrite. It is believed that the leaching rate of chalcopyrite is very low due to the formation of a surface layer on the particles (Biegler and Horne, 1985; Hackl et al., 1995; Nazari et al., 2012a, 2012b). However, the composition of the surface layer, often referred to as a passivation layer is still under debate. Elemental sulfur (Ghahremaninezhad et al., 2015; Klauber et al., 2001; Nazari et al., 2012a); copper-rich sulfides (Hackl et al., 1995) and jarosites (Parker et al., 2003; Cordoba et al., 2009a) have all been proposed as passivating candidates.

Various additives have been investigated for consideration as potential catalysts for copper extraction from chalcopyrite. Some of the

additives include Ag ions (Miller and Portillo, 1979; Nazari et al., 2012a; Yuehua et al., 2002; Johnson et al., 2008) and other metal ions, surfactants (Sandoval et al., 1990), carbon particles (Wan et al., 1984a, 1984b; Nakazawa et al., 2016), iron powder (Sanchez et al., 1996), suspended Cu particles (Baur et al., 1974) and pyrite (Dixon et al., 2008). Carbon particles reportedly improved chalcopyrite leaching by increasing the surface conductivity and acting as nucleation sites for elemental sulfur formation. This reportedly prevents chalcopyrite surface coverage by elemental sulfur (Wan et al., 1984a, 1984b). In a study where MnO<sub>2</sub> was added to a chalcopyrite leach, carbon black was reported to improve electrical contact between MnO<sub>2</sub> and chalcopyrite to establish galvanic coupling (Nakazawa et al., 2016). Surfactants have been found to reduce the hydrophobicity of the chalcopyrite surface caused by interfacial tension (Duncan et al., 1964; Sandoval et al., 1990). However, in other studies, surfactants had no significant effect on chalcopyrite leaching (Torma et al., 1976; Schultze et al., 1995).

In some studies, adding iron powder to a chloride leach of chalcopyrite concentrates improved copper extraction (Sanchez et al., 1996). Baur et al. (1974) had earlier proposed that the presence of suspended iron particles increased the leaching rate via conversion of chalcopyrite to chalcocite. The potential catalytic benefit of pyrite has also been investigated. Pyrite was reported to enhance the extraction of Cu from chalcopyrite due to the establishment of galvanic couples between

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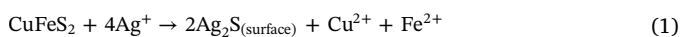
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pyrite and chalcopyrite (Berry et al., 1978; Klauber, 2008; Dixon et al., 2008; Koleini et al., 2011). It has been reported that pyrite increases the dissolution rate of chalcopyrite by a factor of 18 (Abraitis et al., 2004). The influence of pyrite in permanent contact with chalcopyrite was reported to vary with the amount of pyrite present (Majuste et al., 2012). However, it was also reported that the catalytic effect of pyrite on chalcopyrite leaching was realised only if the pyrite was pre-treated with silver (Nazari et al., 2012a, 2012b).

As a result of water restrictions in some locations, the use of saline and seawater is being considered as an option for hydrometallurgical operations (Veloso et al., 2016). It is therefore essential to gain a better understanding of combined sulfate-chloride leaching as the presence of chloride ions has important implications on leaching and downstream processes (Veloso et al., 2016). Investigations on chloride-assisted bioleaching of chalcopyrite revealed that chloride ions enhanced chalcopyrite leaching at 67 °C and 87 °C (Kinnunen and Puhakka, 2004). In that study, it was also reported that 0.25 g Cl<sup>-</sup>/gram of concentrate increased Cu extraction from 60% to 100% in 2 weeks at 90 °C. These authors observed that chloride ions had a negative effect on chalcopyrite leaching at 50 °C. In a different study carried out at 95 °C, it was reported that adding NaCl to a sulfate leach increased the extent of Cu extraction from 45% in the absence of chloride to over 90% in the presence of 1–2 M NaCl (Carneiro and Leão, 2007). Chloride ions are believed to promote the formation of a porous sulfur product as opposed to a dense sulfur layer (Kinnunen and Puhakka, 2004). Such a porous sulfur product is believed to have a weaker passivation effect (Lu et al., 2000). Chalcopyrite is therefore expected to leach more rapidly in the presence of chloride ions than in their absence (Lu et al., 2000). However, it has also been reported that sulfur is not responsible for passivation of chalcopyrite (Nicol, 2017) and such a conclusion implies that the morphology of the S has no effect on chalcopyrite leaching. The pre-treatment of copper sulfide ores with NaCl and H<sub>2</sub>SO<sub>4</sub> followed by leaching in a NaCl-H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub> medium was reported to enhance Cu extraction (Herrerros and Vinals, 2007). One theoretical benefit of introducing chloride ions to the leach solution has been suggested to be the ability of Cl<sup>-</sup> to complex Cu<sup>+</sup> ions and as a result, increase the Cu<sup>+</sup> solubility (Carneiro and Leão, 2007). However, it is considered unlikely this would occur in practice due to the highly oxidising conditions used in leaching (Carneiro and Leão, 2007).

Pioneering studies on the catalytic effects of metal ions were carried out on ZnS and it was proposed that the catalytic effect was probably due to the establishment of galvanic effects between the catalyst ions and the sulfide mineral (Scott and Dyson, 1968). It was proposed that the ideal catalyst ions should activate the sulfide by incorporating themselves into the crystal lattice of the surface layers. Additionally, the ideal catalyst should participate in the electrochemical reactions between the sulfide and the oxidising agent (Scott and Dyson, 1968). Ballester et al. (1992) tested the catalytic effect of several ions on chalcopyrite leaching and only Ag, Hg, Bi and Sn ions had a significant effect. It has now been established that of these additives, Ag ions have the strongest catalytic effect on chalcopyrite dissolution. The leaching rate of chalcopyrite increases dramatically in the presence of Ag ions (Miller and Portillo, 1979; Ahonen and Tuovinen, 1990; Blazquez et al., 1999; Hiroyoshi et al., 2002; Munoz et al., 2007a; Ballester et al., 2007; Ghahremaninezhad et al., 2015). However, Ag ions have not been used as a catalyst in commercial operations due to their high cost (Hiroyoshi et al., 2002).

