KINETICS OF LEACHING OF COVELLITE IN FERRIC-SULFATE-SULFURIC ACID MEDIA

by

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Abstract

Hydrometallurgy methods to extract copper are becoming more frequently applied in modern industry. However, the leaching kinetics for certain minerals like covellite is poorly understood. This thesis investigates the kinetics of covellite leaching in a ferric-sulfate-sulfuric acid media, with an emphasis first placed on the understanding of the effect of the most common variables such as temperature and redox potential.

A natural mineral sample of covellite and an ore sample from the Oyu Tolgoi project in Mongolia were obtained for the leaching studies. The leaching temperature was varied from 20° to 90°C, the total iron concentration varied from 0.1 mol/L to 0.5 mol/L, the Fe$^{+3}$/Fe$^{+2}$ ratios varied from 0.1 to 10.

The leaching results showed that an increase in temperature will result in an increase in the rate and extent of copper extraction. However, the redox potential or Fe$^{+3}$/Fe$^{+2}$ ratio have little to no effect on the final copper extraction. These factors had only a modest impact on copper leach kinetics. The final copper extractions for covellite from Butte, Montana and covellite containing ore from Oyu Tolgoi at the same temperature were very similar.

The key factor to improve copper extraction from covellite containing ores is to maximize the leach temperature. The other factors appear to be much less important. These findings provide the basis for process design and optimization of industrial leaching processes of covellite.
Preface

Financial support for this work was provided by Rio Tinto. I was responsible for conducting the research, preparing and analyzing the results, and writing progress reports and this thesis. The work was done under the supervision of Dr. David Dreisinger.
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<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SX</td>
<td>Solvent Extraction</td>
</tr>
<tr>
<td>EW</td>
<td>Electrowinning</td>
</tr>
<tr>
<td>MTPD</td>
<td>Metric Tons per Day</td>
</tr>
<tr>
<td>PLS</td>
<td>Pregnant Leach Solution</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-Density Polyethylene</td>
</tr>
<tr>
<td>AA</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td>PPM</td>
<td>Parts Per Million</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>ORP</td>
<td>Oxidation-Reduction Potential</td>
</tr>
</tbody>
</table>
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I would like to express my deepest gratitude to my supervisor Dr. David Dreisinger for his constant support, guidance, understanding and patience thought the course of my study. He continuously showed the deep love he has for research and teaching and also for his family and students.

I would like to extend my appreciation to the people at Rio Tinto specially Ralph Hackl, Paul Brown, Lucy Esdaile and Mike Rockandel for supporting and sponsoring my research. The knowledge and deep analysis obtained from our progress meetings were fundamental.

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I owe a deep sense of gratitude to my previous bosses at AMEC, William Colquhoun and Niresh Deonarain for their endless support.

Last but not least, it’s my privilege to thank my wife Patricia for her constant encouragement and support throughout my research period.
Dedication

To Patricia, my amazing wife.

My parents and brothers for their deep support.

And to Dr. David Dreisinger for not only been my mentor but also my friend.
Chapter 1: Introduction

Most copper ores contain only small amounts of this metal. This means that the recovery processes have to be constantly improving to sustain profitable earnings. Another fact that affects the copper processing industry is the continuous reduction of this even low copper ore grades. At this point the average grade of copper ore in the 21st century is now below 0.6% copper [1].

The most successful processing methods for these low grades copper ores are dump and heap leaching. The most successful heap leaching operations have been those for oxide and secondary sulfide minerals such as chalcocite and covellite. Copper dump and heap leaching of the low grade ores contributes more than 20% of the annual world copper production [2]. These large hydrometallurgy operations are very common in countries such as Chile and Peru with large low grade copper orebodies.

In order to keep the operational costs as low as possible the most common leaching system comprises acidified ferric sulfate solutions. These solutions are inexpensive and constitute a potent lixiviant that can extract copper from both oxide and secondary sulfide minerals. The use of ferric sulfate in leaching to extract copper from low grades ores by dump or heap leaching is becoming more and more frequent. During the ferric leaching process, the sulfide mineral sulfur reports almost completely as elemental sulfur with small amounts of soluble sulfate formed [2]. The elemental sulfur can be oxidized and used to produce acid which will reduce the amount to be purchased.

With the growing of the hydrometallurgical copper processing industry it’s crucial to have a better understanding about the leaching chemistry of a variety of secondary copper sulfides. The leaching of chalcocite dominates the secondary sulfide leaching process. However,
covellite is a very important mineral for the low grade copper industry. The lack of information on the leaching behavior of covellite in ferric sulfate – sulfuric acid leaching solutions is a limitation to exploitation of these ores. Accordingly, this research is meant to help understand the leaching behavior of covellite and to define the best conditions for leach extraction.

1.1 Scope of Present Study and Research Objectives

Very few studies about the leaching kinetics of covellite with acidified ferric/ferrous solutions or with oxygen gas as the oxidant have been published. This work is designed to fill this gap and identify the most relevant conditions for commercial covellite leaching.

Another factor to consider is that most of the previous work has been done on synthetic covellite but that information is not very relevant to the industry. Therefore this work will use natural covellite samples including a relatively pure sample of covellite from Butte, Montana and a covellite-containing ore sample from the Oyu Tolgoi project. The first sample contains very low impurity values and the second sample represents an available covellite ore for leaching.

The study will focus on the covellite leaching at temperatures between 20ºC and 90ºC with an emphasis at 40ºC because that’s a reference for heap leaching. The obtained information will be used to define the best conditions to leach covellite.

The effect of different Fe$^{+3}$/Fe$^{+2}$ concentrations will also be studied for both covellite from Butte, Montana and covellite ore from the Oyu Tolgoi project.

In the following chapters the most relevant information about previous work done on covellite and also the results and analysis from this present research will be presented.
Chapter 2: Literature Review

2.1 General Copper Information

Copper as metal and its alloys have been used for thousands of years. It’s considered to be the oldest metal used by man, dating back more than 10,000 years. From the old civilizations to our modern times, copper has always been a key element for humans. The word copper comes from “Cyprus”, the island where the Romans found it. [3]

Copper is the 26th most abundant element on Earth, but it is rare to find as a pure metal [4]. It’s mostly found in many different types of mineral ores, many of them are close to the surface (open pit mines) with relatively easy extraction methods while others are deeper from surface (underground mines) with more complicated extraction methods. It’s common that the open pit mines contain around 0.5% Cu while underground mines have between 1 and 2% Cu[2].

Copper is usually found in two types of ores: (1) sulfide ores, containing minerals such as covellite (CuS), chalcopyrite (CuFeS2), bornite (Cu8FeS4), chalcocite (Cu2S), and enargite (Cu3AsS4); and (2) oxidized ores, containing minerals such as tenorite (CuO), malachite (CuCO3.Cu(OH)2), azurite (2CuCO3.Cu(OH)2), cuprite (Cu2O), chrysocolla (CuO.SiO2.2H2O), and brochanite (CuSO4.3Cu(OH)2). [39].

Around 80% of the world copper production is obtained by a flotation, smelting and refining from Cu-Fe-S ores. The other 20% is obtained by the hydrometallurgical method. The election between pyrometallurgy and hydrometallurgy is based in several aspects such as type of copper mineral, copper grade, market price and many others.
While some copper minerals are preferred for pyrometallurgy (Figure 2.1) i.e. chalcopyrite (the most common copper mineral - CuFeS$_2$) others prefer the hydrometallurgical way (Figure 2.2) due to low grade minerals and economic restrictions i.e chalcocite, covellite, bornite.

Copper production by hydrometallurgy can generally be broken down in these steps:

- Copper leaching using sulfuric acid. The mineral from the ore first must be crushed and leached. An impure copper bearing aqueous solution will be generated.
- Copper is transferred from the impure solution to a pure or high grade copper electrolyte via solvent extraction.
- The pure copper cathode is then electroplated to produce a copper product that is +99.99% pure.

