The development of an effective technology for heap leaching of chalcopyrite ores by the use of synergistic catalytic additives

Jake Sheean

“A report submitted to the School of Engineering and Information Technology, Murdoch University in partial fulfilment of the requirements for the degree of Bachelor of Engineering”

Unit Coordinators: Dr. Gareth Lee and Professor Parisa Arabzadeh Bahr
Supervisors: Dr Aleks Nikoloski & Mr Tendekayi Tapera
Declaration

I hereby declare that this project is my own work and it hasn’t been submitted previously for a degree. I have referenced all contributions by others.

Word Count: 11,123
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 chalcocpyrite 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 thesis 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 chalcocpyrite 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.
Acknowledgements

I would like to send my sincere thanks and acknowledge the following people for their help and support during my time at Murdoch University:

Dr Aleks Nikoloski and Mr Tendekayi Tapera, thank you both for the opportunity to work with your supervision, support and motivation.

I would like to thank Rio Tinto for the samples that were key to this project.

My partner, family and friends, thank you very much for your encouragement, love and support.
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# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Cl</td>
<td>Chloride</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
1. Introduction

There is an ever-increasing demand for copper driven by its application in a range of industries including electronics and telecommunications. Copper occurs naturally as native copper or in copper containing minerals generally classified as copper sulfides, copper carbonates and copper oxides. A breakdown of the main minerals can be seen in Table 1. Chalcopyrite is the principal copper-containing mineral, accounting for 70% of all copper minerals. The majority of chalcopyrite deposits remaining are low grade, with the bulk of current reserves containing around 0.5% Cu. These reserves are continually getting lower with time and aren’t suitable for traditional flotation and pyrometallurgical processing routes (Ayres et al., 2002; Norgate and Jahanshahi, 2010).

Table 1. Common copper containing minerals.

<table>
<thead>
<tr>
<th>Copper Sulfide Minerals</th>
<th>Mineral Name</th>
<th>Mineral Formula</th>
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<tbody>
<tr>
<td></td>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
</tr>
<tr>
<td></td>
<td>Chalcocite</td>
<td>Cu₂S</td>
</tr>
<tr>
<td></td>
<td>Covellite</td>
<td>CuS</td>
</tr>
<tr>
<td></td>
<td>Bornite</td>
<td>Cu₅FeS₄</td>
</tr>
<tr>
<td></td>
<td>Enargite</td>
<td>Cu₃AsS₄</td>
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<table>
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<tr>
<th>Copper Carbonate Minerals</th>
</tr>
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<tbody>
<tr>
<td>Azurite</td>
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<tr>
<td>Malachite</td>
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<table>
<thead>
<tr>
<th>Copper Oxide Minerals</th>
</tr>
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<tbody>
<tr>
<td>Cuprite</td>
</tr>
<tr>
<td>Tenorite</td>
</tr>
<tr>
<td>Chrysocolla</td>
</tr>
</tbody>
</table>
Traditionally copper is produced via smelting however, hydrometallurgical methods have offered an economic advantage over pyrometallurgical refinement in an increasing emission conscience society. Hydrometallurgical techniques avoid SO$_2$ emissions that can incur costly penalties during production. A metallurgical challenge for the leaching of primary copper sulfides is the slow leaching kinetics they display at ambient conditions. The refractory properties, slow leaching kinetics and poor extraction associated with chalcopyrite and enargite makes understanding the leaching mechanism a considerable research interest. Past studies observed passivation as the main problem, the leaching reaction is impeded by the formation of a product layer on the surface of the mineral grains (Hackl et al., 1995; Córdoba et al., 2009b; Rivera-Vasquez and Dixon, 2015; Wang et al., 2016). The composition and formation mechanism of this layer is not widely agreed upon.

This thesis is a part of a larger study that has investigated the effect of a range of conditions and additives on the copper and iron extraction from chalcopyrite and enargite. This thesis studies the effect of silver and other additives on the leaching kinetics and copper extraction. Improvements on dissolution rate and extraction will be of significant value. Additives have been identified as a promising way to overcome the challenges posed by passivation and poor extraction of copper. Past research has observed that several additives have successfully promoted copper extraction from chalcopyrite and enargite. These additives include metal ions (Ag$^+$, Bi$^{3+}$, Cu$^{2+}$, Ni$^{2+}$), chloride ions (Cl$^-$), specific minerals, wetting agents and activated carbon (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).
Several factors contribute to the success of an additive. Silver has shown the promise however, the high cost of silver reduces its viability unless a method is devised to reliably recycle the silver. Some studies have under certain conditions, recycled 90% of the silver. This would increase the economic feasibility of silver as an additive (Nazari et al., 2012). Additional challenges associated with the additive also require consideration. The involvement of bacteria in the process raises the challenge of silver toxicity, however studies observed that the bacteria could build resistance to the silver (Sugio et al., 1981; Tevors, 1987). Numerous studies have obtained positive results and proposed mechanisms describing how silver catalyses chalcopyrite leaching. (Ahonen and Tuovinen, 1990a, 1990b; Blázquez et al., (1999); Córdoba et al., 2008, 2009a; Feng et al., 2013; Gómez et al., 1997a, 1997b, 1999; Muñoz et al., 1998, 2007a, 2007xb, 2008). As a result, improvements on dissolution rate and extraction will be of significant value.
2. Objectives

From the uses of several bench scale leach tests, to try and increase copper extraction from a chalcopyrite ore by the uses of various additives. Primary copper sulfide leaching displays slow kinetics and optimisation of copper extraction is a valuable avenue for companies to explore. A baseline test will be undertaken to analyse whether replicable results were made. Four additives being tested are silver ions, chloride ions, ethylene glycol (EG) and a wetting agent (BASF RD203322). Silver has been extensively investigated and its positive effects on the extraction of copper are well documented. Initially a silver additive will be used in three concentrations; low, medium and high. Upon analysis, the most effective quantity will be used for further combination tests. The goal of the project is to:

- To devise a solution which could allow currently uneconomic copper mineral resources to be rendered economic by effectively applying low cost leaching technology

This has been pursued in the present study by:

- Studying the effects of specific additives on the extent and kinetics of copper leaching from chalcopyrite in acidic ferric sulfate media
- Optimising the reagent addition and identifying potential synergies.
3. Literature review

3.1 Introduction

Copper is an essential metal in the development of modern technologies worldwide. As the higher copper bearing deposits are being processed, companies are looking to the future and being able to process lower copper containing ores to maintain production. Chalcopyrite (CuFeS$_2$) makes up approximately 70% of the world copper resources (Dutrizac & MacDonald, 2013). Traditionally copper is produced via smelting however, hydrometallurgical methods have offered an economic advantage over pyrometallurgical refinement in an increasing emission conscience society. Hydrometallurgical techniques avoid SO$_2$ emissions that can incur costly penalties during production. A metallurgical challenge for the leaching of primary copper sulfides is the slow leaching kinetics they display at ambient conditions. As a result, improvements on dissolution rate and extraction will be of significant value.

3.2 Experimental Considerations

The scope of this review is to explore the literature surrounding the leaching of chalcopyrite and the effects of a variety of parameters on extraction. Leaching performed at atmospheric pressure and in acidified ferric sulphate media will be the major focus. However, chloride leaching will be looked at briefly. Much of the early research had used chalcopyrite concentrates as feed. As ore deposits are depleted over time the focus will shift to lower grade ores and the data collected may require a movement towards test work on these ores to allow for these changes. The oxidation of chalcopyrite for the extraction of copper is commonly performed in sulfuric acid-ferric sulphate (H$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$) media due to its economic nature compared to alternative systems. Financial feasibility
of reported effects was not examined in this review as the economics of copper demand and ore availability will likely change in due course.

