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The Acidic Ferric Sulfate Leaching of Primary Copper Sulfides under Recycle Solution Conditions observed in Heap Leaching. Part 1: The Effect of Silver

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Abstract

The current focus for the treatment of low-grade copper resources is through heap leaching with the aid of bacteria. However, it is well known that chalcopyrite and other copper sulfide minerals such as enargite are refractory and suffer from slow leaching kinetics and poor overall extraction due to becoming passivated. Researchers have observed that certain additives such as silver can considerably improve the extraction. What is less understood is if additives like silver can effectively promote the extraction under recycle heap leach conditions, and if so, the mechanism of its action. The study reported in this paper addresses these questions. The standard leaching conditions used were based on a simulated long term recycle solution composition. It was observed that silver addition greatly promoted the extraction of copper from the ore samples under those conditions. Experiments at varied silver concentrations showed that there is a minimum concentration of silver needed to achieve a significant enhancement in the rate and extent of the extraction of copper. For example, for the leaching of the chalcopyrite ore tested in the present study a silver addition of 0.02 g/L resulted in 25% copper extraction in 10 days, whereas 0.05 g/L Ag resulted in over 90% extraction in the same period. It has also been shown that the silver needs to be present at the start of the leaching or precipitated onto the surface of the minerals before adding the lixiviant, to achieve the catalytic effect. Iron extraction appeared to be retarded in the presence of silver, which suggests that silver not only catalyses chalcopyrite and enargite leaching but it may also be galvanically protecting pyrite from dissolution, although the lower iron observed is at least partly attributable to the formation of argentojarosite.

Highlights

- Chalcopyrite and enargite ores tested under recycle heap leach conditions
- Small silver addition enabled full extraction of copper from both minerals
- Model is proposed for the catalytic effect of silver on the leaching process
- Catalytic effect is attributed to silver metal increasing surface conductivity
- Optimal benefit of addition is when silver is added at the start of a leach

1 Introduction

Copper is a versatile metal used in a range of applications (Biswas and Davenport, 1994) including the electrical, electronics and tele-communications industries. To meet the ever-
increasing demand for copper, it is important to be able to effectively extract it from the earth’s crust. The dominant copper mineral in the earth’s crust is chalcopyrite but the vast majority of it is found in low grade deposits, not suitable for traditional flotation and pyrometallurgical processing. To meet the ever-increasing demand for copper, it is important to be able to effectively extract copper from the earth’s crust. Copper in the earth’s crust occurs as native copper or in minerals such as the copper sulfides (for example, chalcopyrite (CuFeS$_2$), chalcocite (Cu$_2$S), covellite (CuS), bornite (Cu$_5$FeS$_4$) or enargite (Cu$_3$AsS$_4$)), the copper carbonates (azurite (Cu$_3$(CO$_3$)$_2$(OH)$_2$) or malachite (Cu$_2$CO$_3$(OH)$_2$)), and the copper oxide minerals (cuprite (Cu$_2$O), tenorite (CuO) or chrysocolla (Cu$_2$O$(H_2$O))$_2$). Chalcopyrite is the most abundant of these copper minerals, accounting for 70% of all copper-containing minerals in the earth’s crust, but the majority of the current reserves are hovering around 0.5% Cu and are continually getting lower with time (Ayres et al., 2002; Norgate and Jahanshahi, 2010). Such resources are not economically suitable for the traditional flotation and pyrometallurgical processing so hydrometallurgical solutions are being investigated to determine if the copper could be extracted through heap leaching. However, both chalcopyrite and enargite are refractory and suffer from slow leaching kinetics and poor overall extraction, so understanding the mechanism of how these minerals leach has generated considerable research interest. The main problem identified is apparent passivation where a product layer is formed on the surface of the grains of the mineral being leached that hinders the leaching reaction (Hackl et al., 1995; Córdoba et al., 2009b; Rivera-Vasquez and Dixon, 2015; Wang et al., 2016). There is much debate as to how this layer is formed and what it comprises. This article is part of a larger study that has investigated the effect on copper and iron extraction from chalcopyrite and enargite of a range of conditions, common species and additives under recycle heap leach solution conditions. Specifically, this article examines the effect of silver on the process chemistry.

One way to overcome the passivation and improve the extraction of copper from these refractory copper minerals is with additives. A number of additives have been shown to promote the extraction of copper from chalcopyrite and enargite, including metal ions (Ag$^+$, Bi$^{3+}$, Cu$^{2+}$, Ni$^{2+}$), minerals (pyrite or pyrolusite), chloride ions, activated carbon and wetting agents (Ahmadi et al., 2010; Ballester et al., 1992; Ballester et al., 2007; Ghanad, 2011; Hiroyoshi et al., 2007; Koleini et al., 2011; Mier et al., 1995; Muñoz et al., 2007a,b; Nicol et al., 2010; Qiu et al., 2007; Rivera-Vasquez and Dixon, 2015; Zhang and Gu, 2007). The most promising of these additives is silver, but it is considered too expensive unless the silver can be recycled. Some recent research has shown that 90% of the silver could be recyclable under certain process conditions, which makes this process more economically feasible (Nazari et al., 2012). There has also been concerns raised relating to silver toxicity given the process involves bacteria, but bacteria have been shown to build resistance to silver (Sugio et al., 1981; Tenvors, 1987). The positive catalytic effect of silver ions on the bioleaching or leaching of chalcopyrite has been demonstrated in several studies (Ahonen and Tuovinen, 1990a, b; Blázquez et al., 1999; Córdoba et al., 2008, 2009a; Feng et al., 2013; Gómez et al., 1997a,b, 1999; Muñoz et al., 1998, 2007a,b, 2008). The use of silver has also been incorporated in the IBES (Indirect Bioleaching with Effects Separation) process and the BRISA (Bioleaching Rapid Indirect with Separation Actions) for the treatment of sulfide concentrates (Carranza et al. 1997; Carranza et al., 2004).