The most common copper ores treated by hydrometallurgy are:

- Oxides copper minerals, carbonates, silicates, sulfates
- Secondary sulfide copper minerals containing chalcocite (Cu$_2$S)
Figure 2.1 Main Processes for extracting Copper from sulfide ores. [2]
Figure 2.2 Flowsheet for leaching oxide and Copper sulfide ores. The dissolved Cu is recovered by solvent extraction purification/strengthening then electrowinning. Leaching accounts for 20% of primary (from ore) copper production. [2]
Table 2.1 Principal Commercial Copper Minerals [2]

<table>
<thead>
<tr>
<th>Type</th>
<th>Common Minerals</th>
<th>Chemical Formula</th>
<th>Theoretical %Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary Sulfides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minerals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS$_2$</td>
<td>34.6</td>
<td></td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu$_5$FeS$_4$</td>
<td>63.3</td>
<td></td>
</tr>
<tr>
<td><strong>Secondary Minerals</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supergene Sulfides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Cu$_2$S</td>
<td>79.9</td>
<td></td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>66.5</td>
<td></td>
</tr>
<tr>
<td>Native Copper</td>
<td>Metal</td>
<td>Cu</td>
<td>100.0</td>
</tr>
<tr>
<td>Carbonates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malachite</td>
<td>CuCO$_3$Cu(OH)$_2$</td>
<td>57.5</td>
<td></td>
</tr>
<tr>
<td>Azurite</td>
<td>2CuCO$_3$Cu(OH)$_2$</td>
<td>55.3</td>
<td></td>
</tr>
<tr>
<td>Hydroxy-silicates</td>
<td>Chrysocolla</td>
<td>CuO.SiO$_2$.2H$_2$O</td>
<td>36.2</td>
</tr>
<tr>
<td>Hydroxy-Chlorides</td>
<td>Atacamite</td>
<td>Cu$_2$Cl(OH)$_3$</td>
<td>59.5</td>
</tr>
<tr>
<td>Oxides</td>
<td>Cuprite</td>
<td>Cu$_2$O</td>
<td>88.8</td>
</tr>
<tr>
<td></td>
<td>Tenorite</td>
<td>CuO</td>
<td>79.9</td>
</tr>
<tr>
<td>Sulfates</td>
<td>Antlerite</td>
<td>CuSO$_4$.2Cu(OH)$_2$</td>
<td>53.7</td>
</tr>
<tr>
<td></td>
<td>Brochantite</td>
<td>CuSO$_4$.3Cu(OH)$_2$</td>
<td>56.2</td>
</tr>
</tbody>
</table>

2.2 Copper Price

The selling price for a metal is always important in the decision making for the mining industry, whether to increase or decrease production or even close mines. The real copper price since 1950 is shown in Figure 2.3. From 1960 to 2003 the price was relatively constant at an average of $\sim 1$ $$/lb (except for period of 1965-1975). Since 2003 the price increased quickly to
around 3.5 $/lb. The reason for the steep rise is generally believed due to rapidly increasing consumption in China and other developing economies. Copper is a metal with a relatively low market price and that is in part because of its large production (approaching 20 million tonnes per year). Any excess of supply over demand makes it very difficult for producers but beneficial to users. Any excess of demand is of course beneficial to the producers. In Rio Tinto’s statement, “long run price levels are the outcome of a continuous tussle between demand and supply” [5].

![Copper price since 1950 to 2010](image)

**Figure 2.3 Copper price since 1950 to 2010 [2]**

Another factor to consider along with fast growing production and consumption of this important metal are the barriers to growing the copper production base. The constant decrease in the grade of copper ores over time (Figure 2.4) creates challenges in exploration (finding new ore sources) and economics (cost effective processing of lower grade ores). Exploration has become a crucial activity for the copper market to sustain the increased supply. The economics of the
copper ore treatment are favoured with metallurgical developments to increase the copper extraction or recovery and at the same time increase in ore treatment volumes. These are key factors to keep in focus to increase production. This means that mining companies constantly implement new technologies and extractions methods that allow them to recover greater amounts of metal using the same amount of ore (i.e. a better reagent combination in the flotation stage will allow more valuable metal to be recovered).

The requirement of better technologies and new and better recovery methods for more complex ores are some of the keys factors to keep mining companies working competitively.

Figure 2.4 Weighted average percentage head grades of copper mines, 1970 onwards [46]

Figure 2.4 shows the weighted average percentage head grade of copper mines over time for the last 140 years. After 1970 to the early 2000 the copper ore grades were constantly struggling with a small 1% average. Although is not show in the figure, a curious fact happened
in the late 1920’s, while the US was struggling with the worst economic depression in its history the richest deposits of the 20th century were exploited. The 21st century is characterized by the lowest copper ores grade in history with an average value around 0.6%.

2.3 Covellite

Covellite (CuS) is a copper sulfide mineral which contains 66% copper and it is now considered as dimer (2 molecules of CuS attach to form Cu$_2$S$_2$) with the copper existing as copper (I). Covellite occurs very often in nature associated with chalcopyrite and chalcocite which are the main primary and secondary copper sulfides for the copper industry, respectively [2]. It’s rarely found in nature as a primary mineral in copper deposits. The leaching process of covellite is considered slow and if it’s compared with chalcopyrite and chalcocite, covellite leaches slower than chalcocite but faster than chalcopyrite [6].

Covellite is stable at room temperature. It’s a blue-black mineral with a unique hexagonal or monoclinic crystal structure. Covellite is insoluble in water even at high temperatures, but it is soluble in alkali cyanides and ammonia solutions with complex ion formation. Covellite is also oxidized in hot nitric acid. Although covellite is not directly soluble in sulfuric acid the most common method to leach covellite involves the use of sulfuric acid to provide an acidic media. Sulfuric acid is the preferred acid for copper leaching because of its low cost.
2.3.1 Research on Covellite Leaching

The first controlled study to leach covellite in an acidic ferric sulfate media was done in 1930 by Sullivan [6] who also discovered that covellite under these conditions produced elemental sulfur according to the reaction:

\[ CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S^0 \]  

(1)

Sullivan [6] studied many aspects of covellite leaching that are the topic of the present work. He discovered that covellite has a very slow dissolution rate at temperatures around 50° or less, although at temperatures close to the water boiling point the dissolution was quite fast. He also advised about the requirements of agitation to accelerate the process.

Sullivan [6] discovered that covellite leaching rate was practically independent of acid concentration if the ferric iron concentration was kept at 1%, however, if this concentration dropped so does the dissolution rate. This represents a process advantage because that means leaching covellite in acidic media is a robust process.

Sullivan [6] compared leaching covellite in excess sulfuric acid in the presence of excess dissolved atmospheric oxygen and leaching covellite with only with ferric sulfate. The evidence showed that the rate of copper leaching in sulfuric acid in combination with excess oxygen is only half the rate obtained for ferric sulfate. He also compared ferric sulfate and ferric chloride solutions, finding that at low temperatures (35°C) ferric sulfate leaching is more rapid but at high temperatures (98°C) the rate is virtually the same.

Sullivan [6] and Dutrizac’s [7] experiments showed that synthetic covellite dissolved at a much faster rate than natural covellite. Both attributed this to a widely varying amount of other minerals that are commonly associated with natural covellite i.e. bornite, chalcocite and others.
Various papers reported on the effect of temperature and this resulted in activation energies in the range of 33 to 121 kJ/mol; which suggests that the rate of covellite leaching is controlled by slow chemical and/or/electrochemical steps. Sullivan and Dutrizac experiments showed up the very slow dissolution rate of covellite. The experimental results of Sullivan, Dutrizac and others are summarized in table 2-2.

Thomas and Ingraham [8] leached synthetic covellite using rotating disks in acidified ferric sulfate solutions in a wide range of temperature from 25 to 80°C. This work done 37 years after Sullivan [6] verified the covellite reaction with ferric. However, the reported dissolution rates were very different, Sullivan’s work showed a very slow dissolution rate for synthetic covellite and Thomas and Ingraham reported much faster rates. They found that only 4% of the reacted sulfur reported as sulfate; the remainder was in elemental form. Their leaching rate curves showed extremely slow reactions below 60°C and faster ones over 60°C. Below 60°C a chemically controlled process takes place on the covellite surface with an apparent activation energy of 92 kJ/mol. Over 60°C the reaction is controlled by the mass transfer (deduced by the high dissolution speed) with an apparent activation energy of 33 kJ/mol. Thomas and Ingraham have been the only one with results showing a dual mechanism of covellite leaching in acidic ferric media. Thomas and Ingraham discovered that the leaching rate was almost directly proportional to the ferric concentration at diluted solutions (concentrations below 0.005M) but at high concentrations the dissolution rate is almost independent of ferric concentration.
Table 2.2 Leaching Kinetics observed for Covellite dissolution in acidified ferric sulfate solutions