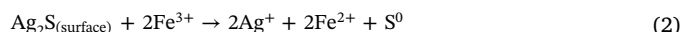
In the absence of an oxidising agent, the reaction of the Ag ions with chalcopyrite has been proposed to be an exchange reaction as shown in Eq. (1) (Miller and Portillo, 1979).



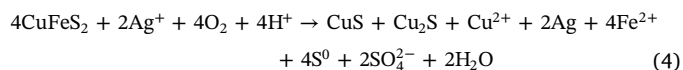
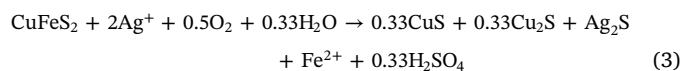
Eq. (1) was reported to have  $\Delta G^\circ = -227.702 \text{ kJ/mol}$  (Miller and Portillo, 1979) and this suggests that the formation of Ag<sub>2</sub>S is thermodynamically feasible. The Ag<sub>2</sub>S rapidly forms on the surface as a

greyish layer (Ahonen and Tuovinen, 1990) or a bluish-black layer (Price and Warren, 1986; Miller et al., 1981). The production of a layer of Ag<sub>2</sub>S several hundred nanometres thick was found to occur in < 30 min (Parker et al., 2003). The growing thickness of such a layer implies that diffusion becomes important in the overall leaching rate (Ghahremaninezhad et al., 2015). The Ag<sub>2</sub>S layer is believed to be porous, unlike elemental sulfur and is therefore less passivating than elemental sulfur (Munoz et al., 2007a). It has also been reported that there is a galvanic interaction between Ag<sub>2</sub>S and CuFeS<sub>2</sub>, where the Ag<sub>2</sub>S behaves cathodically while CuFeS<sub>2</sub> behaves anodically and is preferentially dissolved (Ahonen and Tuovinen, 1990; Parker et al., 1981). In such a case the Ag<sub>2</sub>S facilitates a fast electron transfer (Scaini et al., 1995; Parker et al., 1981).

It has been suggested that there is rapid reaction of the Ag<sub>2</sub>S film with ferric ions according to Eq. (2) (Miller et al., 1981).



Eq. (2) suggests that the Ag<sup>+</sup> ions are regenerated in this way to become available for further reaction with chalcopyrite according to Eq. (1). However, Eq. (2) was reported to give negligible Ag<sub>2</sub>S dissolution in sulfate media at temperatures below 100 °C (Dutrizac, 1994). In addition, Nazari et al. (2012a) have suggested that the Ag<sub>2</sub>S formed is not oxidised by Fe<sup>3+</sup> because the reaction shown by Eq. (2) is not thermodynamically feasible at 25 °C with  $\Delta G_0 = +45.927 \text{ kJ/mol}$ . However, it has been argued that the reaction can become thermodynamically favourable at high ferric concentrations and low Ag concentrations (Ghahremaninezhad et al., 2015). Parker et al. (2003) disputed the feasibility of Eq. (2) because they did not observe elemental S during an x-ray photoelectron spectroscopy (XPS) study. It was recently proposed from thermodynamic data that chalcopyrite can react with Ag to form intermediate copper sulfides as shown in the following equations (Cordoba et al., 2009b; Nikoloski et al., 2017):



Eq. (3) has a  $\Delta G = -302.6 \text{ kJ/mol}$  (Cordoba et al., 2009b) or  $-294 \text{ kJ/mol}$  (Nikoloski et al., 2017). On the other hand, Eq. (4) has a  $\Delta G = -449.7 \text{ kJ/mol}$  (Nikoloski et al., 2017). It was also reported that Eq. (4) has a greater likelihood of metallic Ag formation than Ag<sub>2</sub>S formation (Nikoloski et al., 2017). Metallic silver particles were also detected on the surface of a chalcopyrite electrode treated in acidic sulfate solutions containing silver ions at 50 °C (Tapera and Nikoloski, 2016). Recent studies have shown that there is a minimum Ag<sup>+</sup> dosage needed to give improved rates and extents of copper extraction under heap leaching conditions (Nikoloski et al., 2017). In that study, it was discovered that 0.02 g/L Ag resulted in 25% extraction whereas 0.05 g/L resulted in over 90% extraction. In addition, it was shown that Ag needs to be present on a particle surface or precipitated onto the surface prior to introducing the lixiviant in order to achieve a catalytic effect (Nikoloski et al., 2017). It was proposed that Ag, in the form of Ag<sub>2</sub>S or silver metal, becomes incorporated in the passivating layer during chalcocite, covellite or sulfur formation (Nikoloski et al., 2017). After dissolution of these Ag species, there are pores that form in the surface layer, leaving a porous layer that enables fast transport of dissolved species to and from the mineral surface. When Ag metal is re-deposited, there will be improved electron transfer due to the high conductivity of Ag metal (Nikoloski et al., 2017).

The present study provides further information on the catalytic effect of Ag on leaching of low grade chalcopyrite ores. The study investigates a possible synergistic effect on Cu extraction between Ag and several additives that have previously been observed to have a positive effect on chalcopyrite leaching. These additives include ethylene glycol,

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