A mechanism as to how silver catalyses chalcopyrite leaching was first proposed by Miller and Portillo (1979) and Miller et al. (1981) and is based on the Ag$^+$ ions forming Ag-sulfide on the chalcopyrite surface (equation 1), followed by Fe$^{3+}$-mediated oxidation to return the silver ions to solution (equation 2):
CuFeS₂ + 4Ag⁺ → Cu²⁺ + Fe²⁺ + 2Ag₂S \hspace{1cm} (1)

Ag₂S + 2Fe³⁺ → 2Ag⁺ + 2Fe²⁺ + S⁰ \hspace{1cm} (2)

Silver recirculates between the solution and solid phase reactions and the overall sum of the chalcopyrite reaction yields elemental sulfur (equation 3) which has been shown to be porous:

CuFeS₂ + 4Fe³⁺ → Cu²⁺ + 5Fe²⁺ + 2S⁰ \hspace{1cm} (3)

Elemental sulfur has also been proposed to form via equation 4 (Price and Warren, 1986):

CuFeS₂ + 4Ag⁺ → Cu²⁺ + Fe²⁺ + 4Ag + 2S⁰ \hspace{1cm} (4)

Price and Warren (1986) added to this theory by proposing that the elemental sulfur layer, in addition to having greater porosity, also possesses a higher electrical conductivity which allows for more efficient electron transport through this surface layer on the chalcopyrite and promotes catalytic leaching. This view of improved electrical conductivity is shared by Nazari et al. (2012) who found silver decreased the resistivity of the sulfur product layer within the Galvanox™ process. They observed that silver increased the catalytic properties of pyrite and enhanced the rate of ferric reduction on the surface of silver-doped pyrite so that it was faster than on the surface of natural pyrite.

Polysulfide and sulfur passive films have been shown to form on chalcopyrite surfaces (Harmer et al., 2006; Klauber et al., 2001; Todd et al., 2003). Córdoba et al.’s (2008, 2009a) leaching model (equations 5 & 6) helps to explain their formation. According to their model, chalcopyrite reacts with silver in solution to form covellite (CuS) and chalcocite (Cu₂S), which subsequently reacts with ferric ions to produce sulfur on the reacting surface (equations 7 and 8).

CuFeS₂ + 2Ag⁺ → CuS + Ag₂S + Fe²⁺ \hspace{1cm} (5)

3CuFeS₂ + 6Ag⁺ + 1.5O₂ + H₂O → CuS + Cu₂S + 3Ag₂S + 3Fe²⁺ + H₂SO₄ \hspace{1cm} (6)

CuS + 2Fe³⁺ → Cu²⁺ + 2Fe²⁺ + S⁰ \hspace{1cm} (7)

Cu₂S + 4Fe³⁺ → 2Cu²⁺ + 4Fe²⁺ + S⁰ \hspace{1cm} (8)

Hiroyoshi et al. (2002) proposed a different reaction model for the catalytic effect of Ag⁺ ions in sulfuric acid solutions which is an extension of their standard two-step model for Fe²⁺-induced dissolution of chalcopyrite (Hiroyoshi et al., 2000, 2001). The Fe²⁺-induced dissolution model assumes that the chalcopyrite and copper in solution is reduced by ferrous ions to form chalcocite (Cu₂S) (equation 9), which is more rapidly leached by ferric ions and/or dissolved oxygen to release cupric ions.

CuFeS₂ + 3Cu²⁺ + 3Fe²⁺ → 2Cu₂S + 4Fe³⁺ \hspace{1cm} (9)

According to the modified model to explain silver catalysed chalcopyrite leaching, the iron within the chalcopyrite is initially reduced to release H₂S into the aqueous phase (equation 10) and the Ag⁺ in solution reacts with this hydrogen sulfide to form Ag₂S precipitate (equation 11) which acts as the anode for chalcopyrite dissolution (equation 12). This causes a rise in the critical potential for formation of Cu₂S and a broadening of the potential range that causes rapid copper extraction to take place.

2CuFeS₂ + 6H⁺ + 2e⁻ → Cu₂S + 2Fe²⁺ + 3H₂S \hspace{1cm} (10)
H₂S + 2Ag⁺ → Ag₂S + 2H⁺  
\[ (11) \]
Ag₂S → 2Ag⁺ + S + 2e⁻  
\[ (12) \]

One of the problems with the above models is they do not explain the porous nature of the sulfur film that has been shown to form on the chalcopyrite surface (Miller et al., 1981; Price and Warren, 1986). Ghahremaninezhad et al. (2015) have proposed an explanation in which the silver cations adsorb on the passivating surface and are incorporated into it, forming Ag₂S. The formation of Ag₂S in the surface layer requires the creation of a sulfur vacancy and a pair of holes in the passive film and proposed by Ghahremaninezhad et al. (2015) as an explanation for the increase in porosity which increases the dissolution kinetics of chalcopyrite in the presence of silver ions. However, this model would not explain the improved electrical conductivity of the surface layer as the low temperature polymorph of Ag₂S which is proposed to form under the leach conditions is not very conductive (Morrison, 2009).

To better explain what mechanism is responsible for the catalytic dissolution of copper sulfide minerals ones, surface examination studies are needed. Surface studies of chalcopyrite in the presence of silver have mainly detected Ag₂S (Muñoz et al., 1981; Price and Warren, 1986; Muñoz et al., 1998; Blázquez et al. 1999). The Ag₂S would redissolve via equation 2, which is verified by the fact that increasing the Fe³⁺ concentration in the leach increases the extraction of copper, as equation 2 indicates that the silver regeneration would be more favourable at a high Fe³⁺/Fe²⁺ ratio (Córdoba et al., 2009a). However, Córdoba et al. (2009a) also noted that the dissolution of silver sulfate by oxygen (equation 13) is more thermodynamically favourable than dissolution by ferric ions. So the dissolved oxygen concentration is also an important parameter in the silver-catalysed chalcopyrite dissolution process.

\[ 2Ag₂S + O₂ + 4H⁺ → 4Ag⁺ + 2S^0 + 2H₂O \]  
\[ (13) \]

The work of Dutrizac (1994) and Bolorunduro et al. (2003) showed that silver sulfide dissolution was very slow below 100 °C in even concentrated acidic ferric sulfate solutions (4 M (223 g/L) Fe³⁺ in 4 M (392 g/L) H₂SO₄). However, bacterial leaching studies that have used either silver sulfide or concentrates containing silver sulfides have shown silver sulfide indeed catalyses the dissolution of chalcopyrite, which would suggest this dissolution has taken place through the catalysed action of the bacteria (Hu et al., 2002; Zhao et al., 2015).