<table>
<thead>
<tr>
<th>Material</th>
<th>Fe$^{3+}$ dependence on rate</th>
<th>Activation Energy (kJ/mol)</th>
<th>Temperature (°C)</th>
<th>Rate Controlling process</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural ores of different purities</td>
<td>No effect for Fe$^{3+}$&gt;1%</td>
<td>88-117 (calculated)</td>
<td>25-95</td>
<td>Not defined</td>
<td>6</td>
</tr>
<tr>
<td>Synthetic</td>
<td>No effect for Fe$^{3+}$&gt;0.005M Fe$^{3+}$ directly proportional to Fe$^{3+}$ conc. at lower levels</td>
<td>92</td>
<td>25-60</td>
<td>Essentially linear kinetics (surface reaction)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Solution transport with linear kinetics</td>
<td>8</td>
</tr>
<tr>
<td>Intermediate product from the leaching of pure synthetic Cu$_2$S</td>
<td>Increased with increasing Fe$^{3+}$ conc. in the range 0.25-1.0M</td>
<td>100-121</td>
<td>20-80</td>
<td>Chemically controlled</td>
<td>9</td>
</tr>
<tr>
<td>Mounted natural crystals</td>
<td>Increased gradually between 0.0064M and 0.212M Fe$^{3+}$</td>
<td>57</td>
<td>40-70</td>
<td>Chemisorption process with linear kinetics</td>
<td>10</td>
</tr>
<tr>
<td>Synthetic powders</td>
<td>Fe$^{3+}$&gt;0.005M, no effect. Fe$^{3+}$&lt;0.005M, rate proportional to ferric strength</td>
<td>84</td>
<td>30-90</td>
<td>Slow chemical step with linear kinetics</td>
<td>11</td>
</tr>
<tr>
<td>Pure synthetic natural crystals</td>
<td>No effect for Fe$^{3+}$&gt;0.005M directly proportional to Fe$^{3+}$ conc. at lower levels</td>
<td>75</td>
<td>25-95</td>
<td>Rates increased slightly with time; kinetics essentially linear; chemically controlled</td>
<td>7</td>
</tr>
<tr>
<td>Synthetic</td>
<td>-</td>
<td>46-71</td>
<td>25-50</td>
<td>Essentially linear kinetics (surface reaction)</td>
<td>12</td>
</tr>
<tr>
<td>Blaubleibender</td>
<td>-</td>
<td>46-59</td>
<td>25-50</td>
<td>Essentially linear kinetics (surface reaction)</td>
<td>12</td>
</tr>
</tbody>
</table>
King et al. [9] studied the leaching of chalcocite in acidic ferric chloride solutions and the covellite formed as an intermediate product during the reaction. The rate controlling process is chemical controlled by the reaction of $S^{2-}$ ions on the covellite surface to form elemental sulfur. The apparent activation energy for the covellite leaching as a second stage of the chalcocite leaching was in the range of 100 to 121 kJ/mol. As Sullivan [6], King [9] also found that the dissolution rate of covellite is similar for hydrochloric and sulfuric solutions at high temperatures (anionic concentrations below 1M).

Lowe [10] studied the leaching of covellite mounted specimens in acidified ferric sulfate solutions at temperatures between 35 and 68°C. The rate controlling step was chemisorption occurring at the surface of the covellite with apparent activation energy of 57 kJ/mol. The leaching rate increased slightly with increasing ferric sulfate concentration for cases between 0.0064M and 0.212M. The dissolution rate was found to be unaffected by the sulfuric acid concentration. They found that cupric ion/elemental sulfur ratio during was 1:1. The overall leaching reaction proposed was identical to Sullivan’s work.

Mulak [11] studied the leaching of synthetic covellite in acidified ferric sulfate solutions at temperatures between 30 and 90°C. The leaching rate proved to be linear and independent of stirring rate with apparent activation energy of 84 kJ/mol. Due to slow reaction rates, Mulak defined the reaction as chemical controlled by the surface reaction of covellite. The leaching rate was independent of sulfuric acid concentration for pH below 3 and also independent of ferric sulfate concentration for cases over 0.005M Fe$^{3+}$. For cases below 0.005M Fe$^{3+}$ the reaction rate depended directly of ferric concentration.

Walsh et al. [12] studied the leaching rate of synthetic covellite and blaubleibender covellite with ferric iron in acidic chloride solution at pH 2.0 for temperatures between 25 and
50°C. Blableibender covellite proved to leach faster than synthetic covellite. However, both had high apparent activation energy of 46-59 kJ/mol for blableibender covellite and 46-71 kJ/mol for synthetic covellite. He concluded that due to high activation energies the rate controlling process is chemical controlled by the reaction on the covellite surface.

Dixon et al. [45] studied the blableibender covellite oxidation with ferric sulfate and discovered a slow process, controlled by the rate of charge transfer in the anodic decomposition process with an extremely high activation energy (80-100 kJ/mol). The kinetic is limited by the slow mineral kinetic of the blableibender.

### 2.3.2 Covellite Leaching

Covellite, as for the rest of copper sulfides, requires the presence of Fe$^{+3}$ and an oxidizing agent (usually oxygen) for ferric regeneration for leaching to occur. Covellite is oxidized by Fe$^{+3}$ resulting in Fe$^{+2}$ which may be reoxidized to Fe$^{+3}$ by oxygen in a commercial circuit. The Fe$^{+3}$/Fe$^{+2}$ redox couple acts in a catalytic manner in these reactions.

These are the chemical reactions for ferric catalyzed oxygen leaching of covellite:

$$(i) CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + S$$  \hspace{1cm} (2)

$$(ii) 2FeSO_4 + 0.5O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$$  \hspace{1cm} (3)

$$(overall) CuS + 0.5O_2 + H_2SO_4 \rightarrow CuSO_4 + S + H_2O$$  \hspace{1cm} (4)

The reaction show elemental sulfur production which was verified by King et al. [9] and also by Thomas and Ingraham [8] who discovered that only 4% of the reacted sulfur reported as sulfate; the remainder was in elemental form. It is also possible to obtain sulfuric acid instead of element sulfur, but that may involve the use of bacteria (or some special conditions).

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$  \hspace{1cm} (5)
Pourbaix diagrams, also known as Eh/pH diagram, show the stable phases of an aqueous electrochemical system. These diagrams are particularly useful for leaching because it shows the reactions that are favorable under different conditions. However, these diagrams do not provide kinetic information. I.e. the reaction may be favorable but if the kinetics is too slow, then the reaction will not take place. In the case of covellite, the diagram shows that leaching covellite will produce Cu$_2$S initially, however this reaction does not happen in most leaching systems because the oxidation of sulfur to sulfate (required to form Cu$_2$S from CuS) is very unfavorable kinetically.

Figure 2.5 shows a Pourbaix diagram for Cu-Fe-S-O-H$_2$O which is the system used on this research.

Figure 2.5 Pourbaix diagram of the Cu-Fe-S-O-H$_2$O system at 25°C [Cu]=0.01M; [Fe]=[S]=0.1 M [2]
The majority of copper recovered by hydrometallurgy comes from heap leaching and the same applies for covellite. The process is divided into 3 stages: (1) heap leach, where the dissolution of copper in weak sulfuric acid solutions takes place; (2) solvent extraction (SX), where the solution obtained by heap leaching will be upgraded and purified to produce an electrolyte suitable for electrowinning; and (3) electrowinning (EW), where the purified electrolyte from SX is reduced to copper metal by the application of an electrical current. Figure 2.6 shows a copper heap leach/solvent extraction/electrowinning flowsheet.

In 2011 leaching (both heap leaching and in-situ leaching) produced 3.4 million metric tons of copper, 22 percent of world production [13]. The largest copper heap leach operations are in Chile, Peru, and the southwestern United States.

Other copper leaching methods include:

- In-Situ leaching
- Dump leaching
- Vat leaching
- Agitation leaching
- Pressure oxidation leaching
Figure 2.6 Copper Heap Leach/Solvent extraction/Electrowinning flowsheet [2]
2.3.3 Covellite Industrial Leaching Operations

Cerro Verde is one of the most important copper leaching operations in the world. It is located approximately 20 miles southwest of Arequipa Peru. The concentration facility treats 120,000 metric tons per day (MTPD) and is expanding to 360,000 MTPD by the end of 2015; a $4.6 billion project. Cerro Verde will produce annually 600 million pounds of copper and 15 million pounds of molybdenum by 2016 and with that it will become one of the world’s largest concentration complexes [14].

Cerro Verde mine is a porphyry copper deposit that has oxide and secondary sulfide mineralization, and primary sulfide mineralization. The predominant oxide copper minerals are brochanite, chrysocolla, malachite and copper “pitch.” Chalcocite and covellite are the most important secondary copper sulfide minerals. Chalcopyrite and molybdenite are the dominant primary sulfides [14].

Cerro Verde facilities include Solvent Extraction/Electrowinning (SX/EW) like the example shown in Figure 2.6. Figure 2.7 shows the Cerro Verde processing plant.

The following data [2] is from 2010:

- **Operation:**
  - 1.5t/t Cu consumed of H₂SO₄.

- **Ore feed to leach:**
  - Mineralogy: chalcocite, covellite, chalcopyrite
  - 0.64% average Cu grade
  - 0.54% average leachable Cu
  - 85% Leachable Cu recovered to PLS
• Ore Preparation
  o Crush and agglomerated in rotating drum

• Operation
  o 9.5 mm for 10-15% Ore

• Heap
  o Permanent
  o 1,000,000 m$^2$ of leach area
  o 45 cells under leach
  o 7m lift height
  o Aeration with pipes beneath heap
  o HDPE used as material for liners
  o 1.5 mm liners thickness

• Acid Cure
  o Applied on Rotating drum
  o 3.5 Kg H$_2$SO$_4$/t ore

• Lixiviant
  o Uses raffinate or recirculated PLS
  o 4-8 g/L of H$_2$SO$_4$
  o 0.3 g Cu/L

• PLS
  o 3-4 g/L of H$_2$SO$_4$
  o 3 g Cu/L
  o 19-25 ºC
2.4 Summary of Literature Review

There is very little literature for covellite which represent a problem in the industry. Covellite leaching is considered to be slow below 50ºC and faster at temperatures close to water boiling and the ferric concentration has very little or no effect on the leaching kinetics. Most of the previous work was done on high grade natural covellite or synthetic covellite, however there is little information about covellite from an actual mining operation.