The generally accepted reactions for the extraction of copper from chalcopyrite via oxidation can be given by equations 1-3.

\[
\begin{align*}
\text{CuFeS}_2 + 2\text{Fe}_2(\text{SO}_4)_3 & = \text{CuSO}_4 + 5\text{FeSO}_4 + 2\text{S}^0 \quad (1) \\
\text{CuFeS}_2 + \text{O}_2 + 2\text{H}_2\text{SO}_4 & = \text{CuSO}_4 + \text{FeSO}_4 + 2\text{S}^0 + 2\text{H}_2\text{O} \quad (2) \\
4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{O}_2 & = 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \quad (3)
\end{align*}
\]

3.2.1 Reaction Mechanisms

Temperature, agitation, activation energy and particle size are all factors that influence leaching mechanisms of chalcopyrite. The pattern of copper dissolution is used to determine the overall effects of these variables. Klauber (Klauber, 2008) modelled the dissolution of chalcopyrite as occurring in four discrete stages:

1. The initial reaction on the ‘fresh’ chalcopyrite surface. This is characterised by high reaction rate and low \( E_a \). Sample preparation has the greatest effect on this stage.
2. A solid layer of elemental sulphur impedes dissolution. The electron transport results in a low reaction rate and a high \( E_a \). The parabolic rate curve continues if the leaching conditions don’t favour sulphur removal.
3. If the leaching conditions favour the removal of the sulphur layer the reaction rate increases according to a linear rate curve. This is characterised by a high reaction rate and a high \( E_a \).
4. In the absence of iron and pH control jarosites are spontaneously formed. These can independently precipitate from the chalcopyrite resulting in a linear rate curve. If the precipitate coats the chalcopyrite the rate curve is parabolic.

Step two of the model describes oxidation on the surface of chalcopyrite forming the intermediate product elemental sulphur. The elemental sulphur coating the chalcopyrite surface is also a product of chalcopyrite reduction. Low redox conditions are particularly favourable for this mechanism (Vilcáez, et al., 2009). Diffusion models are typically complex and Wen (Wen, 1968) proposed alternative dissolution steps. The slowest step is considered to be the rate-determining step.

1. Fluid reactants diffuse through the fluid film coating the solid particle

2. Fluid diffusion through a porous solid layer

3. Adsorption of fluid products from the solid surface

4. Chemical reaction on the solid surface

5. Desorption of fluid reactants from the reaction surface

6. Diffusion away from the reaction surface through the porous solid media and the fluid film coating the solid.

The literature indicated that the particle size of chalcopyrite was a significant factor in the leaching dissolution model.

Acid attack can promote the dissolution of chalcopyrite and other sulfides including galena and sphalerite. These sulfides follow the polysulfide mechanism (equations 4-6).

\[
\text{nMS} + (2n - 2)\text{Fe}^{3+} + 2\text{H}^+ \rightarrow \text{nM}^{2+} + \text{H}_2\text{S}_n + (2n - 2)\text{Fe}^{2+} \quad (n \geq 2)
\]  

\[
\text{H}_2\text{S}_n + 2\text{Fe}^{3+} \rightarrow \frac{n}{8} \text{S}_8^{0} + 2\text{Fe}^{2+} + 2\text{H}^+ 
\]  

\[
\frac{n}{8} \text{S}_8^{0} + 1.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ 
\]
3.2.2 Passivation

Studies generally accept that the slow dissolution of chalcopyrite in ferric sulphate leaching is the result of passivation. Numerous studies have noted the formation of different passivation layers depending on the leaching conditions. Jarosite, chalcocite, covellite, and elemental sulphur have all been observed as passivation layers (Pradhan, et al., 2008), (Watling, 2006), (Karimi, et al., 2010), (Gericke, et al., 2010), (Gómez, et al., 1996). The significant layers are elemental sulphur and jarosite as these products have been noted to inhibit leaching by coating the chalcopyrite surface. However, recent research by Debernardi and Carlesi (Debernardi & Carlesi, 2012) has questioned the interpretation of chalcopyrite passivation data. The elemental sulphur formation occurs according to the following reactions (Li, et al., 2013).

\[
\begin{align*}
\text{CuFeS}_2(s) + \text{Fe}^{2+} + \text{Cu}^{2+} + 2\text{H}^+ & \rightarrow \text{Cu}_2\text{S}_2(s) + 2\text{Fe}^{3+} + \text{H}_2\text{S} & \text{(7)} \\
\text{Cu}_2\text{S}_2(s) + 4\text{Fe}^{3-} & \rightarrow 2\text{Cu}^{2+} + 4\text{Fe}^{2+} + \text{S}^0(s) & \text{(8)} \\
\text{H}_2\text{S} + 2\text{Fe}^{3+} & \rightarrow 2\text{Fe}^{2+} + 2\text{H}^+ + \text{S}^0(s) & \text{(9)}
\end{align*}
\]

The elemental sulphur passivation layer on chalcopyrite surfaces may inhibit leaching. The sulphur obstructs the electron and oxidant flow to and from the surface of the (Pradhan, et al., 2008). The presence of bacteria encourages sulphur oxidation. Sulphate and Fe\textsuperscript{3+} ions are products of the bacterial action. Suitable conditions, predominantly a pH of 1.9–2.2 and high $E_h$ promote the precipitation of jarosite (Pradhan, et al., 2008), (Kono & Okusawa, 1974). Precipitated jarosite coats the chalcopyrite surface inhibiting reactions on the surface of chalcopyrite.

\[
3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} + \text{M}^+ \rightarrow \text{MFe}_3(\text{SO}_4)_2(\text{OH})_6(s) + 6\text{H}^+ \quad \text{(10)}
\]

Where: $\text{M} = \text{K}^+, \text{Na}^+, \text{H}_3\text{O}^+$ or $\text{NH}_4^+$
3.2.3 Effect of Particle Size

Particle size is an important parameter to be considered for leaching test work, especially when there’s a potential for upscaling the process. Studies suggest that when the particles size is reduced the sample experiences a faster dissolution rate (Adebayo, et al., 2003), (Sokic, et al., 2009), (Nicol, et al., 2010). This is likely a result of the smaller particle size resulting in a larger particle surface area to volume ratio. Determination of the ideal size range is important because increased grinding correlates to higher power consumption in the grinding circuits, it affects the leaching choice of reactor design and preparation required prior to leaching (Dreisinger & Abed, 2002). One study tested the copper recovery at three different size fractions -74+53, -53+38, and -38 μm over time. Constant solution potential, temperature and stirring speed of 440 mV, 50°C and 800 rpm respectively was maintained for the test work. The results indicated that copper increased with decreased particle size (Figure 1.) (Salehi, et al., 2017).