The second form of silver that has been detected on the surface of chalcopyrite as metallic silver (Muñoz et al., 1981; Price and Warren, 1986; Muñoz et al., 1998; Blázquez et al. 1999). Silver metal dissolution in acidic sulfate solutions is known to be fast (equation 14) with an activation energy of 28 kJ/mol (Morrison, 1989).

\[ \text{Ag} + \text{Fe}^{3+} \rightarrow \text{Ag}^+ + \text{Fe}^{2+} \]  
\[ (14) \]

Morrison (1989) found the rate was independent of the ferric concentration as long as this was higher than 0.5 M (~28 g/L Fe), but at lower concentrations the rate depended upon the 0.65 power of the ferric ion concentration. Morrison (1989) also discovered that the rate was affected by the sulfate ion concentration which dramatically slowed this dissolution reaction. The rate was approximately first order with respect to the sulfate ion concentration within solution, which slowed the reaction rate to just over half in the presence of 1 M (~100 g/L) SO₄²⁻. This is most likely due to the competing reaction of silver sulfate formation (equation 15).

The third form of silver that has been detected on the surface of chalcopyrite is silver sulfate (Ag₂SO₄) (Córdoba et al., 2009a; Muñoz et al., 1998; Zhao et al., 2015). Silver sulfate could form through silver reacting with sulfate within the solution (equations 15 & 16) or through
silver dissolution with sulfuric acid (equations 17 & 18). Silver sulfate is likely to be an aqueous species or weak complex and not a real precipitate, and is therefore unlikely to passivate the surface or catalyse reactions. Silver metal, silver or silver sulfate ions are thermodynamically more likely to form in the typical pH region (0.5-2)/Eh (0.5-0.8 V) for heap leaching than silver sulfide, which forms at much lower reducing potentials (< 0.4 V) (equation 19) (Figure 1).

\begin{align*}
2\text{Ag}^+ + \text{SO}_4^{2-} & \rightarrow \text{Ag}_2\text{SO}_4 & (15) \\
\text{Ag}^+ + \text{SO}_4^{2-} & \rightarrow \text{AgSO}_4^- & (16) \\
2\text{Ag} + 2\text{H}_2\text{SO}_4 & \rightarrow \text{Ag}_2\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} & (17) \\
2\text{Ag} + \text{H}_2\text{SO}_4 & \rightarrow \text{Ag}_2\text{SO}_4 + \text{H}_2 & (18) \\
2\text{Ag} + \text{S}^0 & \rightarrow \text{Ag}_2\text{S} & (19)
\end{align*}

Figure 1: $E_\text{h}$-pH Diagram for Silver in Acidic Sulfate Solution (1 mM Ag & 2 M S) at 50°C. Pourbaix Diagrams produced in HSC Chemistry 7.1.1 (Royne, 2011).

However, Córdoba et al. (2009a) observed that the presence of a large excess of silver ions facilitated transformation of the chalcopyrite surface into covellite (CuS) and geerite (Cu$_8$S$_5$ – supposedly chalcocite, Cu$_2$S), that passivated the surface and prevented the electrical galvanic contact between CuFeS$_2$ and Ag$_2$S and, in turn, the regeneration of silver ions. Under such conditions, they found the silver did not catalyse the chalcopyrite dissolution. Muñoz et al. (1998) observed that in the presence of high concentrations of silver, the current from the oxidation reaction fell considerably and attributed this to a compound passivation layer on the chalcopyrite surface of silver sulfate and silver sulfide. Other researchers investigating the leaching of chalcopyrite, or concentrates thereof, have also reported observing a similar effect. That is, they observed an increase in copper extraction with increasing silver addition except for very high silver additions, where the extraction was retarded (Muñoz et al., 2007a; Feng et al., 2013; Abdollahi et al., 2015).

However, Ag$_2$S can also form chemically through reactions with sulfide oxidation products. Sulfur chemistry is very complex as there are a myriad of reactions that could take place to form a range of sulfur species and thiosalts through reactions with acid or oxygen, reactions between other sulfur compounds, and through disproportionation or decomposition. The work
of Mizoguchi et al. (1976) best describes how these various sulfur species can behave under acidic conditions to form a complex mix of sulfur species in solution (Figure 2).

![Disproportionation of Sulfur Species in Acid (Mizoguchi et al., 1976).](image1.png)

**Figure 2: Disproportionation of Sulfur Species in Acid (Mizoguchi et al., 1976).**

During sulfide oxidation, the sulfur is transformed through a series of sulfur species to finally convert to the most stable oxidised form, sulfate (Figure 3). These series of redox reactions are best described in a Latimer diagram which shows the oxidation of species from right to left. So, if the voltage to the right of the species in question is greater than the voltage to the left of the species, that species is said to be unstable with respect to disproportionation. As evident from Figure 3 there are several sulfur compounds that can disproportionate.

![Latimer Diagram for Sulfur in Acidic Solution.](image2.png)

**Figure 3: Latimer Diagram for Sulfur in Acidic Solution.**

These sulfur species can also react with other cations such as ferric ions which are regularly present in the chalcopyrite leach system, to form other sulfur compounds. Druschel et al. (2003) studied the oxidation of tetrathionate and trithionate in the presence of oxygen and ferric ions under acidic solutions (pH 0.4 to 2) and proposed a reaction mechanism based on their observations (Figure 4). Trithionate oxidation was found to be several orders of magnitude faster than tetrathionate oxidation, but both were reported to be orders of magnitude slower than the oxidation of thiosulfate under these conditions. This would suggest tetrathionate and possibly trithionate would persist in heap leach or leaching environments, so ferric ions is not only necessary for the extraction of copper but plays an important role in the generation and oxidation of many polythionates.
Figure 4: Proposed Pathway for the Reaction of Tetrathionate with Ferric Ions at Low pH in the Presence of Oxygen (Druschel et al., 2003).

While Latimer diagrams show the series of steps during the oxidation of species, Pourbaix diagrams better portray the likely stable species in solution. Based on calculated thermodynamic data (Figure 5), the sulfate to bisulfate equilibrium is above pH 2 and it appears that only bisulfate ions should be stable under the typical leaching window of pH 0.5-2 and $E_h$ 0.5-0.8V. However, while it is not clear why, the thermodynamic data fails to accurately describe the actual conditions in typical solutions in heap leaching, where experience shows that the sulfate to bisulfate equilibrium reduces to much lower pH of about 0.8 to 1. Thus, in practical solutions the dominant form of sulfur is sulfate. In addition, if one excludes the sulfate and bisulfate ions (second graph) then tetrathionate and hydrogen sulfate can be seen to exist within this region. Sulfur is likely to be stable under more reducing conditions ($< 0.3$ V) but it is known to be present on the surface of chalcopyrite particles (Córdoba et al., 2009a; Harmer et al., 2006; Klauber et al., 2001; Muñoz et al., 1979).
Figure 5: $E_h$-pH Diagram for Sulfur (2 M S) in Acidic Sulfate Solution (second graph excludes $SO_4^{2-}$ at 50°C. Pourbaix Diagrams Produced in HSC Chemistry 7.1.1 (Royne, 2011).