The objective of the present work was to investigate the kinetics of covellite leaching in a ferric-sulfate-sulfuric acid media with emphasis in understanding the most common variables such as temperature and redox potential. The experimental procedures required to achieve this objective are presented in the following Chapter.
Chapter 3: Objectives

The experimental program was designed to understand the leaching behavior of covellite and ores containing covellite under acid, ferric sulfate leaching conditions.

The experimental program designed for this study can be divided in phases:

1. Leaching of covellite with only ferric in solution. For this phase, temperature was controlled and oxygen was used as an oxidant.

2. Leaching of covellite with ferric and ferrous in solution. Again temperature was controlled and oxygen used as an oxidant to maintain ferric in solution.

3. Leaching of covellite with ferric and ferrous in solution. Temperature was controlled and permanganate was substituted for oxygen as an oxidant to maintain ferric levels in solution.

4. Leaching of ore sample containing covellite from the Oyu Tolgoi deposit in Mongolia with ferric and ferrous in solution. Temperature was controlled and permanganate was used as an oxidant to maintain ferric levels in solution.
Chapter 4: Experimental Procedures

Two experimental methods were used for studying the covellite leaching. The first one used oxygen as the oxidant and the second one used potassium permanganate as the oxidant. Both methods will be explained in this chapter.

4.1 Materials

Covellite samples used in this work have different origins. Most of the experiments were conducted with a high grade, high purity covellite mineral sample from Butte, Montana. The final experiments were conducted with a sample provided by Rio Tinto from the Oyu Tolgoi Project in Mongolia. The different experimental conditions were designed to provide a better understanding of copper extraction from covellite using common acid ferric leaching conditions.

The work on the sample from the Oyu Tolgoi project was an attempt to bridge the investigation to the industrial application.

4.2 Experimental Conditions

The experimental conditions were chosen based on previous researches and also based on Dr. David Dreisinger’s experience and Rio Tinto advice.

4.2.1 Temperature

One of the easiest parameters to adjust and control is the temperature of the reaction. Due to equipment limits in the laboratory the investigation covered temperatures from 20 to 90°C at atmospheric pressure. Previous work [7] reported that the covellite reaction rate for the range 25-95°C is relatively slow and increases at higher temperature.
4.2.2 Ferric/Ferrous Concentration

For both systems (high grade sample and Oyu Tolgoi sample) it is important to study the effect of ferric and ferrous ion concentration on the leach kinetics. This research focused on the effect of concentrations above 0.1 M Fe$^{+3}$. Previous work done [7] reveals that the rate varied directly with the ferric concentration for initial concentrations below 0.005 M Fe$^{+3}$ but was insensitive to higher ferric strengths. For each system the effect of total iron concentration and ferric/ferrous couple on the leach kinetics were investigated.

In most of cases for copper leaching, there’s an important relationship between the leaching rate and the Fe$^{+3}$/Fe$^{+2}$ couple. However for covellite there is almost no published information on this parameter.

4.2.3 Potential

For covellite leaching, the mixed potential theory may apply because the reduction of the oxidant and the oxidation of the mineral take place at the mineral surface via an expected electrochemical mechanism. Therefore, a continuous measure of the slurry potential during leaching was thought to be useful to understand the controlling step for the reaction. Again, there’s little information about this in the literature.

4.2.4 Sulfuric Acid Concentration – pH Control

Another important condition is the sulfuric acid concentration, there are several reports about the effects of changing the acid concentration [7, 15, 16 and 17]. In this work, some experiments were conducted with pH control. The experiments with permanganate as oxidant used pH control. Experiments that used oxygen as an oxidant did not have pH control.
4.2.5 Particle Size

The general experience in leaching studies is that smaller particle sizes improve the reaction rate. For this research, the sample from Butte, Montana had a $P_{80}$ of 68 microns and the sample from Oyu Tolgoi had a $P_{80}$ of 47 microns.

4.2.6 Stirring Speed and Effect on Mixing

Stirring speed was easily controlled with the current laboratory equipment. The importance of mixing in this study was to ensure particle suspension, solid-liquid mixing and gas-liquid mixing for re-oxidation of ferrous to ferric with molecular oxygen. For this research the stirring speed was generally held at 900 RPM.

4.3 Samples Preparation

The sample of covellite was obtained from Butte, Montana. This sample was a high grade and high purity covellite. The as-received sample was in the form of coarse rocks and was ground and screened to a range of -230 +270 mesh. Ground mineral was stored in sealed containers and kept away from sunlight to minimize oxidation of the mineral surface.

Particle size analysis was conducted in the Coal Laboratory of the University of British Columbia. Measurements were conducted with a MasterSizer system which use particle refraction index to achieve better results than conventional screen analysis. A dispersant was used for the analysis to ensure particle separation and particles were assumed to be spherical. The cumulative particle size distribution for the Butte Montana ground sample was determined by this method and is plotted in Figure 4.1.
Figure 4.1 Cumulative particle size distribution of the mineral sample from Butte, Montana, \( P_{90} = 68.0 \) microns

The covellite sample from Oyu Tolgoi was provided by Rio Tinto. The as-received sample was already ground and screen. The cumulative particle size distribution for covellite sample from Oyu Tolgoi sample was determined by the method previously described and is plotted in Figure 4.2.
Figure 4.2 Cumulative particle size distribution of the mineral sample from Oyu Tolgoi, Pₘₐₓ=47.0 microns

4.4 Chemical Analysis of the Mineral Sample

Samples were sent to Acme Labs in Richmond, British Columbia (also called Inspectorate) for chemical analysis. The results of the chemical analysis provided was crucial to define the amount of mineral that would be used for each leaching experiment. Analysis of the sample was done in duplicate by Acme Labs to ensure quality of the analysis.
Table 4.1 Results of Chemical analysis for the Covellite samples used for the experiments

*Sample from the Oyu Tolgoi Project was provided by Rio Tinto.

<table>
<thead>
<tr>
<th>Element</th>
<th>Covellite from Butte, Montana</th>
<th>Covellite from Oyu Tolgoi Project*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>56.95 %</td>
<td>0.62 %</td>
</tr>
<tr>
<td>Fe</td>
<td>2.45 %</td>
<td>4.65 %</td>
</tr>
<tr>
<td>S</td>
<td>15.50 %</td>
<td>5.30 %</td>
</tr>
<tr>
<td>K</td>
<td>0.02 %</td>
<td>2.33 %</td>
</tr>
<tr>
<td>Al</td>
<td>0.07 %</td>
<td>0.50 %</td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>0.13 %</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>0.06 %</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>0.06 %</td>
</tr>
<tr>
<td>Mg</td>
<td>-</td>
<td>0.05 %</td>
</tr>
<tr>
<td>Ba</td>
<td></td>
<td>0.05 %</td>
</tr>
<tr>
<td>As</td>
<td>30.0 ppm</td>
<td>0.03 %</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
<td>0.02 %</td>
</tr>
<tr>
<td>Cr</td>
<td>10.0 ppm</td>
<td>0.02 %</td>
</tr>
<tr>
<td>Sr</td>
<td>-</td>
<td>0.02 %</td>
</tr>
<tr>
<td>Ni</td>
<td>4.5 ppm</td>
<td>0.02 %</td>
</tr>
<tr>
<td>Zn</td>
<td>0.17 %</td>
<td>82.0 ppm</td>
</tr>
<tr>
<td>Pb</td>
<td>0.07 %</td>
<td>81.4 ppm</td>
</tr>
<tr>
<td>Mo</td>
<td>5.6 ppm</td>
<td>79.2 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>17 ppm</td>
<td>47.0 ppm</td>
</tr>
<tr>
<td>Co</td>
<td>2.0 ppm</td>
<td>30.0 ppm</td>
</tr>
<tr>
<td>Zr</td>
<td>-</td>
<td>24.0 ppm</td>
</tr>
<tr>
<td>La</td>
<td>-</td>
<td>2.9 ppm</td>
</tr>
</tbody>
</table>
### 4.5 Mineralogical Characterization of the Sample

In order to corroborate the chemical analyses and to obtain the phase abundance, qualitative analysis by X-ray power diffractometry (XRD) was carried out at the Department of Earth, Ocean & Atmospheric Sciences of UBC. The XRD analysis was useful in determining the initial phases for the minerals before leaching.

The samples were reduced to the optimum grain-size range for quantitative X-ray analysis (<10 μm) by grinding under ethanol in a vibratory McCrone Micronizing Mill for 10 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-80°2θ with CoKα radiation on a Bruker D8 Advance Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye-XE detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°.