![Figure 1. The effect of particle size on copper recovery over time adopted from (Salehi, et al., 2017)](image)

(Watling, et al., 2014) also concluded that particle size has a significant effect on copper extraction. It was found that 25 μm particles resulted in 70% copper extraction while only 25% of copper was recovered for particles sized at 125 μm at consistent leaching
conditions (Watling, et al., 2014). Dutrizac suggested that copper extraction and surface area are independent when exposed to ferric sulfate and ferric chloride systems (Dutrizac, 1989). For particles below 75 μm the dissolution becomes efficient with potassium dichromate (Dutrizac, 1981). However, the results of Padilla et al (Padilla, et al., 2008) provided no clear-cut effects on the kinetics of particles sized between 49-89 μm. These results are different to the studies previously discussed; however, they aren’t conclusive. This could be because smaller chalcopyrite particles can become completely covered with an elemental sulfur layer that hinders dissolution (Klauber, 2008).
3.2.4 Effect of Temperature

Reaction rates of chemical processes typically increase at higher temperatures. The effect of temperature on the extraction of copper from chalcopyrite concentrate hasn’t been widely studied. Lu et al. (Lu, et al., 2000) measured the percentage of copper extracted (%) over time (h) for particles of a standard size at 60°C, 70°C, 85°C and 95°C (Figure 2). The results indicate that temperature had a noticeable effect on copper extraction when the temperature is increased from 60°C to 70°C and 70°C to 85°C. However, copper dissolution increased minimally when the process was run at 95°C compared to 85°C.

![Figure 2. The effect of temperature on the leaching of chalcopyrite over time (h) (Lu, et al., 2000).](image)

Al-Harasheh et al. (Al-Harasheh, et al., 2008) found that the overall reaction of chalcopyrite leaching in acidic ferric chloride was sensitive to temperature. Copper recovery was measured as the fraction of copper reacted during chalcopyrite leaching in ferric chloride. Chalcopyrite particles of 38 µm were leached at temperatures 70 °C, 80 °C and 90 °C over a period of 3 hours. When the experiment was run at 70 °C roughly 7.4% of the copper was recovered after the 3 hours. At 90 °C 22% of copper was extracted over the same period of time. The results indicate that temperature had a significant effect on the copper recovery (Figure 3).
The studies suggested possible explanations for the diminishing effect of temperature on copper recovery at high temperatures. Reduced oxygen solubility at high temperatures is one possible reason (Lu, et al., 2000). Research indicates the kinetics of chalcopyrite leaching in acidic ferric chloride follow the shrinking core model due to sulfur formation on the chalcopyrite surface. These results indicate that the process is predominantly chemically controlled at low temperatures and diffusion controlled at high temperatures (Lu, et al., 2000), (Al-Harasheh, et al., 2008).

Kinetic studies on chalcopyrite leaching typically focus on the determination of activation energy ($E_a$) rather than the effect of temperature. However, the significant variation in the published values indicates differences in the studies. The discrepancies in the values could result from some researchers not taking into consideration the two mechanisms proposed by Havlik and Kammel (Havlik, 2008) for chalcopyrite leaching. Authors using different mechanisms can result in error determining the rate-limiting step. This contributes to incorrect calculations of the rate constant and the activation energy (Al-Harasheh, et al., 2008), (Prosser, 1996).
3.2.5 Effect of Acid Concentration

The acidity of a leach and its effects on reaction kinetics of chalcopyrite leaching is an area that has explored extensively. Acid concentration is an area of focus due to the economic weighting it carries in terms of dissolution rate. Sulfuric acid is a commonly used lixiviant for the leaching of primary copper sulfides (Adebayo, et al., 2003), (Padilla, et al., 2008), (Hiroyoshi, et al., 2004), (Senanayake, 2009). Leach rate appears to increase with sulfuric acid concentration, Dreisinger and Abed (Dreisinger & Abed, 2002) proposed that an acceptable H\(^+\) concentration range is 0.1-1.0 M (Dreisinger & Abed, 2002). Antonijević and Bogdanović (Antonijević & Bogdanović, 2004) had work that suggests that at higher concentrations passivation occurs due to competition between ferric and hydrogen ions on the iron deficient surface (Antonijević & Bogdanović, 2004). Additionally, it was observed at concentrations of 3-5 M H\(^+\) this passivation becomes more obvious. Interestingly, with an acid concentration of 6 M, extraction of copper reached 80% within 30 minutes. This was attributed to the result of increased redox potential of H\(_2\)O\(_2\) from higher hydrogen ion concentration and that an increased dissolution rate was observed with a sulfuric acid concentration of below 1.0 M (Adebayo, et al., 2003). Vilcaez (Vilcáez, et al., 2009) found that a lower pH increased copper dissolution dramatically at pH 1 compared to pH 1.5 as shown in Figure 4.
Vilcaez (Vilcáez, et al., 2009) attributed the difference in copper extraction to passivating iron precipitate on the surface of the mineral in the pH 1.5 tests.

3.2.6 Effect of Redox Potential

Redox potential (Eₚ) and its effects on the dissolution of chalcopyrite have been researched due to the electrochemical nature of the leaching process. There is discussion in the literature with respect to whether high or low redox potential is more effective, usually depending on the temperature that the leach is performed at. Sandström et al. (Sandström, et al., 2005) propose that a small Eₚ of 620 mV (SHE) yields greater results than a higher Eₚ of 800 mV (SHE) in sulfuric acid media (Sandström, et al., 2005). Nazari et al. (Nazari & Asselin, 2009) suggests that the active to passive region at low temperature (25 °C) seemed to transition in the range of 600-700 mV (SHE) (Nazari & Asselin, 2009). Chalcopyrite leached in sulfuric acid media was found to be effective in Eₚ below 685 mV (SHE) regardless of temperature, impurities or acidity according to Viramontes-Gamboa et al. (Viramontes-Gamboa, et al., 2010), (Viramontes-Gamboa, et al., 2007). Viramontes-Gamboa et al. also suggest that between 685 and 755 mV (SHE)
chalcopyrite could be passive or active, above 755 mV (SHE) chalcopyrite leaching was found to exhibit strong passivating characteristics resulting in slow leach kinetics. Hiroyoshi et al. (Hiroyoshi, et al., 2002), (Hiroyoshi, et al., 1997), (Hiroyoshi, et al., 2001) suggests that the oxidation of chalcopyrite in sulfuric acid media with oxygen as the oxidant can be given by equations 11 and 12, which Holliday and Richmond also proposed (Holliday & Richmond, 1990).

\[
\text{CuFeS}_2(S) + 4H^+ + O_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}_0^0 + 2\text{H}_2\text{O} \quad (11)
\]

\[
4\text{Fe}^{2+} + 4H^+ + O_2 \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (12)
\]

Koleini et al. (Koleini, et al., 2011) determined that the greatest Cu recovery could be obtained in the range of 610–640 mV (SHE). Comparable findings have been reported by (Sandström, et al., 2005), (Viramontes-Gamboa, et al., 2010), (Viramontes-Gamboa, et al., 2007), (Koleini, et al., 2011), (Kamentani & Aoki, 1985) although the overall reaction (equation 13) would suggest that a high redox potential and thus high concentration of ferric ions would result in the most rapid copper leaching (Hiroyoshi, et al., 2002), (Hackl, et al., 1995), (Dutrizac, 1981).

\[
\text{CuFeS}_2(S) + 4\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}_0^0 \quad (13)
\]

Hiroyoshi et al. (Hiroyoshi, et al., 2001) also reported that leach rate was increased significantly with the addition Fe\(^{2+}\), Cu\(^{2+}\) and Fe\(^{3+}\) (Hiroyoshi, et al., 2008). This implies that equation (13) is not an accurate model of dissolution as ferrous and cupric ions would drive the leach in the opposite direction. Thus, a two-step reaction model was put forward to capture this detail given by equations 14 and 15.

\[
\text{CuFeS}_2(S) + 3\text{Cu}^{2+} + 3\text{Fe}^{2+} \rightarrow 4\text{Fe}^{3+} + \text{Cu}_2\text{S}_0(S) \quad (14)
\]

\[
\text{Cu}_2\text{S}_0(S) + 4\text{Fe}^{3+} \rightarrow 2\text{Cu}^{2+} + 4\text{Fe}^{2+} + \text{S}_0^0 \quad (15)
\]

Despite the abundance of literature surrounding redox potential control, it is apparent that the mechanisms are not fully understood. Additionally, there is a degree of uncertainty
surrounding the optimal $E_h$ range obtained experimentally matching with the respective reaction models.