Therefore, it is highly likely that the $Ag_2S$ observed on the surface of chalcopyrite in many studies is formed through reactions with sulfur compounds such as tetrathionate in solution (equation 20).

$$2Ag^+ + S_4O_6^{2-} + 2H_2O \rightarrow Ag_2S + 2SO_4^{2-} + S^0 + 4H^+$$ (20)
Given this pathway seems likely to be the main method of Ag₂S formation on the surface of chalcopyrite in silver-catalysed acidic ferric sulfate leaching, none of the currently proposed dissolution mechanisms explain the observed catalytic dissolution or the increase in the electrical conductivity.

Table 1 summarises all the possible reactions between chalcopyrite and silver ions. During dissolution, chalcopyrite is known to form covellite, chalcocite and copper(II) ions in solution. While all these reactions are thermodynamically feasible, this information does provide an indication to the most likely dissolution mechanism. In the presence of silver, the solid-state transformation of chalcopyrite thermodynamically favours the formation of a mixture of copper-rich sulfides (equations 6 and 24) rather than direct dissolution to cupric ions or to either chalcocite (Cu₂S) or covellite (CuS). The silver is also thermodynamically more likely to be reduced to metallic silver than to form a silver sulfide. This supports the surface characterisation studies which show that chalcopyrite converts to covellite and chalcocite derivatives (i.e., geerite) (Córdoba et al., 2009a; Ghahremaninezhad et al., 2013). Equation 24 is more in line with the observed results, given the higher electrical conductance of silver metal than Ag₂S (Price and Warren, 1986; Nazari et al., 2012), and in fact metallic silver has the highest electrical and thermal conductivity of all metals (Myers, 2009). Equation 24 also explains the leaching observations where the pH increases with the consumption of protons, and the importance of oxygen in the system. However, this reaction can be expected to be kinetically slow under atmospheric conditions such that ferric oxidation would likely dominate. The limited detection of silver metal on the surface is likely due to the fact that silver is highly soluble in acidic ferric sulfate solution and does not persist on the chalcopyrite surface for observation.

Table 1: Proposed Reactions for chalcopyrite and corresponding Gibbs Free energy at 298K.

<table>
<thead>
<tr>
<th>Equations</th>
<th>ΔG° (kJ/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFeS₂ + 2Ag⁺ → 0.5Cu₂S + Fe²⁺ + 2Ag + 1.5S⁰</td>
<td>-99.6</td>
<td>Royne (2011)</td>
</tr>
<tr>
<td>CuFeS₂ + 2Ag⁺ → CuS + Fe²⁺ + 2Ag + S⁰</td>
<td>-109.0</td>
<td>Royne (2011)</td>
</tr>
<tr>
<td>CuFeS₂ + 2Ag⁺ → 0.5Cu₂S + Ag₂S + Fe²⁺ + 0.5S⁰</td>
<td>-140.0</td>
<td>Royne (2011)</td>
</tr>
<tr>
<td>CuFeS₂ + 4Ag⁺ → Cu²⁺ + Fe²⁺ + 4Ag + 2S⁰</td>
<td>-149.2</td>
<td>Price and Warren (1986)</td>
</tr>
<tr>
<td>CuFeS₂ + 2Ag⁺ → CuS + Ag₂S + Fe²⁺</td>
<td>-152.4</td>
<td>Royne (2011)</td>
</tr>
<tr>
<td>CuFeS₂ + 4Ag⁺ → Cu²⁺ + Fe²⁺ + 2Ag₂S</td>
<td>-229.6</td>
<td>Price and Warren (1986)</td>
</tr>
<tr>
<td>CuFeS₂ + 2Ag⁺ + 0.5O₂ + 0.33H₂O → 0.33CuS + 0.33Cu₂S + Ag₂S + Fe²⁺ + 0.33H₂SO₄</td>
<td>-302.6</td>
<td>Córdoba et al. (2009a)</td>
</tr>
<tr>
<td>CuFeS₂ + 0.5Ag⁺ + O₂ + H⁺ → 0.25CuS + 0.25Cu₂S + 0.25Cu²⁺ + 0.5Ag + Fe²⁺ + S⁰ + 0.5SO₄²⁻ + 0.5H₂O</td>
<td>-449.7</td>
<td>Royne (2011)</td>
</tr>
</tbody>
</table>
It is highly likely that the leaching reactions of enargite in the presence of silver ions are similar to the leaching reactions of chalcopyrite in the presence of silver, as summarised in Table 2. These reactions are also thermodynamically feasible. Similar to chalcopyrite, they show that the solid-state transformation of enargite thermodynamically favours a mixture of copper-rich sulfides (equations 29 and 33) rather than its dissolution to cupric ions or to either chalcocite (Cu$_2$S) or covellite (CuS). However, the silver ions in these reactions would favour forming silver sulfide precipitate rather than silver metal, given the more favourable Gibbs free energies. This may be occurring via equation 25 which would explain the lower energy to precipitate silver ($\Delta G^o = 20.2 \text{ kJ/mol}$).

$$2\text{Ag} + S^o \rightarrow \text{Ag}_2S$$  \hspace{1cm} (25)