The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF-4 and Search-Match software by Bruker. X-ray powder-diffraction data of the samples were refined with Rietveld program Topas 4.2 (Bruker AXS). The results of quantitative phase analysis by Rietveld refinements are given in Table 4-2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>32.5 ppm</td>
</tr>
<tr>
<td>W</td>
<td>2.6 ppm</td>
</tr>
<tr>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>11.8 ppm</td>
</tr>
<tr>
<td>Ag</td>
<td>37 ppm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>2.1 ppm</td>
</tr>
<tr>
<td>Y</td>
<td>2.0 ppm</td>
</tr>
<tr>
<td>Sn</td>
<td>1.6 ppm</td>
</tr>
<tr>
<td>Ag</td>
<td>1.6 ppm</td>
</tr>
</tbody>
</table>
**Table 4.2 Results of Mineralogical composition of the Covellite samples**

*Sample from the Oyu Tolgoi Project was provided by Rio Tinto.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Covellite from Butte, Montana</th>
<th>Covellite from Oyu Tolgoi Project*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alunite</td>
<td>$K_2Al_6(SO_4)<em>{12}(OH)</em>{12}$</td>
<td>-</td>
<td>4.0 %</td>
</tr>
<tr>
<td>Antlerite</td>
<td>$Cu^{2+3}(SO_4)(OH)_4$</td>
<td>16.4 %</td>
<td>-</td>
</tr>
<tr>
<td>Chalcanthite</td>
<td>$CuSO_4\cdot 5H_2O$</td>
<td>11.4 %</td>
<td>-</td>
</tr>
<tr>
<td>Covellite</td>
<td>$CuS$</td>
<td>62.6 %</td>
<td>0.4 %</td>
</tr>
<tr>
<td>Illite-Muscovite 2M1</td>
<td>$K_{0.65}Al_{2.0}Al_{0.65}Si_{3.35}O_{10}(OH)_{2}$</td>
<td>-</td>
<td>26.6 %</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$Al_2Si_2O_5(OH)_4$</td>
<td>-</td>
<td>6.7 %</td>
</tr>
<tr>
<td>Pyrite</td>
<td>$FeS_2$</td>
<td>7.7 %</td>
<td>9.8 %</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>$Al_2Si_4O_{10}(OH)_2$</td>
<td>-</td>
<td>3.2 %</td>
</tr>
<tr>
<td>Quartz</td>
<td>$SiO_2$</td>
<td>1.9 %</td>
<td>48.3 %</td>
</tr>
<tr>
<td>Rutile</td>
<td>$TiO_2$</td>
<td>-</td>
<td>1.0 %</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>100.0 %</strong></td>
<td><strong>100.0 %</strong></td>
</tr>
</tbody>
</table>

For the sample from Butte, Montana the mineralogical composition showed a calculated grade of 53.33, 3.58 and 28.06 % of Cu, Fe and S compared to 59.95, 2.45 and 15.50 % respectively for ICP.

For the sample from the Oyu Tolgoi project the mineralogical composition showed a grade of 0.31, 4.56 and 6.00 % of Cu, Fe and S compared to 0.62, 4.65 and 5.30 % respectively for ICP.

In both cases, the analysis results obtained from the mineralogical composition are similar to the ones obtained by ICP.

30
4.5.1 Acid Soluble Copper

The covellite sample from Butte, Montana contained acid soluble copper. However the sample from the Oyu Tolgoi project doesn’t. The species that contain acid soluble copper are antlerite and chalcanthite.

The percentage of copper in antlerite is 53.7% in mass and copper in chalcanthite is 25.5% in mass.

A simple mass balance determined that the sample from Butte, Montana contain 11.71% of acid soluble copper which represent a 22% of all the copper present in the sample.

4.6 Equipment and Experimental Set-up

The laboratory-scale unit for the leaching studies consisted of a 3-litre glass reactor with 2 layers of glass (2 chambers – 1 inside, 1 outside). The operating temperature was maintained at a pre-established value using recirculating water from a hot water bath. The temperature range for leaching ranged from 20 °C (room temperature) to 90°C. The hot water from the water bath was pumped to the external chamber while the leaching solution is in the internal chamber.

The solution redox potential was controlled at pre-established set points. The initial redox potential was defined after adding all reagents to the leach reactor (eg. ferric and ferrous salts and sulfuric acid). After the leach reactor was closed and secure, the stirrer was turned on. The best results for redox measurement were maintained once the system was stabilized for 5 to 10 minutes. The redox potential was measured by a combination ORP electrode using the Ag/AgCl reference. The experiments were conducted to control the redox or ORP at the initial value.

For the initial experiments, pure oxygen was used as the oxidant for ferric regeneration. The addition of oxygen was totally automated. A computer controlled electronic device detected the changes in the ORP (measured with an ORP electrode) and sent the signal to a feedback
mechanical system (essentially a software-controlled mass flow controller), which fed oxygen to
the system as required to maintain the potential at the desired value. A data acquisition system
recorded the ORP every 30 seconds and exported to an EXCEL spreadsheet.

For a second generation of experiments, potassium permanganate was used as oxidant. For these experiments the ORP control was basically the same as that used for oxygen. The only difference was that for this case it was possible to also record potassium permanganate consumption with time by weighing (continuously) the potassium permanganate solution storage vessel. The potassium permanganate concentration was 0.2M for all experiments. Preparation of the potassium permanganate is described in section 3.6.1.

The working pH for these experiments was between 1 and 1.5 (measured with a pH electrode). pH was not controlled when oxygen was the oxidant. For the cases where permanganate was the oxidant the pH was controlled. The pH was maintained by delivery of 1 N sulfuric acid solution into the reactor. Acid addition with time was also recorded. The stirring was controlled at pre-established set points. An electronic device connected to a calibrated motor provided a range from 1 to 2000 RPM.

Covellite samples are high-grade purity covellite from Butte, Montana with a P$_{80}$ of 68µm. A ground mineral sample from the Oyu Tolgoi deposit with a P$_{80}$ of 47 microns was also used for a series of experiments.
Figure 4.3 Typical Equipment Set-up for Oxygen as oxidant

Figure 4.4 Typical Equipment Set-up for Permanganate as oxidant
4.6.1 Permanganate use as Oxidant

Volumetric and potentiometric titrations of Fe\(^{2+}\) with MnO\(_4^-\) are well known and established analytical methods, where the ferrous ions instantaneously and stoichiometrically are oxidized to ferric ions by the permanganate according to

\[ \text{Fe}^{+2} + \frac{1}{5}\text{MnO}_4^- + \frac{8}{5}\text{H}^+ \rightarrow \text{Fe}^{+3} + \frac{1}{5}\text{Mn}^{+2} + \frac{4}{5}\text{H}_2\text{O} \]  \hspace{1cm} (6)

The redox potential in solution is determined by the Fe\(^{3+}/\text{Fe}^{2+}\) ratio. Therefore, the leaching proceeds via equations (1) and (6), giving the following sum equations (7), which were used for evaluation of the chemical leaching experiments:

\[ \text{CuS} + \frac{2}{5}\text{MnO}_4^- + \frac{16}{5}\text{H}^+ \rightarrow \text{Cu}^{+2} + \frac{2}{5}\text{Mn}^{+2} + \frac{8}{5}\text{H}_2\text{O} + S^0 \]  \hspace{1cm} (7)

The KMnO\(_4\) used for the experiments was prepared according to the following steps:

- Permanganate preparation – 0.2 M
  - Weigh 31.6 g KMnO\(_4\)
  - Dissolve in 1L distillated water (2 L beaker)
  - Cover the beaker with a watchglass and boil the solution for 20 min
  - Cool the solution
  - Filter through glass wool into a clean amber glass storage bottle
  - Label

- Permanganate Titration
  - Prepare 1 L of 1 M H\(_2\)SO\(_4\) by slowly adding 60 mL of concentrated acid to about 700 mL of water then diluting to 1 L.
  - Dry about 1.5 g of primary – standard sodium oxalate, Na\(_2\)C\(_2\)O\(_4\), at about 110°C for at least 1 h.
Cool in the desiccator

Weigh

After preparing and titrating the KMnO₄, it was placed in a dark bottle and covered with aluminum foil to avoid decomposition by sunlight. Consumption of KMnO₄ as a function of time was recorded during the leaching experiments. Figure 4.4 shows the setup used when working with permanganate.

4.7 Leaching Procedure

Once the equipment was set-up as previously described, mineral sample was added to the system. Every recording system was then started (i.e. ORP, pH, weigh scales). Experiment duration was defined depending on our previous experiences. Some experiments can be run for as little as 72 hours and others can go for over 168 hours.

Liquid samples were taken during the experiment and also at the end. Solids were also recovered.

4.8 Sampling Program

Liquid samples taken during the experiment were filtered or centrifuged and separated from solids. Solids went back to the reactor and liquid samples were labelled and saved for future analysis. The number of liquid samples obtained depended on the duration of the experiment.

Final solids were also recovered from the experiment. After the experiment ended, final solutions containing solids were filtered in order to separate solids from liquid. The final liquid volume was measured as well as the weight. The final solids were washed to remove any liquid residues that might affect the future analysis and dried at low temperatures.
4.9 Sampling Analysis

For every experiment, liquid and solid samples were produced for analysis. Liquid samples were generally analyzed at UBC using the Atomic Absorption Spectroscopy system. Solid samples were sent to a third party laboratory specialized in mineral digestion and ICP analysis.