### 3.2.7 Effect of Agitation

It has been noted that chalcopyrite dissolution in ferric sulfate or ferric chloride media is independent of stirring speed (Dutrizac, 1981). Additionally, the effects of agitation speed on the rate of oxidation of chalcopyrite in sulfuric acid media with the presence of ferric ions were independent of one another (Antonijević & Bogdanović, 2004). Alternatively, Sokic observed a slightly negative effect on leach rate as stirring speed increased in sulfuric acid with added sodium chloride (Sokic, et al., 2009). The reasoning for this was postulated that the faster stirring speed decreased contact between particle and oxidant between speeds of 100-450 rpm. Similar results were found in a hydrogen peroxide-glycol system (Mahajan, et al., 2007). Aydogan found that the dissolution rate in a sulfuric acid-potassium dichromate system increased with stirring speed until 400 rpm whereby the rate decayed considerably (Aydogan, et al., 2006). Harmer reported similar findings leaching chalcopyrite with perchloric acid with the addition and omission of ferric ions. Harmer also noted that mixing was inadequate at stirring speeds under 500 rpm (Harmer, 2002).

In a Brønsted acidic ionic liquid Dong reported that at copper dissolution was affected at speeds less than 600 rpm however no difference was reported in the 600-800 rpm range (Dong, et al., 2009). Lu (Lu, et al., 2000) reported the effects of agitation on an atmospheric leach depicted in Figure 5.
Figure 5. Copper extraction over time for varying agitation speeds. (Lu, et al., 2000).
3.3 Additives

The use of additives and their effect on the leaching kinetics of primary copper sulfides is an area of invested interest. Literature focusing on additives was reasonably scarce, especially regarding acidified ferric sulfate systems. Not all additives will be economically feasible and this could be a reason for the lack of literature focusing on them. Furthermore, it could be argued that much of the literature was focussing on developing accurate models that fit the leaching kinetics and mechanisms of chalcopyrite and introducing additives could create unwanted noise.

3.3.1 Silver Ions

The catalytic effect of silver ions on the leaching process has been thoroughly researched by Ballester (Ballester, et al., 1992). The silver (Ag⁺) ions react with the surface of the chalcopyrite producing a layer of silver sulfide (Ag₂S) on the sulfide mineral surface (Reaction 16). Reaction 17 shows the oxidation of the intermediate product, Ag₂S in the presence of ferric ions (Miller & Portillo, 1979). However, the mechanism is relatively simplistic and doesn’t account for every observation. An example of this is Ag₂S oxidation with ferric ions (Reaction 17) requiring temperatures over 100 °C (Dutrizac, 1994). Parker et al. (Parker, et al., 2003) was unable to detect elemental sulfur on the surface of the chalcopyrite after the catalysed leaching (Reactions 17 and 18). This contradicts the theoretical results of the reaction scheme (Reactions 16 – 22). This implies that further research should be done into determination of the silver catalysis mechanism in order to completely understand the catalytic effect. However, the costs associated with using silver as an additive is high and this means it isn’t a cost-effective catalyst. If silver is naturally present in an ore the catalytic effect would be beneficial and the process more economical (Klauber, 2008).
\[ \text{CuFeS}_2 + 4\text{Ag}^+ \rightarrow 2\text{Ag}_2\text{S}_{\text{(on chalcopyrite surface)}} + \text{Cu}^{2+} + \text{Fe}^{2+} \quad (16) \]
\[ 2\text{Fe}^{3+} + \text{Ag}_2\text{S} \rightarrow 2\text{Ag}^+_{\text{(regenerated catalyst)}} + \text{S}_0 + 2\text{Fe}^{2+} \quad (17) \]
\[ \text{CuFeS}_2 + 4\text{Ag}^+ ightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 4\text{Ag}^0 + 2\text{S}^0 \quad (18) \]
\[ \text{Ag}^+ + \text{Fe}^{2+} \rightarrow \text{Ag}^0 + \text{Fe}^{3+} \quad (19) \]
\[ 2\text{AgCl} \rightarrow \text{Ag}^0 + \text{Cl}_2_{\text{(photochemical decomposition)}} \quad (20) \]
\[ 2\text{CuFeS}_2 + 4\text{Ag}^+ ightarrow \text{Cu}_2\text{S} + 2\text{Fe}^{2+} + 2\text{Ag}_2\text{S} + \text{S}^0 \quad (21) \]
\[ \text{Cu}_2\text{S} + 4\text{Fe}^{3+} \rightarrow 2\text{Cu}^{2+} + 4\text{Fe}^{2+} + \text{S}^0 \quad (22) \]

An alternative reaction scheme proposed by Hiroyoshi et al. (Hiroyoshi, et al., 2002), detailed a system with a low solution potential. The chalcopyrite reduced to chalcocite while the silver ions and hydrogen sulfide also react. Chalcocite is more prone to oxidation when leached with ferric ions than chalcopyrite, providing an easier ‘alternative’ reaction pathway that increases the leaching rate. Pawlek (Pawlek, 1976) concluded that silver is an effective additive by pressure leaching two powdered chalcopyrite samples at 120°C and 0.2 MPa of O₂ for 30 minutes. The control test with no additive experienced 25% recovery for the coarser sample while 51% of copper was extracted from the finer sample. The test with silver addition achieved 95% chalcopyrite extraction in the same period of time for both the coarse and fine samples. This supports the notion that silver is an effective catalyst for chalcopyrite leaching.

3.3.2 Chloride Ions

Lima et al. (de Lima, et al., 2012) researched kinetic calculations associated with chalcopyrite leaching proposed that chloride ions could be an appropriate additive. The calculations suggest that water molecules and chloride ions compete for iron sites on the surface of chalcopyrite. This was attributed to similar adsorption energies and
chalcopyrite surface ‘reconstructions’. Dutrizac (Dutrizac, 1981) converted a sulfate system (0.1M Fe$_2$(SO$_4$)$_3$; 0.3M H$_2$SO$_4$; at 90°C) to a pseudo-chloride system using 1-4M lithium chloride as an additive. The lithium chloride addition increased the chloride concentration in the system without encouraging jarosite compound formation; an issue encountered with sodium or potassium chlorides addition. The use of a chloride ion additive resulted in the leaching rate increasing, with the 4M-lithium chloride system up to 2.6 times higher than the control with no chloride addition. However, excess chloride can result in the unintentional precipitation of lithium sulfate (Watling, et al., 2014).