<table>
<thead>
<tr>
<th>Equations</th>
<th>$\Delta G^o$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_3$AsS$_4$ + Ag$^+$ + H$_2$O + O$_2$ + H$^+$ → Cu$_2$S + Cu$^{2+}$ + H$_3$AsO$_3$ + Ag + 3S$^o$</td>
<td>-542.3</td>
</tr>
<tr>
<td>Cu$_3$AsS$_4$ + Ag$^+$ + 3H$^+$ + 1.5O$_2$ → CuS + 2Cu$^{2+}$ + H$_3$AsO$_3$ + Ag + 3S$^o$</td>
<td>-679.5</td>
</tr>
<tr>
<td>Cu$_3$AsS$_4$ + 3Ag$^+$ + 3H$^+$ + 1.5O$_2$ → 3Cu$^{2+}$ + H$_3$AsO$_3$ + 3Ag + 4O$^-$</td>
<td>-714.9</td>
</tr>
<tr>
<td>Cu$_3$AsS$_4$ + Ag$^+$ + 2.75O$_2$ + 1.5H$_2$O → 0.5CuS + 0.5Cu$_2$S + 1.5Cu$^{2+}$ + H$_3$AsO$_3$ + Ag + 2S$^o$ + SO$_4^{2-}$</td>
<td>-1118.1</td>
</tr>
<tr>
<td>Cu$_3$AsS$_4$ + 2Ag$^+$ + 1.5H$_2$O + 0.75O$_2$ → Cu$_2$S + Cu$^{2+}$ + H$_3$AsO$_3$ + Ag$_2$S + 2S$^o$</td>
<td>-541.2</td>
</tr>
<tr>
<td>Cu$_3$AsS$_4$ + Ag$^+$ + 3H$^+$ + 1.5O$_2$ → CuS + 2Cu$^{2+}$ + H$_3$AsO$_3$ + 0.5Ag$_2$S + 2.5S$^o$</td>
<td>-699.7</td>
</tr>
<tr>
<td>Cu$_3$AsS$_4$ + 3Ag$^+$ + 3H$^+$ + 1.5O$_2$ → 3Cu$^{2+}$ + H$_3$AsO$_3$ + 1.5Ag$_2$S + 2.5S$^o$</td>
<td>-775.5</td>
</tr>
<tr>
<td>Cu$_3$AsS$_4$ + Ag$^+$ + 2.75O$_2$ + 1.5H$_2$O → 0.5CuS + 0.5Cu$_2$S + 1.5Cu$^{2+}$ + H$_3$AsO$_3$ + 0.5Ag$_2$S + 1.5S$^o$ + SO$_4^{2-}$</td>
<td>-1138.3</td>
</tr>
</tbody>
</table>

All of these models have been proposed from studies with initial leaching conditions. None of these studies were conducted using recycle leach solution conditions in ferric sulfate media, and therefore, they may not apply well to practical heap leach conditions. The purpose of the research reported in this paper therefore is to show how low grade chalcopyrite and enargite ores behave in such a system, with special focus on the effect of adding silver ions on the kinetics and the chemistry of the leaching process. Separate reports to follow will provide further detailed information on the mineralogical changes that take place during the leaching, the formation of intermediate species and the semiconductor behaviour of the target minerals.

2 Materials and Methods

2.1 Ore Samples

A chalcopyrite-dominant and an enargite-dominant ore sample were used in this test work. The chemical composition of the predominantly chalcopyrite ore sample is given in Table 3, and of the predominantly enargite ore sample in Table 4. The main elements in the two ores were silicon (~32 %) and aluminium (~8 %). Besides this, the predominantly chalcopyrite ore
contained 3.53 % Fe and 0.85 % Cu, and the predominantly enargite ore contained 3.66 % Fe and 1.02 % Cu.

**Table 3: Bulk Chemical Analysis of the Chalcopyrite Sample.**

<table>
<thead>
<tr>
<th>Element</th>
<th>(%)</th>
<th>Element</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>32.73</td>
<td>Cu</td>
<td>0.85</td>
</tr>
<tr>
<td>Al</td>
<td>7.76</td>
<td>Mg</td>
<td>0.36</td>
</tr>
<tr>
<td>S</td>
<td>3.79</td>
<td>Ca</td>
<td>0.032</td>
</tr>
<tr>
<td>Fe</td>
<td>3.53</td>
<td>As</td>
<td>0.017</td>
</tr>
<tr>
<td>K</td>
<td>3.09</td>
<td>Remaining</td>
<td>0.53</td>
</tr>
</tbody>
</table>

**Table 4: Bulk Chemical Analysis of the Enargite Sample.**

<table>
<thead>
<tr>
<th>Element</th>
<th>(%)</th>
<th>Element</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>32.20</td>
<td>Cu</td>
<td>1.02</td>
</tr>
<tr>
<td>Al</td>
<td>8.05</td>
<td>As</td>
<td>0.246</td>
</tr>
<tr>
<td>S</td>
<td>4.03</td>
<td>Mg</td>
<td>0.197</td>
</tr>
<tr>
<td>Fe</td>
<td>3.66</td>
<td>Ca</td>
<td>0.074</td>
</tr>
<tr>
<td>K</td>
<td>3.06</td>
<td>Remaining</td>
<td>1.65</td>
</tr>
</tbody>
</table>

A summary of the mineralogical information is given in Table 5 for the chalcopyrite sample and Table 6 for the enargite sample. The chalcopyrite-dominant ore contained 2.47 % copper minerals with the main gangue species being quartz (45.4 %) and muscovite (40.4 %). Pyrite was the main sulfide mineral which accounted for 6.87 % of the mineral content. The copper mineral content is largely chalcopyrite (87.7 %), with the remaining 12.3 % comprising other copper minerals (8 %), chalcocite (2 %), covellite (1 %), and enargite, copper oxide and copper clay minerals (1 %).

The enargite-dominant ore contained 1.98 % copper minerals with the main gangue species being quartz (44.7 %), muscovite (40.1 %) and pyrophyllite (3.2 %). Pyrite was also the main sulfide mineral which accounted for 7.04 % of the mineral content. The copper mineral content is largely enargite (67.1 %) with the remaining 32.9 % comprising other copper minerals (8.7 %), covellite (8.7 %), copper oxides (6.4 %), chalcopyrite (4.3 %), chalcocite (2.4 %) and copper clay minerals (2.4 %).

A total of 20 feed samples for the chalcopyrite sample were assayed which gave an average grade for copper of 0.85 %, and average grade for iron of 3.53 %. Five feed samples of the enargite ore were assayed and showed an average grade for copper of 1.00 % and average grade for iron of 3.66 %. The P₈₀ of the ground chalcopyrite ore sample was 42 µm and for the ground enargite ore sample was 38 µm, as determined by laser sizing.

**Table 5: Mineralogical Analysis of the Chalcopyrite Sample.**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>(%)</th>
<th>Mineral</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>45.4</td>
<td>Remaining</td>
<td>1.61</td>
</tr>
<tr>
<td>Muscovite</td>
<td>40.4</td>
<td>K-Feldspar</td>
<td>0.28</td>
</tr>
<tr>
<td>Pyrite</td>
<td>6.87</td>
<td>Other Cu Minerals</td>
<td>0.22</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>2.99</td>
<td>Chalcocite</td>
<td>0.05</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>2.16</td>
<td>Covellite</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Table 6: Mineralogical Analysis of the Enargite Sample.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>(%)</th>
<th>Mineral</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>44.7</td>
<td>Kaolinite</td>
<td>0.54</td>
</tr>
<tr>
<td>Muscovite</td>
<td>40.1</td>
<td>K-Feldspar</td>
<td>0.26</td>
</tr>
<tr>
<td>Pyrite</td>
<td>7.04</td>
<td>Other Cu Minerals</td>
<td>0.17</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>3.24</td>
<td>Covellite</td>
<td>0.17</td>
</tr>
<tr>
<td>Remaining</td>
<td>2.18</td>
<td>Copper Oxides</td>
<td>0.13</td>
</tr>
<tr>
<td>Enargite</td>
<td>1.33</td>
<td>Chalcopyrite</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chalcocite</td>
<td>0.05</td>
</tr>
</tbody>
</table>