4.9.1 Liquid Sample Analysis

In order to analyse the liquid samples, standards were prepared and samples were diluted, as follow:

- **Standards** :
  - 5 standards were prepared: 1, 2, 3, 4 and 5 mg Cu/L
  - Each standard had 0.1 M Fe and 1% nitric acid
  - A blank containing 1% nitric acid was prepared
  - Deionized water was used to dilute.

- **Liquid Samples** :
  - Each sample was diluted in a ratio 1:1000 (some experiments used a 1:200 ratio)
  - Deionized water was used to dilute.
4.10 Sample and Waste Management

Every sample taken in the course of the leaching program was registered in the laboratory sample log. Samples shipped for external analysis were labeled and packaged according to UBC safety rules (MSDS forms were filled for every batch of sample sent). The external laboratory chosen for the different required analysis was Inspectorate Vancouver (now Bureau Veritas).

All liquids for disposal were collected in specially conditioned tanks inside the laboratory. They are intended to be treated via UBC authorities. Solid residues were stored in a dry and safe location.
Chapter 5: Results and Discussion

5.1 Mineralogical Characterization

Analysis of the covellite samples by X-Ray Diffraction (XRD) showed that the sample from Butte, Montana consisted mainly of covellite with antlerite, chalcanthite, quartz and pyrite. The ore sample from Oyu Tolgoi had very little covellite with a majority of quartz.

The analysis also revealed that the pyrite concentration is a little bit higher in the Oyu Tolgoi sample. The covellite sample from Butte, Montana had 7.7% of Pyrite while the one from Oyu Tolgoi had 9.8%. Pyrite may react under different conditions to form acid. The relative amounts of pyrite in each sample may influence the acid balance.

The copper sources between both minerals were different, while the sample from Oyu Tolgoi had only covellite; the sample from Butte, Montana had antlerite (a copper hydroxide) and chalcanthite (a copper sulfate). Antlerite and chalcanthite are both dissolved by sulfuric acid. The X-Ray patterns for covellite from Butte, Montana and Oyu Tolgoi are shown in Figure 5.1 and Figure 5.2 respectively.
Figure 5.1 X-Ray diffraction pattern of Covellite from Butte, Montana
Figure 5.2 X-Ray diffraction pattern of Covellite from Oyu Tolgoi
5.2 Experimental Work Conditions

Table 5.1 shows the different conditions used to run the experiments.

### Table 5.1 Experimental Work Conditions

<table>
<thead>
<tr>
<th></th>
<th>Series 1 – Different Temperature</th>
<th>Series 2 – Different Fe³⁺/Fe²⁺ ratios</th>
<th>Series 3 – KmnO₄</th>
<th>Series 4 – Oyu Tolgoi sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu concentration (g/L)</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>1 (approx. 100g at 1% Cu)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20-90</td>
<td>40</td>
<td>40-90</td>
<td>40</td>
</tr>
<tr>
<td>Initial Solution Volume (L)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulfuric Acid concentration (g/L)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Stirring Rate (RPM)</td>
<td>600</td>
<td>900</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>Fe concentration (M)</td>
<td>0.1 – only Ferric</td>
<td>0.5 – Diff Ratios</td>
<td>0.5 – Diff Ratios</td>
<td>0.5 – Diff Ratios</td>
</tr>
<tr>
<td>Ferric/Ferrous Ratios</td>
<td>No</td>
<td>0.1 to 10</td>
<td>0.1 to 10</td>
<td>0.1 to 10</td>
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<tr>
<td>Oxygen</td>
<td>When required</td>
<td>When required</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>pH</td>
<td>1-1.5</td>
<td>1-1.5</td>
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</tr>
<tr>
<td>pH control</td>
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<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
5.3 Results of the Chemical Leaching Experiments for Covellite from Butte Montana

The results of the leaching experiments on covellite from Butte, Montana are presented in the following sections.

5.3.1 Effect of Temperature Control – Only Ferric in Solution

The effect of temperature for covellite from Butte, Montana is shown in Figure 5.3. The results were obtained by using the same leach solution at different temperatures between 20 and 90ºC. These experiments only contain Ferric with a 0.1 M total concentration in solution. The mechanical agitator was setup at 600 RPM.

Experiment duration was based on the kinetics. Low temperature experiments took longer times than for high temperatures. Experiments between 20 and 50 ºC show a slow recovery rate, while experiments between 60 and 90 ºC show a fast recovery rate. This behavior was expected as it is well known that copper leaching is directly affected by temperature.

For these experiments, pH was not controlled in any way.

Initial redox potential was measured when all salts were in solution (without mineral) and the value obtained was used as a setup value to control the system. However, due to the fact that these systems only contained ferric iron initially, it’s not possible to maintain the initial redox potential value. The chemical reaction between Fe$^{+3}$ and covellite will produce Fe$^{+2}$ in solution and that will change the Redox Potential of the system. The system tried to inject the maximum possible amount of oxygen to keep the redox potential but as discussed this did not work. For that reason all experiments suffered a drop in the redox potential as shown in Figure 5.4.

For the case of pH, while it was not controlled at all, it was still recorded for analysis. All experiments showed a little decrease in the pH value (solution becoming more acidic) at the very
beginning. The value at 0 hours was taken before adding the solids (mineral sample) and with only salts in solution. With the current information is not possible to give a reason for this effect and it’s also possible that the pH variation is due to an experimental error in pH measurement due to the long duration. The effect on the pH is shown in Figure 5.5.

Most of experiments maintain a constant pH after that initial drop, however for the experiment at 80°C there is also another small drop before the end of the experiment. Schoonen et al [18] found that the rate of pyrite oxidation is strongly temperature dependent, which means that at a higher temperature the reaction producing sulfuric acid will be faster which will therefore generate a drop in the pH. However, for the experiment at 90°C the pH is relatively constant after the initial drop. The other possible explanation is that the probe had troubles obtaining the true values due to the high temperature. It is not uncommon for the ORP/pH probes to present problems when working at too high temperatures as in present case.

In conclusion, running the experiments with only Fe⁺³ in the system helped us to make decisions about the path to follow for the future experiments. For future experiments the total concentration of iron (as ferric and ferrous) was increased from 0.1M to 0.5M to make sure the system did not run out of iron by mass transfer limitation; the stirring rate was also increased from 600 to 900 RPM and the total iron concentration will be divided in different Ferric/Ferrous ratios.
Figure 5.3 Effect of temperature on leaching of Butte Montana sample of covellite at 0.1 mol/L ferric and 600 RPM

Figure 5.4 Redox Potential for leaching of covellite from Butte Montana at 0.1 mol/L ferric and 600 RPM
Figure 5.5 pH for leaching of covellite from Butte Montana at 0.1 mol/L ferric and 600 RPM

5.3.2 Mathematical Model for the Butte, Montana sample based on temperature effect

The present mathematical model include the following assumptions:

- The model considers temperature as the only variable for the system. The rest of conditions will continue unchanged.

- All experiments were carried at the same particle size and the oxygen was always in excess, therefore, the model will consider both as constants.

- The model consist of two parts: the first part go from beginning until 6 hours and uses a Shrinking Sphere Model (SS) and the second part which go from 6 hours to the end of the experiment uses a Passivation Shrinking Sphere Model (PSS)
The points represent the values obtained by experimenting while the lines are the values obtained by modeling.

The calculated activation energy ($E_a$) was 33 KJ/Mol.

Figure 5.7 shows the Arrhenius plot obtained for the Butte, Montana sample.
5.3.3 Effect of Ferric/Ferrous Ratio

The effect of ferric/ferrous ratio for covellite from Butte, Montana leaching is shown in Figure 5.8. The results were obtained by using the same leach solution at 40°C. These experiments were only different in Fe\(^{+3}/Fe^{+2}\) ratios with a total of 0.5 M Fe concentration in solution. The mechanical agitator was setup at 900 RPM.

For these experiments, pH was not controlled in any way.

In order to achieve the required Redox Potential, five different Fe\(^{+3}/Fe^{+2}\) ratios were prepared: 0.455/0.045, 0.417/0.083, 0.25/0.25, 0.167/0.333 and 0.045/0.455 corresponding to Fe\(^{+3}/Fe^{+2}\) ratios of 10, 5, 1, 0.5 and 0.1 respectively. The initial redox Potential (Ag/AgCl) of the solutions were 533, 505, 454, 445 and 386 mV at 40°C with only dissolved salts and sulfuric
acid in the system (before adding the mineral sample). The obtained values were used as setup values to control the system ORP. The system used oxygen as oxidant and it was injected into the leach slurry according to the requirements.

Figure 5.8 shows that the mineral reacted very fast at the beginning of the experiment (around 2 hours) but after that the reaction rate started to slow down considerable. This behavior is present in all the five experiments. The final recoveries are between 60 and 70% for a 40°C, which is consistent with the information obtained from the previous experiment. However, the previous experiment only contained Fe$^{+3}$ while in this case is Fe$^{+3}$/Fe$^{+2}$. It’s safe to say that at least for this case, the ORP or different ratios of Fe$^{+3}$/Fe$^{+2}$ had no special effect over the final copper recovery.

