THE MECHANISM OF BORNITE LEACHING:
INSIGHTS FROM MINERALOGICAL AND
TEXTURAL CHARACTERISATION

by

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in the discipline of
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School of Engineering and Information Technology
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Supervisor: Dr. Fang Xia
Perth, Western Australia, December 2018
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Abstract

Copper is a versatile metal used in a range of applications including electronics, electrical and tele-communications industries. The long-term demand for copper has been promising, especially in the development of electric vehicles and renewable energies. To meet the increasing demand of copper, it is important to be able to effectively extract copper from its ores. But the majority of the current reserves for copper minerals are hovering to low grades. Heap leaching is a well-established extractive metallurgy for the processing of various low-grade ores. Additionally, in situ leaching has been suggested as a profitable alternative in recovering inaccessible, deep-seated copper ore bodies, but these processes highly depend on comprehensive understanding of the underlying fundamental leaching mechanism and how it interacts with the mineralogy of the ore body. Bornite (Cu₅FeS₄) is a major copper sulphide in a wide range of copper orebodies, so understanding the mechanism and kinetics of bornite under heap and in situ leaching conditions is therefore important.

Although, there have been various studies in the past that have helped define the phases and reaction sequences involving oxygen as oxidant and ferric ion leaching of bornite, there are still many uncertainties associated with the effect of various parameters on the leaching mechanism and kinetics.

The mechanisms of bornite leaching in this study were revealed by a thorough kinetic, mineralogical and textural study on its grains at 70 °C and 90 °C for particle sizes of -355 + 150 µm and -53 + 38 µm. Different oxidant types were investigated including O₂, Fe³⁺ and H₂O₂ in a sulphuric acid solution. The leached solutions and residues were analysed using atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), reflective light optical microscope and scanning electron microscope (SEM). Based on the quantitative and qualitative analysis of the results, it is found that ferric (III) sulphate as oxidant produced the fastest kinetics and led to the highest recovery out of all the three oxidants that has been investigated. Likewise, using hydrogen peroxide as oxidant produced a faster kinetics than using oxygen at shorter leaching times (<24 hours). Nevertheless, at longer leaching times (≥24 hours) oxygen produced a faster kinetics than using hydrogen peroxide. Furthermore, using temperature of 90 °C produced higher recovery and faster kinetics than 70 °C for all conditions. The extent of kinetics at 90 °C, however, is only 2.17% Cu extracted using oxygen as oxidants than at 70 °C. Furthermore, after 192 hours of leaching using ferric (III) sulphate and hydrogen peroxide there
are only differences of 0.85% and 2.03% Cu extracted, respectively, between two temperatures. From a mineral processing perspective, leaching at 70 °C may be economically desirable than leaching at 90 °C. It is therefore recommended from these results that leaching at 70 °C may be beneficial to save more money as leaching to higher temperatures requires a lot of energy. Moreover, smaller particle size range of -53 + 38 µm produced a higher recovery than -355 + 150 µm, the difference in the recoveries are not that huge. The difference in copper extraction using oxygen, ferric (III) sulphate, and hydrogen peroxide as oxidants between two particle size ranges at 70 °C are 5.93%, 14.84%, and 3.96% and at 90 °C are 6.73%, 15.04%, and 3.12%, respectively. It is therefore recommended for industries to use larger particles of -355 + 150 µm than -53 + 38 µm as it will be more economically beneficial. This is because grinding to finer sizes in the comminution circuit requires a lot of energy, as this can entail high costs in terms of energy consumption and media use. These costs can be minimised by selecting appropriate operating conditions.