2.2 Sample Preparation

The ore samples were stage crushed to -1.0 mm by screening and crushing the +5 mm samples in a Jacques laboratory crusher, followed by a second screening and crushing of the +1 mm sample in a Metso Minerals Marcy gy-roll crusher. The ore was homogenised in a Wallaby Mining Products rotary splitter by combining and re-splitting the ore five times before dividing into 500 g lots. A grind establishment on the 500 g samples was undertaken in a laboratory rod mill at 50 % solids to achieve a P$_{80}$ of 38 µm. When the ore was required for a leach, a 500 g charge was ground to P$_{80}$ of 38 µm and then pressure filtered into a cake. A wedge was taken for moisture determination so the correct mass of wet cake could be added to the leach to achieve the desired percent solids in the leach. The target grind size was confirmed on a Microtrac S3500 laser sizing. All allotments and ground samples were stored in a refrigerator (5 °C) until required.

2.3 Leaching Tests

Each leaching test was run for 10 days in a 1 L thermostatic baffled leaching vessel at 50 °C (± 1 °C) stirred at 600 ± 30 rpm. To avoid vortex formation two opposing baffles were mounted perpendicular to the vessel wall. Airtight lids with a condenser were installed on each leach vessel to minimise evaporation.

For the chalcopyrite sample, different silver concentrations in the leach solution were tested ranging from 1 g/L to 0.005 g/L. Table 7 summarises the silver concentrations in solution in grams per litre, molarity, mass of ore and the mass of copper contained in the ore.

Table 7: The Silver Concentration within the Chalcopyrite Sample Leach.

<table>
<thead>
<tr>
<th>[Ag] (g/L)</th>
<th>[Ag] (mM)</th>
<th>[Ag] (g Ag/kg Ore)</th>
<th>[Ag] (g Ag/kg Cu contained)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>9.27</td>
<td>19</td>
<td>2229</td>
</tr>
<tr>
<td>0.5</td>
<td>4.64</td>
<td>9</td>
<td>1114</td>
</tr>
<tr>
<td>0.25</td>
<td>2.32</td>
<td>5</td>
<td>550</td>
</tr>
<tr>
<td>0.1</td>
<td>0.93</td>
<td>2</td>
<td>222</td>
</tr>
<tr>
<td>0.05</td>
<td>0.46</td>
<td>1</td>
<td>110</td>
</tr>
<tr>
<td>0.02</td>
<td>0.19</td>
<td>0.4</td>
<td>45</td>
</tr>
<tr>
<td>0.005</td>
<td>0.05</td>
<td>0.1</td>
<td>11</td>
</tr>
</tbody>
</table>

For the enargite sample, the silver concentrations tested in the leach solution varied from 1 g/L to 0.1 g/L. Table 8 summarises the silver concentrations in solution in grams per litre, molarity, mass of ore and the mass of copper contained in the ore.
Table 8: The Silver Concentration within the Enargite Sample Leach.

<table>
<thead>
<tr>
<th>[Ag] (g/L)</th>
<th>[Ag] (mM)</th>
<th>[Ag] (g Ag/kg Ore)</th>
<th>[Ag] (g Ag/kg Cu contained)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>9.27</td>
<td>19</td>
<td>2115</td>
</tr>
<tr>
<td>0.5</td>
<td>4.64</td>
<td>10</td>
<td>1049</td>
</tr>
<tr>
<td>0.1</td>
<td>0.93</td>
<td>2</td>
<td>200</td>
</tr>
</tbody>
</table>

The lixiviant was prepared using deionised water and laboratory reagent (LR) grade sulfated salts of iron, magnesium, copper or aluminium either from Chem Supply, Ajax Finechem, Fisher Chemical, or BDH Prolabo. The required mass of chemicals was added to make the desired concentration of metal in the leach solution. The pH of the solution was modified by either adding analytical reagent (AR) grade sulfuric acid (98.3% H₂SO₄) or AR lithium hydroxide (1 M). The value of x in the Fe₂(SO₄)₃.x H₂O reagent was determined to be 6.82 using a gravimetric method (Sohn and Park, 1998) in which a sample of the reagent was heated to 300 °C overnight in an oven to remove the water of crystallisation while preventing the decomposition of the sulfate.

The required amount of silver (as 10 g/L Ag nitrate solution) was added to achieve the concentration of the predicted baseline recycle solution. The baseline conditions were 25 g/L Fe³⁺/²⁺, 10 g/L Al³⁺, 1 g/L Mg²⁺, 0.2 g/L Cu²⁺ and 125 g/L SO₄²⁻ at pH 1.2, Eₚ 700 mV and temperature of 50 °C. All leach experiments were conducted with 5% solids, such that 42 g (dry basis) ore sample was added to 800 mL of lixiviant once the temperature had reached the set point. The Eₚ was monitored using a TPS ORP Ag⁺/AgCl probe and only allowed to vary to within ±10 mV, while pH only varied to within ±0.1 of a unit. If required, adjustments were made by adding sodium metabisulfite or hydrogen peroxide to control the Eₚ, and by adding LiOH or H₂SO₄ to control the pH. The use of LiOH was chosen to minimise the loss of iron as sodium jarosite. All potentials reported have been converted to SHE. All residues were washed in acidified deionised water and collected on Whatman 541 hardened ashless filter papers by vacuum filtration and dried at 60 °C. Solution samples were diluted in acidified deionised water and all residues digested in Aqua Regia and diluted before being analysed on an Agilent technologies 55 atomic absorption spectrometer. The error in extraction was calculated based on the average change in accountability and how that would alter the extraction.

3 Results and Discussion

3.1 Effect of silver concentration on leaching chalcopyrite ore

The effect of the concentration of silver on the extraction of copper and iron from the chalcopyrite sample after 10 days of leaching is presented in Figure 6. It is clear that the addition of silver ions significantly improved the extraction of copper, which increased from 18% in the baseline test that contained no added silver to 98% in the presence of 1 g/L Ag. However, the iron dissolution results show the opposite effect. As the silver concentration was increased the iron extraction decreased from 48% in the baseline test with no added silver to 25% in the presence of 1 g/L Ag. The observed decrease in iron extraction or very little additional iron extraction after the first day was proposed to be the result of jarosite precipitation which plateaued the iron concentration in solution, and was confirmed by X-ray diffraction analysis of the residue samples.
Figure 6: Copper and Iron Leaching Kinetics from Chalcopyrite Ore as a Function of Silver Addition.