Figure 5.9 shows the ORP control for the duration of all experiments. The black dot lines represent the initial ORP values used as setup. From all the experiments, the best redox potential control is for the experiments with Fe$^{+3}$/Fe$^{+2}$ ratio of 1 and 0.5. The reason for this is that the oxidant used, oxygen, had not enough oxidizing power to maintain those high redox potential (for Fe$^{+3}$/Fe$^{+2}$ ratio of 10 and 5). For the lowest redox potential, Fe$^{+3}$/Fe$^{+2}$ ratio of 0.1, the system constantly keeps increasing the redox potential because the ferrous to ferric reaction is faster than the covellite reaction. As explained before, when there is too much ferric compare to the ferrous or vice versa, the redox potential will change because of one reaction being too fast and the other too slow.

The fact that oxygen was not a strong enough oxidant for the higher Fe$^{+3}$/Fe$^{+2}$ ratio experiments was an experimental problem. In order to solve this problem, the next series of experiments used potassium permanganate as an alternative oxidant. As was shown in chapter 3, potassium permanganate chemically oxidizes ferrous to ferric very rapidly in acid media and
maintains a higher ferric to ferrous ratio. The permanganate oxidation potential allows a higher ORP (redox potential) in the leach reactor which in turn means that the experiments operated with better redox potential control.

The pH was not controlled but was monitored. The pH values with time are shown in Figure 5.10. All experiments still indicated a slight decrease in the pH value at the very beginning of the experiment. At this time, is not clear the reason for such behavior. It should be noted that the pH electrode is prone to some drifting with time when used at high temperature under aggressive leaching conditions.

As a final observation it is worth mentioning that the speed increase in the agitator from 600 to 900 RPM appeared to provide better mixing of the reagents and a more stable leaching condition.

![Figure 5.8 Effect of Ferric/Ferrous ratio for covellite from Butte Montana at 0.5 mol/L Fe, 900 RPM and 40°C](image)
Figure 5.9 Redox Potential for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 40°C

Figure 5.10 pH for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 40°C
5.3.4 Effect of Ferric/Ferrous Ratio at 40ºC using Permanganate

The effect of ferric/ferrous ratio for covellite from Butte, Montana leaching is shown in Figure 5.11. The results were obtained by using the same leach solution composition as used previously at 40ºC but now using potassium permanganate as the oxidant. These experiments had variation of the initial $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios with a 0.5 M total iron concentration in solution. The mechanical agitator was setup at 900 RPM.

For these experiments, pH was controlled using reagent grade sulfuric acid of 1N composition.

In order to achieve the required redox potential, five different $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios were prepared: 0.455/0.045, 0.417/0.083, 0.25/0.25, 0.167/0.333 and 0.045/0.455 corresponding to Fe$^{3+}$/Fe$^{2+}$ ratios of 10, 5, 1, 0.5 and 0.1 respectively. The initial redox potential (versus Ag/AgCl) of the solutions were 539, 517, 465, 446 and 401 mV at 40ºC with only dissolved salts and sulfuric acid in the system (before adding the mineral sample). The obtained values were used as setup values to control the system ORP. Potassium permanganate was used as the oxidant and was injected into the slurry according to the requirements. An illustration of the system setup is in Figure 4.3 in Chapter 4.

Figure 5.11 shows that some reactions were faster in the first 2 hours of experiment, however as it was calculated in 3.5.1, the total amount of acid soluble copper is 22% which means that this difference in reaction speed is only due to the speed at which the mineral liberates the acid soluble copper. The difference in reaction rate is bigger after the first 20 hours of experiment where the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of 0.5 seems to be the fastest while the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of 10 looks as the slowest. The final recoveries are between 55% and 65% for 40ºC, which is not so
far from the range obtained in the previous two series of experiments. It is notable that the reactions after 72 hours tend to slow down becoming in some cases almost linear.

Figure 5.12 shows the ORP control for the duration of all experiments. The black dot lines represent the initial ORP values used as setup. For the four highest Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios (10, 5, 1 and 0.5) the redox potential is very well controlled and maintained proving that the use of potassium permanganate to replace oxygen was a good decision. However, for the experiment with a Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio of 0.1 it was still difficult to maintain a constant redox potential for the duration of the experiment. The Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio of 0.1 has a redox potential too low for the system to be able to maintain a steady value. It is possible that atmospheric oxygen ingress to the leach reactor may have been responsible for oxidation of ferrous and generation of a higher ferric/ferrous ratio.

For the case of pH, the usage of sulfuric acid addition to control pH had a positive effect. The small decrease of pH at the very beginning of the experiment is still happening as in previous cases. After that initial decrease the pH control is very good, keeping steady pH values during the full duration of the experiments. The pH with time plots are shown in Figure 5.13.

One of the reasons for using sulfuric acid to control these experiments was to avoid the production of jarosite. Jarosite is a potassium and iron precipitate formed from soluble iron in solution. The reaction to produce jarosite is as follow:

\[ 3Fe_2(SO_4)_3 + K_2SO_4 + 12H_2O \rightarrow 2KFe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \]  

Nazari et al. [19] reported that the precipitation of ferric ions increased at elevated pH values in the atmospheric leaching of copper. She also found that the precipitation will start around pH 1.3. The results obtained by Nazari are particularly important for this work because the experiments performed were similarly done with copper and iron sulfides in solution.
According to Figure 5.13, the maximum pH during the full duration of the experiments didn’t go over pH 1.2 successfully avoiding jarosite precipitation.

Figure 5.11 Effect of Ferric/Ferrous ratio for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 40°C
Figure 5.12 Redox Potential for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 40°C

Figure 5.13 pH for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 40°C
5.3.5 Effect of Ferric/Ferrous Ratio at 50°C using Permanganate

The results for leaching of covellite from Butte, Montana at 50 °C are shown in Figure 5.14. These experiments were conducted at the same conditions as the lower temperature experiments.

The initial redox potential (vs. Ag/AgCl) of the solutions were 548, 532, 480, 443 and 405 mV at 50°C with only dissolved salts and sulfuric acid in the system (before adding the mineral sample) for Fe\(^{3+}/Fe^{2+}\) ratios of 10, 5, 1, 0.5 and 0.1 respectively.

Figure 5.14 shows that some reactions happened faster in the first 2 hours of experiment due to the difference in speed at which the acid soluble copper is liberated. The liberation speed for the acid soluble copper is greater at 50°C if compared with 40°C which means that the temperature increase have a positive impact. The difference in reaction rate is bigger after the first 12 hours of experiment where the Fe\(^{3+}/Fe^{2+}\) ratio of 10 seems to be the fastest while the Fe\(^{3+}/Fe^{2+}\) ratio of 5 looks as the slowest. The final copper extractions are between 75% and 85% for 50°C, which is not so far from the information obtained in the first series of experiments. It is notable that the reactions after 36 hours tended to slow down, becoming in some cases almost linear.

Figure 5.15 shows the ORP control for the duration of all experiments. The black dot lines represent the initial ORP values used as setup. For the top 2 Fe\(^{3+}/Fe^{2+}\) ratios (10 and 5) the redox potential is very well controlled and maintained. For Fe\(^{3+}/Fe^{2+}\) ratios of 1 and 0.5 the redox potential control is good but still moved a little higher than the setup value. For Fe\(^{3+}/Fe^{2+}\) ratio of 0.1 the system is still not able to maintain a constant redox potential for the duration of the experiment. The Fe\(^{3+}/Fe^{2+}\) ratio of 0.1 has a redox potential too low for the system to be able to maintain it.
For the case of pH, the small decrease of pH at the very beginning of the experiment is still happening as in previous cases. After that initial decrease the pH control is very good, keeping steady pH’s during the full duration of the experiments. However, for the experiment at Fe$^{3+}$/Fe$^{2+}$ ratio of 0.1 the pH is maintain a little bit higher than 1.3 and according to Nazari et al [19] some jarosite may start precipitating but would be expected to be very little or none since this experiment was run at 50ºC with a low ferric ion concentration. At 50 ºC the iron solubility is high. The pH values with time are shown in Figure 5.16.

![Figure 5.14 Effect of Ferric/Ferrous ratio for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 50ºC](image-url)
Figure 5.15 Redox Potential for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 50°C

Figure 5.16 pH for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 50°C
5.3.6 Effect of Ferric/Ferrous Ratio at 60°C using Permanganate

The results for leaching of covellite at 60 °C from Butte, Montana are shown in Figure 5.17. These experiments were conducted at the same conditions as the lower temperature experiments.

The initial redox potential (Ag/AgCl) of the solutions were 559, 523, 475, 446 and 405 mV at 60°C with only dissolved salts and sulfuric acid in the system (before adding the mineral sample) for Fe³⁺/Fe²⁺ ratios of 10, 5, 1, 0.5 and 0.1 respectively.

The pattern of the experiments in Figure 5.17 was similar to that observed previously. The final copper extractions were between 85% and 90% for 60°C.

The pattern of the ORP control in Figure 5.18 was similar to that observed previously.