Based on quantitative and qualitative analysis, a mechanism has been proposed for the reactions taking place during the leaching of bornite in this study. For oxygen as oxidant, transformation of the original orthorhombic crystal bornite structure to secondary bornite of a cubic crystal system belonging to F-43m space group with unit cell parameter of a=10.70 Å, then to covellite and chalcopyrite and finally to sulphur has been proposed. For ferric (III) sulphate as oxidant, the bornite evolution from primary to secondary, and then the formation of chalcopyrite lamellae, and finally the transformation into sulphur has been proposed. For hydrogen peroxide as oxidant, mineral transformation is the evolution of initial bornite to a secondary bornite, and then the formation of the covellite, and finally the slow formation of chalcopyrite exsolution lamellae has been proposed. Such mineral replacement processes have been very well recognised in Earth sciences, but they are less known to extractive metallurgists, which makes this study more significant as these same processes prevail in hydrometallurgical processing. The clear mechanism and the associated kinetic data in this study can be further applied to optimise the operation conditions in industrial leaching to improve process efficiency and Cu recovery from bornite.
Acknowledgements

I am indebted to the support and expertise of many enthusiastic people with a variety of geological and Engineering knowledge and further encouraging backup and generosity of friends and family. They have given me numerous encouragement throughout the completion of this thesis. Firstly, I would like to express my deepest gratitude to my supervisor Dr Fang Xia for introducing me to this project and for his endless support, patience, hard-work and invaluable advices throughout this thesis. Thank you for the friendly and supportive environment, that always kept me grounded. Without your amazing knowledge, I would never have obtained the success of this thesis.

I am also particularly grateful to Idowu Abiodun Adegoke for his endless support and guidance. I can’t thank you enough on how much you have helped me throughout my thesis and experiments. I would like to extend my gratitude to Fatemeh Nikkhou, Muhammet Kartal, Xizhi Yao and Manuel Knorsch for some insightful discussions and suggestions, or experimental advice. I would also like to acknowledge the amazing staff of Murdoch University, especially to Dr Juita Juita, Miss Jacqueline Briggs, and Mr Stewart Kelly for training and assisting me with analytical instruments.

A special thanks to my friends within and outside university. Thank you for understanding of my busy schedule through stressful times.

Finally, I wish to thank my family for the undying love and support throughout these years. Thank you for opening the world to me and for supporting me with every single endeavour I want to pursuit. My family is my greatest supporter, and this is all for them.
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Chapter 1

Introduction
Chapter 1 Introduction

1.1 Background

Leaching of copper involves a process of dissolving Cu\(^{2+}\) (or Cu\(^{+}\)) from copper-containing minerals into an aqueous H\(_2\)SO\(_4\) solution, known as a lixiviant, to produce a pregnant leach solution (PLS) (Schlesinger et al., 2011). In addition to copper, this PLS also contain other impurities, such as Fe, Co, Al, Mn, etc., that may be present in the ore and are leached with the copper. The solids remaining after leaching (residue) contains gangue or waste minerals, such as silica, alumina, and insoluble iron oxides/hydroxides/sulphates. The gangue is usually disposed of in tailing dumps or dams. The PLS is fed to the solvent-extraction then to the electrowinning circuit (Davenport et al., 2002). Leaching can also take place in nature where rocks are dissolve by water. Copper iron sulphides such as chalcopyrite and bornite are often replaced by secondary minerals such as azurite, chalcocite, chrysocolla, covellite, cuprite and malachite (Figure 1) (Schouten, 1934).

![Figure 1: Supergene enrichment in copper minerals (http://en.archaeometallurgie.de/gossan-iron-cap/).](http://en.archaeometallurgie.de/gossan-iron-cap/)
Bornite, $\text{Cu}_5\text{FeS}_4$, is associated with several copper sulphide minerals and may be found in equilibrium with several copper sulphide minerals (Pesic and Olson, 1983). Understanding the mechanism of leaching of specific minerals such as bornite is important to gain a better understanding of an overall ore body containing given minerals of importance.

Although leaching of copper minerals has been practiced and studied for many years, much remains unknown concerning the chemistry of dissolution of various sulphide minerals, particularly the Cu-Fe sulphides that are of great commercial importance (Pesic and Olson, 1984). Table 1 shows that there have only been few studies on the leaching of bornite compared to chalcopyrite, covellite and chalcocite. As a result, there are still many uncertainties associated on the effect of various parameters and a clear mechanism has not been established. No detailed studies and examinations of mineralogy and mineral texture, but insights of the evolution of mineralogy and texture can provide a better understanding on the leaching behaviour of bornite.