3.3.3 Activated Carbon

The reactivity of activated carbon leads to it forming galvanic couples with chalcopyrite and sphalerite. Chalcopyrite and sphalerite will act as the anode and the activated carbon as the cathode (Liu, et al., 2007). Activated carbon is an effective additive to a system with low redox potentials because it promotes chalcocite oxidation (Liang, et al., 2010). Chalcopyrite when exposed to Fe$^{3+}$ and dissolved O$_2$ oxidises at high redox potential when no activated carbon is present (Reactions 23 and 24).

$$\text{CuFeS}_2(\text{s}) + 4\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}_0(\text{s}) \quad (23)$$

$$\text{CuFeS}_2(\text{s}) + 4\text{H}^+ + \text{O}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}_0(\text{s}) + 2\text{H}_2\text{O} \quad (24)$$

The addition of 2 g/L of activated carbon to chalcopyrite bioleaching systems has been found to increase copper recovery. The amount of copper extracted from a 10-day leach increased from 64% to 95% with the activated carbon addition (Liang, et al., 2010). The results indicate that the activated carbon acted as the cathode reducing Fe$^{3+}$ (Equation 23). The intermediate species chalcocite, jarosite and S$^0$ were identified and contributed
to the reaction process. The jarosite and $S^0$ typically act as passivation layers but the chalcocite appears to mitigate the passivation to an extent (Li, et al., 2013).

3.4 Conclusion

Copper is an essential metal in development and as a result its future demand should remain. Hydrometallurgical processing methods are seemingly the future of processing lower grade ore bodies as much of the high-grade deposits have been mined. Chalcopyrite, a primary copper sulfide, exhibits slow leach kinetics which is a hydrometallurgical challenge. This review explored areas that need to be considered when looking at the leaching of chalcopyrite such as particle size, temperature, acid concentration, redox potential, agitation and additives.

Chalcopyrite leaching mechanisms were found to be broken into three main models, surface reaction, diffusion and a mixed model incorporating the surface reaction and diffusion models according to (Li, et al., 2013). Klauber (Klauber, 2008) modelled chalcopyrite dissolution in four steps and Wen (Wen, 1968) suggested there may be six steps with the slowest being the rate-determining step. A potential reason for the slow kinetics displayed by chalcopyrite leaching is the formation of passivating layers. These layers can be formed from jarosite, chalcocite, covellite, and elemental (Pradhan, et al., 2008), (Watling, 2006), (Karimi, et al., 2010), (Gericke, et al., 2010), (Gómez, et al., 1996).

Smaller particle size was found to increase dissolution rate (Adebayo, et al., 2003), (Sokic, et al., 2009), (Nicol, et al., 2010). Higher temperature, up until a point, appears to have a positive effect on copper extraction over a period of 9 days (Padilla, et al., 2008). A hydrogen ion concentration of between 0.1-1 M appears to be an effective acid concentration with multiple sources in agreement (Vilcáez, et al., 2009), (Adebayo, et al.,
Redox potential, like acid concentration, has an effective range. Koleini et al. (Koleini, et al., 2011) stated that copper recovery would be greatest between 610–640 mV (SHE) which was supported by similar findings by (Sandström, et al., 2005), (Viramontes-Gamboa, et al., 2010), (Koleini, et al., 2011), (Kamentani & Aoki, 1985). Agitation had some conflicting conclusions, varying from chalcopyrite oxidation and agitation speed being independent (Dutrizac, 1981), (Antonijević & Bogdanović, 2004). In contrast, Sokic et al. (Sokic, et al., 2009) observed a slightly negative effect on leach rate as stirring speed increased in sulfuric acid with added sodium chloride.

The effects of additives, specifically silver ions, chloride ions and activated carbon. Ballester et al. (Ballester, et al., 1992) proposed a series of mechanisms from the addition of silver and Pawlek (Pawlek, 1976) found silver to be an effective catalyst on the dissolution of copper from chalcopyrite. Chloride ions increased copper extracted during a 10-day leach from 64% to 95% with the addition of activated carbon (Liang, et al., 2010).
4. Materials and Methods

4.1 Ore Sample Preparation

The chalcopyrite ore sample provided from Rio Tinto had been crushed, screened and homogenised in a rotary splitter into 500 g sample bags. To prepare the sample for leaching tests 500 g would be ground in a laboratory rod mill at 50% solids to achieve a \( \text{P}_{80} \) of 38 \( \mu \text{m} \). After the sample had been reduced to the required size it was placed in a pressure filter and filtered to produce a wet cake. Required masses for leach tests were cut from the filter cake as wedges with an additional slice used to determine moisture content in each instance so as to achieve the required leach pulp density. The ore and filter cake were kept sealed and were stored in a cold room in the meantime.

4.2 Chemicals

The metal species used were metal sulfate salts. Set concentrations were required for the tests in g/L of metal in the leach solution; the required value was accurately weighed for addition. The metal species used as additives were laboratory grade and sourced from Chem Supply, Fisher Chemical. Additional additives (AgNO\(_3\), LiCl) were of analytical grade. BASF was the supplier of the wetting agent (RD 203322) utilised in the tests.

4.3 Leaching Tests

The leaching tests were performed in 1L reactors which can be observed in Figure 5. The reactors were agitated using a stirrer at approximately 600 rpm with three baffles on the edge of the reactor. Air was sparged through each reactor from an air cylinder using a rotameter to regulate airflow. Baseline conditions required the temperature to be set at 50
°C. The mass of chemicals required reach the set metal concentration in the leach solution (g/L) was weighed and added. This lixiviant was prepared using deionised water and laboratory grade sulfate salts of the metals i.e. iron, magnesium, copper or aluminium. Analytical grade sulfuric acid (98.3% H₂SO₄) or lithium hydroxide (3M) were used to alter the pH of the solution depending on whether a decrease or increase was required. The baseline used were: 25 g/L Fe³+/²⁺, 10 g/L Al³⁺, 1 g/L Mg²⁺, 0.2 g/L Cu²⁺ and 125 g/L SO₄²⁻ with pH 1.2 and Eₐ 700 mV (SHE). Every leach test was undertaken with a target pulp density of 5 % solids.

The leach tests were monitored over time and samples collected periodically over 10 days. The solids and solution samples were assayed for Cu. The results were plotted as leach curves. Both the Eₐ and pH were maintained at 700 mV and 1.2 respectively. The values were monitored with sensors and hydrogen peroxide was used to adjust for potential control or pH control with LiOH or H₂SO₄. LiOH was selected instead of NaOH to minimise the iron precipitation into jarosite. The potentials measured in this report were converted to SHE. Acidified deionised water was used to wash the solid residues collected, filter papers were used for the vacuum filtration and left to dry in an oven at 50 °C. Acidified deionised water was used to dilute the solution samples. All of the residues were digested in aqua regia and diluted prior to analysis on an ICP-MS.
4.3.1 Leach Set-up

Figure 5. An image of the leach reactor (left) and temperature controller (right).
4.4 Instrumental Analysis

4.4.1 ICP-MS

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an analytical technique; it is used for elemental determinations. Samples are introduced into the ICP as an aerosol. This occurs by either directly converting solid samples into an aerosol using a laser or aspirating the liquid or the dissolved solid sample into a nebulizer. The aerosol sample is introduced into the torch of the ICP. Elements present in the sample are first converted into gaseous atoms before being ionized towards the end of the plasma. The atoms are converted to ions that can be separated and detected by the mass spectrometer (Wolf, 2005). The solution samples were appropriately diluted prior to testing and the solid samples required dissolution and dilution.