The pH behavior Figure 5.19 was similar to that observed at lower temperatures with an initial dip followed by a relatively steady value. According to Nazari [19] no jarosite is precipitated.
Figure 5.17 Effect of Ferric/Ferrous ratio for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 60°C

Figure 5.18 Redox Potential for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 60°C
5.3.7 **Effect of Ferric/Ferrous Ratio at 70°C using Permanganate**

The results for leaching of covellite from Butte, Montana at 70 °C are shown in Figure 5.20. These experiments were conducted at the same conditions as the lower temperature experiments.

The initial redox potential (Ag/AgCl) of the solutions were 560, 528, 475, 443 and 400 mV at 70°C with only dissolved salts and sulfuric acid in the system (before adding the mineral sample) for Fe$^{3+}$/Fe$^{2+}$ ratios of 10, 5, 1, 0.5 and 0.1 respectively.

The pattern of the experiments in Figure 5.20 was similar to that observed previously. The final copper extractions were between 85% and 95% for 70°C.

The pattern of the ORP control in Figure 5.21 was similar to that observed previously.
The pH behavior Figure 5.22 was similar to that observed at lower temperatures with an initial dip followed by a relatively steady value. According to Nazari [19] no jarosite is precipitated under these conditions.

![Figure 5.20 Effect of Ferric/Ferrous ratio for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 70°C](image)
Figure 5.21 Redox Potential for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 70°C

Figure 5.22 pH for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 70°C
5.3.8 Effect of Ferric/Ferrous Ratio at 80°C using Permanganate

The results for leaching of covellite from Butte, Montana at 80 °C are shown in Figure 5.23. These experiments were conducted at the same conditions as the lower temperature experiments.

The initial redox Potential (Ag/AgCl) of the solutions were 550, 525, 475, 445 and 405 mV at 80°C with only dissolved salts and sulfuric acid in the system (before adding the mineral sample) for Fe³⁺/Fe²⁺ ratios of 10, 5, 1, 0.5 and 0.1 respectively.

The pattern of the experiments in Figure 5.23 was similar to that observed previously. The final copper extractions were between 80% and 95% for 80°C.

The pattern of the ORP control in Figure 5.24 was similar to that observed previously.

The pH behavior Figure 5.25 was similar to that observed at lower temperatures with an initial dip followed by a relatively steady value. According to Nazari [19] no jarosite is precipitated.
Figure 5.23 Effect of Ferric/Ferrous ratio for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 80°C

Figure 5.24 Redox Potential for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 80°C
Figure 5.25 pH for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 80°C

5.3.9 Effect of Ferric/Ferrous Ratio at 90°C using Permanganate

The results for leaching of covellite from Butte, Montana at 90 °C are shown in Figure 5.26. These experiments were conducted at the same conditions as the lower temperature experiments.

The initial redox Potential (Ag/AgCl) of the solutions were 553, 528, 472, 445 and 405 mV at 90°C with only dissolved salts and sulfuric acid in the system (before adding the mineral sample) for Fe³⁺/Fe²⁺ ratios of 10, 5, 1, 0.5 and 0.1 respectively.

The pattern of the experiments in Figure 5.26 was similar to that observed previously. The final copper extractions were around 100% for 90°C.

The pattern of the ORP control in Figure 5.27 was similar to that observed previously.
The pH behavior Figure 5.28 was similar to that observed at lower temperatures with an initial dip followed by a relatively steady value. According to Nazari [19] no jarosite is precipitated.

![Figure 5.26 Effect of Ferric/Ferrous ratio for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 90°C](image)
Figure 5.27 Redox Potential for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 90°C

Figure 5.28 pH for covellite from Butte Montana leaching at 0.5 mol/L Fe, 900 RPM and 90°C
5.4 Results of the Chemical Leaching Experiments: Oyu Tolgoi Covellite

The results for leaching of covellite from Oyu Tolgoi at 40 °C are shown in Figure 5.29. These experiments were conducted at the same conditions as for the covellite from Butte, Montana.

The initial redox potential (versus Ag/AgCl) of the solutions were 534, 495, 472, 458 and 425 mV at 40°C with only dissolved salts and sulfuric acid in the system (before adding the mineral sample) for Fe$^{3+}$/Fe$^{2+}$ ratios of 10, 5, 1, 0.5 and 0.1 respectively.

The pattern of the experiments in Figure 5.29 was similar to that observed previously for the Butte, Montana sample. The final copper extractions were between 70% and 75% for 40°C. Figure 5.30 shows the ORP values for the duration of all experiments. For all the Fe$^{3+}$/Fe$^{2+}$ ratios the redox potential was very well controlled and maintained, even for Fe$^{3+}$/Fe$^{2+}$ ratio of 0.1. Experiments at ratio 0.1 were not able to maintain a constant redox potential when using covellite from Butte, Montana. However, in this case the control is very good. There is no apparent reason for this difference.

For the case of pH, the small decrease of pH at the very beginning of the experiment is still happening as in previous cases. After that initial decrease the pH control is very good, keeping steady pH’s in most cases during the full duration of the experiments. The big difference between all the experiments using covellite from Butte, Montana and this one in terms of pH control, is that for this specific case no sulfuric acid was added to the system; the system was able to control the pH by itself. The pH values with time are shown in Figure 5.31.
Figure 5.29 Effect of Ferric/Ferrous ratio for OT Sample leaching at 0.5 mol/L Fe, 900 RPM and 40°C

Figure 5.30 Redox Potential for OT Sample leaching at 0.5 mol/L Fe, 900 RPM and 40°C
Figure 5.31 pH for OT Sample leaching at 0.5 mol/L Fe, 900 RPM and 40°C
Chapter 6: Conclusions and Recommendations

The objectives defined for this research have been accomplished. The conclusions from this study and how they correspond to the research objectives will be discussed in this chapter. The conclusions will be continued by recommendations for future work.

6.1 Conclusions

- Covellite leaching is very slow when compared to other more common copper minerals such as chalcocite as was reported by Sullivan [6]. Even at high temperatures, it still takes rather long times to achieve full oxidation as it shown in Figure 5.3.
- Comparing results between using only ferric in solution with experiments conducted with both initial ferric and ferrous at the same temperature, it was found that the final copper extractions for the experiments were similar to each other. This was found in spite of the redox potential being initially higher for the experiments with only ferric added initially.
- Maintaining constant conditions during the experiments proved to be very important to be able to obtain consistent results. In multiple occasions the experiments were re-done because the initial results were not as expected, however, results were similar with repeats. The experiments were run from very low to very high values of ORP (around 400 mV to 550 mV) by using different Fe$^{3+}$/Fe$^{2+}$ ratios. These conditions (constant ORP) were not easy to maintain by using only pure oxygen addition as the oxidant and this was the main reason for using potassium permanganate as an alternative. Permanganate use proved to be very effective at maintaining constant ORP, especially for the higher values. In some cases the pH showed drifting over time but is mainly attributed to the long duration experiments under aggressive leaching conditions.
• The covellite leaching reaction happens in a single stage. From Chapter 5 some recovery over time graphics might give the impression of a two stages reactions but the reason to this behavior is found in the XRD analysis presented at the beginning of that same chapter. The sample from Butte, Montana contain acid soluble copper that will dissolve rapidly once the mineral is placed in acid. The sample should have been acid washed but the presence of those acid soluble copper minerals was initially unknown.

• The final extraction of copper from covellite proved to be very little affected or in some cases not affected at all by ORP (different Ferric/Ferrous ratios) at any temperature in a range of 20 to 90°C. This behavior proved that the covellite was not leaching electrochemically which makes this the most important result for this research because the copper sulfides usually leach electrochemically.

• Temperature is the most important variable when leaching covellite. At higher temperatures, higher recoveries were achieved. However working at temperatures over 70°C proved to be challenging because it makes the material harder to manipulate (specially sampling and filtration) and also generate losses from the system; i.e. water losses due to evaporation during the experiments and even during filtration. Water evaporation was probably the most challenging situation during the experiments and it is because even though the leaching tanks are sealed to avoid gas/vapor leaking, when taking samples it is not possible to avoid leaks. Some evaporation also occurred when filtering, since filtration was performed hot to avoid the mineral continuous reaction which would have led to larger errors.
• Comparing results for leaching covellite from Butte, Montana or leaching an ore sample from the Oyu Tolgoi Project, copper recoveries were pretty similar at the same temperature. There is no real difference in final recoveries. The most important difference is that for covellite from Butte, Montana there was an acid consumption to maintain pH constant, however for Oyu Tolgoi sample there was no acid consumption. The reason behind this behavior is still not clear.

6.2 Industrial Applications

• The present study provided the necessary tools to define an operation temperature according to specific process requirements.

6.3 Recommendations for Future Work

• In order to get more precise work, it would be best to work in sealed tanks with automatic sampling to avoid air getting into the system or vapor escaping out of the system.

• It is also required to run more experiments with the Oyu Tolgoi sample as it was only tested at 40ºC due to lack of time and sample. For heap leaching design it is beneficial to have information for temperatures around 20 to 40ºC but for some cases it may be possible to work at still higher temperature.

• If working with a covellite sample with acid soluble copper like the sample from Butte, Montana it would be the best to do a previous acid wash in order to obtain better results.
Bibliography


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