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<td>(Muszer et al., 2013)</td>
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The leaching study for this project was conducted in two specifics but closely related aspects, mineral dissolution and residue study. Based on these results, mechanisms for bornite leaching with oxygen, ferric (III) sulphate and hydrogen peroxide as oxidants are presented.
This project has been established by the Department of Chemical and Metallurgical Engineering and Chemistry from the School of Engineering and Information Technology of Murdoch University, Western Australia. The principal aim is to gain fundamental insights on the mineralogical and textural evolution of bornite leaching under hydrothermal conditions and to reveal the reaction mechanisms.

1.2 Literature Review

This section provides a comprehensive and substantive analysis of the research findings for the project, aiming to identify the knowledge gaps and the relationship of the literature to the experimental program.

1.2.1 Introduction

Copper is one of the first metals used by humans for items such as ornaments and coins at least 10,000 years ago in Western Asia (Group, 2007). Copper has played a significant role in the development of human civilisation since the prehistoric Chalcolithic Period and Bronze Age (Group, 2007). The discoveries and inventions in the late 18th and early 19th centuries of famous scientists like Ampere, Faraday and Ohm regarding magnetism and electricity that helped the onset of industrial revolution has propelled the copper industry into a new era (Purcell and Morin, 2013). Even in the present time, the supply and demand of copper is continuously increasing (Figure 2). It is a versatile metal used in a range of applications including electronics, electrical and tele-communications industries (Davenport et al., 2002).

![Copper supply/demand](image)

**Figure 2**: Supply and demand for copper (million tonnes) (Soirat, 2018).

Long term demand for copper has always been promising, especially for the development of electric vehicles and renewables (Figure 3). The risk of disruption to the global copper supply
is considered low as copper deposits and production is globally dispersed (Figure 4). However, the impact of any copper supply disruption is high. The imbalance between its extraction and discoveries of copper deposits and the increasing demand for this metal require the exploitation of refractory and low-grade ores that has been previously regarded as uneconomical (Northey et al., 2014). To meet the ever-increasing demand for copper, it is therefore important to be able to effectively extract it from the Earth’s crust.

**Table 2**: Selected countries copper mine production (tonnes) in the year 2016 and 2017 with their reserves (tonnes) (Ali et al., 2017).

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<tr>
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<tbody>
<tr>
<td>Australia</td>
<td>948</td>
<td>920</td>
<td>88,000</td>
</tr>
<tr>
<td>Canada</td>
<td>708</td>
<td>620</td>
<td>11,000</td>
</tr>
<tr>
<td>Chile</td>
<td>5,550</td>
<td>5,330</td>
<td>170,000</td>
</tr>
<tr>
<td>China</td>
<td>1,900</td>
<td>1,860</td>
<td>27,000</td>
</tr>
<tr>
<td>Congo (Kinshasa)</td>
<td>846</td>
<td>850</td>
<td>20,000</td>
</tr>
<tr>
<td>Indonesia</td>
<td>727</td>
<td>650</td>
<td>26,000</td>
</tr>
<tr>
<td>Mexico</td>
<td>752</td>
<td>755</td>
<td>46,000</td>
</tr>
<tr>
<td>Peru</td>
<td>2,350</td>
<td>2,390</td>
<td>81,000</td>
</tr>
<tr>
<td>United States</td>
<td>1,430</td>
<td>1,270</td>
<td>45,000</td>
</tr>
<tr>
<td>Zambia</td>
<td>763</td>
<td>755</td>
<td>20,000</td>
</tr>
<tr>
<td>Other countries</td>
<td>4160</td>
<td>4,300</td>
<td>260,000</td>
</tr>
<tr>
<td>World total (rounded)</td>
<td>20,100</td>
<td>19,700</td>
<td>790,000</td>
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*Estimated.