The effect of varying the addition of silver on the final extraction of copper and iron is presented in Figure 7. The copper extraction showed an exponential improvement from no silver addition to 0.05 g/L, after which there was only a gradual improvement of 7% in the extraction with an order of magnitude further increase in silver addition. For the iron extraction there was little change between no silver addition and 0.1 g/L, after which there was a noticeable decrease of ~25% in the extracted iron with increasing silver addition.

Figure 7: Final Copper and Iron Extraction from Chalcopyrite Ore as a Function of Silver Addition.
Figure 8: Initial and Final Copper and Iron Extraction Rate from Chalcopyrite Ore vs. Silver Addition.

Figure 8 illustrates the effect of the silver addition on the rate of copper and iron extraction in the initial (0-2 days) and final period of the leach (4-10 days). It is clear that the silver affected the copper and iron rates of dissolution in the initial period, but in the final stage there was very little difference in the rates of copper or iron extraction for the silver concentrations investigated.

3.2 Effect of varied silver concentration on the enargite sample

The effect of varied concentrations of silver on the extraction of copper and iron from the enargite sample is presented in Figure 9. It is clear that the addition of silver ions significantly improved the extraction of copper from 68 % after 10 days in a baseline test that contained no added silver to 96 % in the test that contained 1 g/L Ag. However, as with the chalcopyrite sample the iron dissolution results show the opposite effect. As the silver concentration increased, the iron extraction decreased from a baseline extraction of 68 % with no silver addition to 45 % in the presence of 1 g/L Ag.
Figure 9: Copper and Iron Leaching Curves in 25 g/L Fe\textsuperscript{3+/2+}, 10 g/L Al\textsuperscript{3+}, 1 g/L Mg\textsuperscript{2+}, 0.2 g/L Cu\textsuperscript{2+}, 125 g/L SO\textsubscript{4}\textsuperscript{2-}, pH of 1.2, E\textsubscript{h} of 700 mV and Temperature of 50°C at Varied Ag Additions for the Enargite Ore.

The effect of varying the addition of silver on the final extraction of copper and iron is shown in Figure 10. The copper extraction showed a significant improvement from no silver addition to 0.1 g/L, after which there was only a gradual improvement of 6% in the extraction with increasing silver addition. For iron, there was a gradual drop in the apparent extraction with increasing silver addition but data scatter makes this trend less definitive.

Figure 10: Final Copper and Iron Extraction Curves at Varied Silver Concentrations for the Enargite Ore.

Figure 11 illustrates the effect of the silver addition on the rate of copper and iron extraction in the initial (0-2 days) and final period of the leach (4-10 days). It is clear that the silver affected
the copper and iron rates of dissolution in the initial period, but in the final stage there was very little difference in the rate of copper or iron extraction over the silver concentration investigated.

![Graph showing copper and iron extraction rates](image1)

**Figure 11**: The Initial and Final Copper and Iron Extraction Rate Curves at Varied Silver Concentrations for the Enargite Ore.

### 3.3 Evaluation of the Initial Rates of Leaching

The initial rates of copper and iron extraction for the enargite and chalcopyrite leaching as a function of silver addition follow a similar trend (Figure 12). The copper dissolution rate increases with increasing silver concentration while the opposite was observed for the iron.

![Graph showing copper and iron extraction rates](image2)

**Figure 12**: The Initial Copper and Iron Extraction Rate Curves at Varied Silver Concentrations.
Figure 13 clearly demonstrates that the reaction was first order with respect to the silver concentration up to a concentration of 0.05 g/L within solution, but the order decreased at higher silver concentrations.

![Graph showing the relationship between ln(rCu) and ln([Ag+]*) with a linear regression line.](image)

**Figure 13: The Initial Copper Extraction Rate Curves for the Chalcopyrite Sample at Varied Silver Concentrations.**

3.4 Proposed Mechanism

It is clear from this present work that silver provides a catalytic benefit under recycle leach conditions for both chalcopyrite and enargite leaching.

Tables 1 & 2 summarises all the possible reactions of chalcopyrite or enargite with silver. While thermodynamically all the reactions were feasible, the current study it is still consistent with the chalcopyrite and enargite minerals leaching according to reactions 24 and 29 respectively, whereby the observed silver sulfide on the surface is from the resulting reaction of silver ions with sulfur species in solution rather than formed during the dissolution reaction.

\[
4\text{CuFeS}_2 + 2\text{Ag}^+ + 4\text{O}_2 + 4\text{H}^+ \rightarrow \text{CuS} + \text{Cu}_2\text{S} + \text{Cu}^{2+} + 2\text{Ag} + 4\text{Fe}^{2+} + 4\text{S}^0 + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} \tag{24}
\]

\[
2\text{Cu}_3\text{AsS}_4 + 2\text{Ag}^+ + 5.5\text{O}_2 + 3\text{H}_2\text{O} \rightarrow \text{CuS} + \text{Cu}_2\text{S} + 3\text{Cu}^{2+} + 2\text{H}_3\text{AsO}_3 + 2\text{Ag} + 4\text{S}^0 + 2\text{SO}_4^{2-} \tag{29}
\]

While thermodynamics explains the reaction pathway they do not explain the observed porous nature of the passivating layer. Ghahremaninezhad et al. (2015) proposed a semiconductor model which forms electron holes in the passivating layer. However, this model is usually applied to a material with a crystal structure and may not be applicable for product layers in the present system. A simpler explanation is that silver, both as silver sulfide or silver metal, is incorporated into the passivation layer during chalcocite, covellite and sulfur formation on the mineral surface. These compounds are subsequently redissolved, leaving pores in that layer which would improve the mass transport of dissolved species to and from the mineral surface. This then allows for the silver to re-deposit and it is the silver metal that improves the electron
transfer, thereby facilitating the electrochemical reaction. This process is illustrated in Figure 14.

Figure 14: Proposed Model for Catalysed Leaching through a Porous Passivating Layer.