4.4.2 XRD Analysis

A GBC Enhanced Multi-Material Analyser (EMMA) was used to perform the XRD analysis at Murdoch University. X-ray absorbing silicon discs within metal sample holders were filled with the samples. The location of the samples was recorded on the computer program. Each analysis was performed using a single pass. A Kα2 strip was run on the diffraction patterns and used the Kα2/Kα1 ratio of 0.51.
5. Results and Discussion

5.1 Sample Characterisation

The XRD analysis of the sample obtained from Rio Tinto confirmed that chalcopyrite was present in the test sample. The sample composition is 2.16% chalcopyrite, 0.05% chalcocite and trace quantities of covellite, copper oxides and clays. Silica was the major mineral, experiencing large peaks while the smaller peaks correspond with chalcopyrite Figure 6. The presence of chalcopyrite is important as this research project focuses on additives to improve chalcopyrite leaching. Figure 7 depicts the XRD analysis on the final residue from one of the performed baseline tests. The chalcopyrite peak heights were reduced indicating that it had been consumed during the leaching process.

Figure 6. XRD analysis on the chalcopyrite ore sample. This represents the feed ore used in subsequent leach tests
Figure 7. XRD analysis on the final leach residue after being subjected to a 10 day leach in an acidic ferric sulfate lixiviant at baseline conditions.
5.2 Baseline

Initially, two leach tests were carried out at baseline conditions which is presented in Figure 8. Baseline tests 1 and 2 targeted identical operating conditions with final copper extraction being 14.8% and 18.0% after 10 days respectively. This provides a basis of comparison for subsequent tests as additives are introduced to later systems. An external baseline test at the same conditions produced a copper extraction of 18% (Nikoloski, et al., 2017). As baseline 2 is the closest to this external baseline, only baseline 2 will be plotted in subsequent figures.

![Copper leaching kinetics from a chalcopyrite ore at baseline conditions.](image-url)
5.3 Iron

Iron dissolution was also researched; some of the iron was anticipated to precipitate out of solution as goethite or jarosite (Equations 25 and 26). Issues were encountered for solids collected and from the test using silver and 5 g/L chloride, the sample resisted filtration and pressure filtration had to be used instead of vacuum filtration. These solids were analysed using XRD (Figure 6). The XRD results of the test with silver and 5 g/L chloride (Figure 6) differed from the feed characterisation (Figure 3). There was a significant reduction in silica, indicated by smaller peaks and peaks identified using red square symbols which correspond to hydroniumjarosite \((2(H_2O)Fe_3(SO_4)_2(OH)_6)\), suggesting that it was precipitated during with silver and 5 g/L chloride (Figure 3 and Equation 26). It was also expected that during the leach some silver will precipitate as argentojarosite \((AgFe_3(SO_4)_2(OH)_6)\) (Equation 27) (Carranza et al., 1997; Bolorunduro et al., 2003; Córdoba et al., 2009a). It’s expected that silver precipitated as argentojarosite will lose its catalytic effect and conditions unfavourable to Equation 27 should be maintained.

\[
Fe_2(SO_4)_3 + 0.5O_2 + 3H_2O \rightarrow 2FeO(OH) + 3H_2SO_4 \quad (25)
\]

\[
3Fe_2(SO_4)_3 + 14H_2O \rightarrow 2(H_2O)Fe_3(SO_4)_2OH_6 + 5H_2SO_4 \quad (26)
\]

\[
Ag^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow AgFe_3(SO_4)_2OH_6 + 6H^+ \quad (27)
\]
The results obtained varied significantly from results obtained in past studies. The strong deviation could be the result of human or experimental error. The results have been omitted due to this difference, further repeats and research to the iron dissolution is recommended.
5.4 Additives

5.4.1 Silver

The effects of silver concentration on the extraction of copper from the chalcopyrite ore are shown in Figure 10. Three different silver dosages were tested; 0.5 g/L, 0.1 g/L and 0.02 g/L. Complete copper dissolution (~99%) was achieved in the 0.5 g/L dosage after 4 days while 0.1 g/L of added silver achieved this extent after day 7. This is slightly higher extraction and faster kinetics than expected as a similar batch of tests attained 98% and 94% copper extraction after 10 days (Nikoloski, et al., 2017). This discrepancy is likely due to error generated during the dilution process of analysis for ICP-MS. However, for additive synergies to be investigated, the 0.02 g/L silver concentration was the point of interest for subsequent tests. As both studies found that silver dosages of 0.5 g/L and 0.1 g/L achieved extraction in excess of 90%, it would be likely that only negative synergy could be detected. It was observed that 0.02 g/L of silver resulted in modest changes to overall extraction and kinetics over the 10-day tests yielding 27.2% copper dissolution. This is comparable to a similar test with the same silver concentration which achieved an extraction of 25% after 10 days (Nikoloski, et al., 2017). Ultimately, the catalytic effect of silver on both extraction kinetics and extent of copper dissolution is evident at the three dosages tested to varying degrees.
Figure 10. Copper leaching kinetics from chalcopyrite at varying silver concentrations.

Table 2. A table containing final copper dissolution extents, initial and final dissolution rates.

<table>
<thead>
<tr>
<th>Additive Tested</th>
<th>Solution Based Extraction</th>
<th>Initial Rate Gradient</th>
<th>Final Rate Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag 0.5 g/L</td>
<td>99.0%</td>
<td>0.429</td>
<td>0.024</td>
</tr>
<tr>
<td>Ag 0.1 g/L</td>
<td>99.0%</td>
<td>0.444</td>
<td>0.048</td>
</tr>
<tr>
<td>Ag 0.02 g/L</td>
<td>27.2%</td>
<td>0.072</td>
<td>0.013</td>
</tr>
<tr>
<td>Baseline</td>
<td>18.0%</td>
<td>0.042</td>
<td>0.007</td>
</tr>
</tbody>
</table>
5.4.2 Chloride

The effects of chloride combined with silver on the extraction of copper from the chalcopyrite sample are depicted in Figure 11. A chloride baseline was carried out using a dosage of 1 g/L, shown in yellow. From the plot, there appears to be no apparent effect on the dissolution of copper at this concentration compared to baseline conditions resulting in an overall extraction of 19.2% compared to 18.0%. However, when combined with silver addition of 0.02 g/L leaching kinetics and extraction were improved at all three concentrations. The kinetic data shows that all chloride-silver combinations stay relatively clustered together over the course of the test. Silver in combination with chloride dosages of 5 g/L, 1 g/L and 0.2 g/L yielded extractions of 23.0%, 23.3% and 21.6% respectively. Despite this increase compared to the chloride baseline, all chloride-silver combination tests resulted in lower overall extraction than 0.02 g/L silver on its own over the 10 days. This indicates that silver is still the dominant catalyst at the tested concentrations and chloride appears to impede the positive effect of the low silver dosage.
Figure 11. Copper leaching kinetics from chalcopyrite at varying chloride concentrations in the presence of silver.

Table 3. A table containing final copper dissolution extents, initial and final dissolution rates for silver and chloride combinations.

<table>
<thead>
<tr>
<th>Additive Tested</th>
<th>Solution Based Extraction</th>
<th>Initial Rate Gradient</th>
<th>Final Rate Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 g/L Ag</td>
<td>27.2</td>
<td>0.072</td>
<td>0.013</td>
</tr>
<tr>
<td>0.02 g/L Ag + 1 g/L Cl</td>
<td>23.3</td>
<td>0.083</td>
<td>0.006</td>
</tr>
<tr>
<td>0.02 g/L Ag + 5 g/L Cl</td>
<td>23.0</td>
<td>0.077</td>
<td>0.008</td>
</tr>
<tr>
<td>0.02 g/L Ag + 0.2 g/L Cl</td>
<td>21.6</td>
<td>0.076</td>
<td>0.005</td>
</tr>
<tr>
<td>1 g/L Cl</td>
<td>19.2</td>
<td>0.039</td>
<td>0.011</td>
</tr>
<tr>
<td>Baseline</td>
<td>18.0</td>
<td>0.042</td>
<td>0.007</td>
</tr>
</tbody>
</table>
5.4.3 Surfactant

The effects of surfactant concentration on the extraction of copper from the chalcopyrite sample are shown in Figure 12. A wetting agent concentration of 1 g/L was tested and resulted in an overall copper extraction of 30.6% after 10 days. The surfactant at 1 g/L offered greater initial kinetics and copper dissolution than 0.02 g/L silver. Notably, when 0.02 g/L of silver was combined with the wetting agent leach kinetics and final copper extraction increased drastically. Interestingly, the highest concentration of wetting agent, 5 g/L, resulted in the lowest extraction out of the three combinations achieving 79.3%. Surfactant addition of 1 g/L and 0.2 g/L resulted in final extractions of 97.5% in both cases. All three surfactant-silver combinations resulted in a significant increase to leaching kinetics compared to the 0.2 g/L silver and 1 g/L wetting agent baselines. Copper extraction after 1 day in all three combination tests exceeded the final extraction achieved by the respective baselines after 10 days of leaching. The surfactant-silver combination tests achieved comparable overall extraction to the 0.1 g/L and 0.5 g/L silver addition tests indicating clear reagent synergy.
Figure 12. Copper leaching kinetics from chalcopyrite at varying surfactant concentrations in the presence of silver.

Table 4. A table containing final copper dissolution extents, initial and final dissolution rates for surfactant (BASF RD203322) and silver combinations.

<table>
<thead>
<tr>
<th>Additive Tested</th>
<th>Solution Based Extraction %</th>
<th>Initial Rate Gradient</th>
<th>Final Rate Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 g/L Ag + 0.2 g/L Wetting Agent</td>
<td>97.5</td>
<td>0.295</td>
<td>0.063</td>
</tr>
<tr>
<td>0.02 g/L Ag + 1 g/L Wetting Agent</td>
<td>97.5</td>
<td>0.235</td>
<td>0.060</td>
</tr>
<tr>
<td>0.02 g/L Ag + 5 g/L Wetting Agent</td>
<td>79.3</td>
<td>0.173</td>
<td>0.059</td>
</tr>
<tr>
<td>1 g/L Surfactant</td>
<td>30.6</td>
<td>0.114</td>
<td>0.006</td>
</tr>
<tr>
<td>0.02 g/L Ag</td>
<td>27.2</td>
<td>0.072</td>
<td>0.013</td>
</tr>
<tr>
<td>Baseline</td>
<td>18.0</td>
<td>0.042</td>
<td>0.007</td>
</tr>
</tbody>
</table>
5.4.4 Ethylene Glycol

The effects of EG concentration on the extraction of copper from the chalcopyrite sample are shown in Figure 13. The three concentrations of EG tested in combination with silver increased final copper dissolution in all cases compared to the silver baseline. Addition of 1 g/L appears to increase kinetics more so than at 5 g/L or 0.2 g/L yielding a final extraction of 44.3% compared to 28.9% and 34.2% respectively. There appears to be a slight positive synergy between EG and silver. Copper leaching kinetics on the 1 g/L dosage of EG were higher than all other combinations achieving 23.4% extraction after one day which is slightly lower than the extent achieved after 10 days in the 0.02 g/L silver baseline.

Figure 13. Copper leaching kinetics from chalcopyrite at varying EG concentrations in the presence of silver.
Table 5. A table containing final copper dissolution extents, initial and final dissolution rates for EG and silver combinations.

<table>
<thead>
<tr>
<th>Additive Tested</th>
<th>Solution Based Extraction</th>
<th>Initial Rate Gradient</th>
<th>Final Rate Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 g/L Ag + 1 g/L EG</td>
<td>44.3</td>
<td>0.119</td>
<td>0.025</td>
</tr>
<tr>
<td>0.02 g/L Ag + 0.2 g/L EG</td>
<td>34.2</td>
<td>0.067</td>
<td>0.029</td>
</tr>
<tr>
<td>0.02 g/L Ag + 5 g/L EG</td>
<td>28.9</td>
<td>0.075</td>
<td>0.020</td>
</tr>
<tr>
<td>0.02 g/L Ag</td>
<td>27.2</td>
<td>0.072</td>
<td>0.013</td>
</tr>
<tr>
<td>Baseline</td>
<td>18.0</td>
<td>0.042</td>
<td>0.007</td>
</tr>
</tbody>
</table>

5.4.5 Combination

Two tests were performed using a combination of three of the additives. Silver was used at a dosage of 0.02 g/L as in previous tests and due to the enhanced extraction shown by the wetting agent additive in combination with silver, the surfactant was kept consistent in the two tests as well at a 1 g/L concentration. The third reagent that was variable in the two tests were 1 g/L of chloride and EG. The kinetic data for the leach has been presented in Figure 14. The combination with EG present performed slightly better achieving 82.8% copper dissolution compared to 72.7% with chloride present. This is an increase compared to all the plotted baselines with faster kinetics. However, the overall leaching kinetics were reduced from silver and surfactant alone at 0.02 g/L and 1 g/L concentrations respectively. Final extraction was also reduced in both cases from 97.5% without the third additive present, Figure 12. It appears that at the tested dosages despite the greater extraction compared to only silver the third reagent is redundant and is reducing performance.
Figure 14. Copper leaching kinetics from chalcopyrite with combinations of additives in the presence of silver.

Table 6. A table containing final copper dissolution extents, initial and final dissolution rates for combinations of silver, surfactant(BASF RD20322), chloride and EG.

<table>
<thead>
<tr>
<th>Additive Tested</th>
<th>Solution Based Extraction</th>
<th>Initial Rate Gradient</th>
<th>Final Rate Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 g/L Ag + 1 g/L Surfactant + 1 g/L EG</td>
<td>82.6</td>
<td>0.176</td>
<td>0.056</td>
</tr>
<tr>
<td>0.02 g/L Ag + 1 g/L Surfactant + 1 g/L Cl</td>
<td>72.7</td>
<td>0.200</td>
<td>0.039</td>
</tr>
<tr>
<td>1 g/L Surfactant</td>
<td>30.6</td>
<td>0.114</td>
<td>0.006</td>
</tr>
<tr>
<td>0.02 g/L Ag</td>
<td>27.2</td>
<td>0.072</td>
<td>0.013</td>
</tr>
<tr>
<td>1 g/L Cl</td>
<td>19.2</td>
<td>0.039</td>
<td>0.011</td>
</tr>
<tr>
<td>Baseline</td>
<td>18.0</td>
<td>0.042</td>
<td>0.007</td>
</tr>
</tbody>
</table>
6. Conclusions and Recommendations

6.1 Conclusions

Hydrometallurgical processing methods are seemingly the future of processing lower grade ore bodies as the higher-grade deposits continue to be processed. Chalcopyrite, a primary copper sulfide, is refractory and exhibits slow leach kinetics at ambient conditions which poses a hydrometallurgical challenge to efficiently process.

A number of mechanisms for the slow kinetics displayed by chalcopyrite leaching have been proposed such as the formation of passivating layers. These layers can be formed from jarosite, chalcocite, covellite, and elemental sulfur (Pradhan, et al., 2008), (Watling, 2006), (Karimi, et al., 2010), (Gericke, et al., 2010), (Gómez, et al., 1996).