The dissolution of iron was also studied under recycle leach conditions. In such an environment it would be expected that some of the iron would precipitate as goethite and/or jarosite (equations 34 and 35) (Figure 15). It is also likely that some of the silver will precipitate as argentojarosite (AgFe$_3$(SO$_4$)$_2$(OH)$_6$) during leaching (equation 36) (Carranza et al., 1997; Bolorunduro et al., 2003; Córdoba et al., 2009a). Once silver becomes locked in argentojarosite, it will most likely lose its catalytic effect on the leaching of chalcopyrite or enargite and resist re-dissolution, effectively eliminating it from the process.

\[
\begin{align*}
\text{Fe}_2(\text{SO}_4)_3 + 0.5\text{SO}_2 + 3\text{H}_2\text{O} & \rightarrow 2\text{FeO(OH)} + 3\text{H}_2\text{SO}_4 \\
3\text{Fe}_2(\text{SO}_4)_3 + 14\text{H}_2\text{O} & \rightarrow 2(\text{H}_2\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 5\text{H}_2\text{SO}_4 \\
\text{Ag}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} & \rightarrow \text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ 
\end{align*}
\]

It was observed there was an apparent retardation in the extraction, or at least a decrease in the concentration, of iron in the presence of high (> 0.05 g/L Ag) concentrations of silver ions in solution. This retardation has also been observed in previous studies that have examined concentrate dissolution or galvanic chalcopyrite/pyrite couples (Ahonen and Tuovinen, 1990a; Muñoz et al., 2008; Nazari et al., 2012). It is proposed that the metallic silver is acting as an electrical conductor enabling galvanic chalcopyrite/pyrite couples to occur above a particular silver concentration in solution. The combined action of the galvanic couples and silver-catalysed dissolution promotes the extraction of copper from either enargite or chalcopyrite. On the other hand, the galvanic protection of pyrite would reduce the supply of iron in solution.
3.5 Effect of Timing of the Addition of Silver and Premixing

Studies reported in the literature have shown that if silver is added during a leaching test with a chalcopyrite ore sample, an improvement in the extraction of copper is observed (Gómez et al., 1997c; Muñoz et al., 2007c). The explanation proposed by Ghahremaninezhad et al. (2015) involves the silver interacting with a sulfur passive layer and reactivating the surface to allow for additional extraction. This mechanism should operate for silver added at any time during a leach. To test this, silver was added after 2 days of leaching. Also, Figures 8 and 11 show silver only affects the initial rate of extraction, so the effect of premixing the ore with silver was tested where the silver was in contact with the ore for two days in a 60% slurry prior to adding this to the leach solution. The results of these tests are presented in Figures 16 and 17.

Figure 15: $E_h$-pH diagram for iron in acidic sulfate solution (0.5 M Fe & 2 M S) at 50°C. Pourbaix diagrams produced in HSC Chemistry 7.1.1 (Royne, 2011) with thermodynamic data for hydronium jarosite obtained from Lemire et al. (2013).
Figure 16: Effect of when the Silver is Added on the Copper and Iron Leaching Curves in 25 g/L Fe$_{3+/2+}$, 10 g/L Al$^3+$, 1 g/L Mg$^2+$, 0.2 g/L Cu$^{2+}$, 125 g/L SO$_4^{2-}$, pH of 1.2, $E_h$ of 700 mV and Temperature of 50°C for the Chalcopyrite Ore.

Figure 17: Effect of Premixing the Silver with the Ore on the Copper and Iron Leaching Curves in 25 g/L Fe$_{3+/2+}$, 10 g/L Al$^3+$, 1 g/L Mg$^2+$, 0.2 g/L Cu$^{2+}$, 125 g/L SO$_4^{2-}$, pH of 1.2, $E_h$ of 700 mV and Temperature of 50°C for the Chalcopyrite Ore.

Figure 16 clearly shows that silver cannot reactivate the chalcopyrite surface once it has been passivated as there is marginal improvement in extraction after the silver is added. Figure 17 clearly shows that premixing the silver with the ore significantly increased the overall extraction of copper from this chalcopyrite ore sample. These results suggest that the silver needs to be present at the start of the leach or precipitated on the surface before adding the lixiviant to have any catalytic effect. Silver ions cannot reactivate a passivated surface as the model proposed by Ghahremaninezhad et al. (2015) would predict.
4 Conclusions

The catalytic effect of silver ions on the leaching of sulfide minerals is well documented but there have not been many studies on the effect of the addition of silver in primary copper sulfide leaching under recycle heap leach conditions and also the mechanism of the process has remained poorly understood. The purpose of the research reported in this paper therefore has been to show how low grade chalcopyrite and enargite ores behave in a system under recycle heap leach conditions using detailed leaching experiments. The study investigated the effect of adding different amounts of silver to the system on the leaching kinetics of copper from a predominately chalcopyrite ore and a predominately enargite ore. The leaching was carried out in the presence of 25 g/L Fe$^{3+}/2+$, 10 g/L Al$^3+$, 1 g/L Mg$^2+$, 0.2 g/L Cu$^{2+}$, 125 g/L SO$_4^{2-}$, with pH 1.2, Eh 700 mV and temperature of 50 °C. The results of the leaching test work have confirmed that the addition of silver ions greatly improves the extraction of copper from either chalcopyrite or enargite under these conditions. Silver additions of less than 0.1 g/L were adequate to significantly catalyse the leaching. It was determined that the rate of extraction of copper from the chalcopyrite was first order with respect to the silver concentration up to 0.05 g/L, after which the order decreased. The catalytic mechanisms could be interpreted using thermodynamic calculations. Based on these findings, a model for the silver catalysed leaching process is proposed which involves metallic silver as the catalyst in the reaction mechanism, and improvement in surface conductivity proposed as the main reason for the faster leaching kinetics in the presence of silver.

The experimental work has shown also that the silver must be introduced to the system at the start of the leach, or precipitated on the surface of the minerals before adding the lixiviant, to achieve the catalytic benefit. The changes in the surface properties that take place during the leaching process and lead to improved surface conductivity are a major contributor to this behaviour. The mineralogical changes, the intermediate species and the semiconductor behaviour of the target minerals have therefore been further investigated using advanced surface characterisation and electrochemical techniques and will be presented in separate reports.

In addition, silver at concentrations of higher than 0.05 g/L was observed to coincide with reduced concentrations of iron in the system. This could be attributed to the observed precipitation of argentojarosite with increasing silver concentration; however, it may also be related to a galvanic interaction of chalcopyrite with pyrite in the presence of silver, resulting in changes in the iron speciation and lower pyrite dissolution. In the absence of detailed data on the mineralogical transformations of pyrite taking place during the leaching and the chemical species formed under these conditions it is difficult to make a definitive statement about the effect of silver on the pyrite dissolution. Further detailed work is required to answer this question.

5 Acknowledgements

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6 References