Silver has been found to catalyse the leaching of chalcopyrite significantly allowing for high extractions and fast kinetics to be attained. However, silver is an expensive catalyst, especially if there is no native silver found in the deposit meaning companies would have to source silver through external means. As a result, the lookout for cheaper alternatives to catalyse the process is a worthwhile investment. Ballester et al. (Ballester, et al., 1992) proposed a series of mechanisms from the addition of silver and Pawlek (Pawlek, 1976) found silver to be an effective catalyst on the dissolution of copper from chalcopyrite.

Chloride ions increased copper extracted during a 10-day leach from 64% to 95% with the addition of activated carbon (Liang, et al., 2010). A recent study found that 0.05 g/L of silver resulted in excess of 90% extraction and 0.02 g/L resulted in 25% copper extraction increased from 18% found at baseline conditions (Nikoloski, et al., 2017).

The aim of the study was to investigate the effects of specific additives on the leaching of a chalcopyrite ore through the series of bench scale laboratory tests. Initially, two tests were performed at baseline conditions. The baseline conditions used were an operating temperature of 50 ºC, a pH target of 1.2 and potential controlled for an $E_h$ of 700 mV.
(SHE) and ran over 10 days. The two baseline leaches resulted in copper extractions of 14.8% and 18.0%. This was comparable to a similar study’s baseline which achieved a copper extraction of 18% (Nikoloski, et al., 2017). The catalytic effect of silver has been discussed throughout this paper and its positive effects on chalcopyrite leaching well documented in literature (Ballester, et al., 1992) (Nikoloski, et al., 2017), to name a few, Three silver concentrations were added to the leach reactors and the kinetic data was plotted, Figure 10. Silver increased copper dissolution in all three concentrations with notably drastic leaching rates with 0.5 g/L and 0.1 g/L silver achieving 99% copper extraction which was comparable with tests at similar conditions resulting in 98% and 94% for the same silver dosage respectively (Nikoloski, et al., 2017). The lowest silver concentration, 0.02 g/L, increased extraction to 27.2% up from 18% without any silver. Again, this was similar to the 25% copper extraction achieved in the same study previously cited (Nikoloski, et al., 2017). The lowest silver concentration was used for subsequent leaching tests utilizing silver addition to allow for any synergies to be more noticeable, positive or negative.

Chloride and its effects on copper extraction were tested in combination with silver. Chloride on its own showed no apparent effect on leaching however when combined with silver an increase was noticed. However, the copper dissolution extent was reduced compared to silver at the same concentration on its own indicating that no positive synergy between silver and chloride at the tested dosages.

A surfactant and its effect on copper extraction were tested in combination with silver with the baseline surfactant dosage of 1 g/L having marginally greater extraction than 0.02 g/L silver. When the two additives were combined however, drastic increases to both kinetics and copper extraction were observed, Figure 12. It is apparent that at the tested dosages of additives, there is a strong positive synergy. Surfactant addition of 1 g/L and
0.2 g/L resulted in final extractions of 97.5% in both cases. All three surfactant-silver combinations resulted in a significant increase to leaching kinetics compared to the 0.2 g/L silver and 1 g/L wetting agent baselines. Copper extraction after 1 day in all three combination tests exceeded the final extraction achieved by the respective baselines after 10 days of leaching.

The effects of EG concentration on the extraction of copper from the chalcopyrite sample are shown in Figure 13. The three concentrations of EG tested in combination with silver increased final copper dissolution in all cases compared to the silver baseline. Addition of 1 g/L appears to increase kinetics more so than at 5 g/L or 0.2 g/L yielding a final extraction of 44.3% compared to 28.9% and 34.2% respectively. There appears to be a slight positive synergy between EG and silver.

Two tests were performed using a combination of three of the additives. Silver was used at a dosage of 0.02 g/L, the surfactant at a 1 g/L concentration and the third reagent that was variable in the two tests were 1 g/L of chloride and EG. The kinetic data for the leach has been presented in Figure 14. The combination with EG present performed slightly better achieving 82.8% copper dissolution compared to 72.7% with chloride present. This is an increase compared to all the plotted baselines with faster kinetics. However, the overall leaching kinetics were reduced from silver and surfactant alone at 0.02 g/L and 1 g/L concentrations respectively.

From the data collected it appears that silver and surfactant had the greatest synergy increasing extraction in all cases. Silver and EG had marginal benefits, particularly at 1 g/L of EG. No apparent synergy is present between chloride and silver at the tested dosages. The combination of the three additives while showing reasonable kinetics and overall extraction was lower than that of surfactant and silver alone.
6.2 Recommendations

The effects of additives and their effect on chalcopyrite leaching were investigated in this study. A few reagent combinations had promising results particularly, between the surfactant and silver. Due to the expensive nature of silver, being able to maintain respectable leaching kinetics and high extraction at lower dosages is significant for the potential development of cost effective leaching technologies. As a result, testing more additive combinations and variations in dosages would be insightful. As more test work is performed, optimisation of these promising additive combinations could be established. Additionally, the length of the leaching tests could be investigated as dosages vary. As seen in some of the more effective combinations in this study, the extraction curves had not begun to plateau after the 10 days. Extending the leach residence time may allow for further dosage optimisation. Eventually larger scale tests will be required to assess whether the systems behave in a similar fashion in set-ups like a column leach. Ultimately, as more test work is undertaken a better understanding of the specific mineralogical transformations as the reactions proceed will be invaluable for potential heap leaching ventures.
References


Table 7. A hazard identification for reagents used during the test work.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Potential Hazards</th>
<th>Action Taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO$_4$·7H$_2$O</td>
<td>Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation</td>
<td>PPE worn: Safety glasses, latex gloves, long sleeve lab coat.</td>
</tr>
<tr>
<td>Al$_2$(SO$_4$)$_3$·18H$_2$O</td>
<td>Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation (lung irritant). Slightly hazardous in case of ingestion</td>
<td>PPE worn: Safety glasses, latex gloves, long sleeve lab coat.</td>
</tr>
<tr>
<td>CuSO$_4$·5H$_2$O</td>
<td>Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation</td>
<td>PPE worn: Safety glasses, latex gloves, long sleeve lab coat.</td>
</tr>
<tr>
<td>FeSO$_4$·7H$_2$O</td>
<td>Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation</td>
<td>PPE worn: Safety glasses, latex gloves, long sleeve lab coat.</td>
</tr>
<tr>
<td>Fe$_2$(SO$_4$)$_3$·xH$_2$O</td>
<td>Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation. Slightly hazardous in case of skin contact (permeator).</td>
<td>PPE worn: Safety glasses, latex gloves, long sleeve lab coat.</td>
</tr>
<tr>
<td>98% H$_2$SO$_4$</td>
<td>Very Hazardous in case of skin contact (Corrosive, irritant, permeator), of eye contact (Irritant, corrosive), of ingestion, of inhalation.</td>
<td>PPE worn: Safety glasses, latex gloves, long sleeve lab coat.</td>
</tr>
<tr>
<td>LiOH</td>
<td>Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.</td>
<td>- Used in fume hood. - PPE worn: Safety glasses, latex gloves, long sleeve lab coat.</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>Very hazardous in case of skin contact (irritant), of eye contact (corrosive). Hazardous in case of skin contact (corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer)</td>
<td>PPE worn: Safety glasses, latex gloves, long sleeve lab coat.</td>
</tr>
</tbody>
</table>