Copper is commonly present in the Earth’s crust as copper-iron-sulphide and copper sulphide minerals that include chalcopyrite, bornite, covellite, chalcocite and digenite. These minerals have abundant reserves (Table 2) but the majority of the current reserves are hovering around 0.5% Cu (open-pit mines) to 1-2% Cu (underground mines) and are continually getting lower with time (Ayres et al., 2002; Norgate and Jahanshahi, 2010). Such resources will no longer economically suitable for the traditional flotation and pyrometallurgical processing. Pyrometallurgical processing in particular involves high energy requirement and are associated with hydrogen-sulphide and sulphur-dioxide production (Feng et al., 2015). As a result, hydrometallurgical solutions are being investigated as it provides two fundamental processes – protecting the energy requirement and the environment. Recently, marked by the worldwide economic recession, it is necessary to consider this problem of complex utilisation of minerals
with minimal financial requirement (Schlesinger et al., 2011). The present of conventional rich deposits of ore of non-ferrous metals have nearly been exhausted (Havlik, 2008). Thus, the processing of complex natures of lean ores is associated with another complication. Therefore, the mineral industries and literature strive in finding the development of more economical methods of processing lean and complex ores for which pyrometallurgical methods of processing are no longer effective.

Figure 3: Positive for long-term copper demand. (a) Global light duty electric vehicles (EV) annual sales forecast (2018-2030). (b) Battery electric vehicles (BEV) copper intensity (kg/unit) by car segment in China (2016). (c) The incremental copper demand from Hybrids and EVs (Henry, 2017).

Heap leaching in particular is a well-established extractive metallurgical beneficiation process that enable economical processing of various low-grade ores, which are difficult to exploit (Schlesinger et al., 2011). Additionally, in situ recovery (ISR), or in situ leaching, has been suggested as a profitable alternative in recovering copper from inaccessible, deep ore bodies (Northey et al., 2014). Despite much progress, these processes remain limited by long extraction times and low recoveries. It is becoming clear that processing using heap leaching, which is both economically viable and environmentally sound, it highly depends on having comprehensive understanding of the underlying fundamental mechanisms of the process and how it interacts with the particular mineralogy of the ore body. It is thus important to understand the mechanism and kinetics of bornite leaching under heap and in situ leaching conditions.
1.2.2 Bornite Crystal Chemistry

Bornite is an orthorhombic, pseudocubic crystal system that is a copper-red to pinchbeck-brown on fresh surfaces but appears tarnishes iridescent purplish in polished section and pinkish brown when fresh. Its streak is pale greyish with a metallic lustre. It has a brittle tenacity and around 3-3.25 hardness (Anthony et al., 2011). Additionally, it has a weak but noticeable pleochroism and weak anisotropism. It has a chemical formula of \( \text{Cu}_5\text{FeS}_4 \) with an elemental breakdown of 63.31% copper, 25.56% sulphur and 11.13% iron (Anthony et al., 2011), as Figure 5 illustrates. Bornite unit cell is also based on a cubic close-packed framework of S atoms, with 75% tetrahedral sites filled with Cu/Fe, and 25% tetrahedral sites left empty as vacancy (Anthony et al., 2011). Bornite is a significant copper ore mineral occurring widely in porphyry copper deposits along with chalcopyrite. Bornite and chalcopyrite are both typically replaced by covellite and chalcocite in the supergene enrichment zone of copper deposits. Bornite is also found disseminated in mafic igneous rocks, in contact metamorphic skarn deposits, in pegmatites, in medium to high temperature deposits in hydrothermal and in sedimentary cupriferous shales; stable below approximately 200 °C (Anthony et al., 2011). It is important as an ore for bornite’s copper content of about 63 percent by mass. It’s nickname peacock copper or peacock ore is due to its striking iridescence. Furthermore, bornite belongs to space group Pbca with unit cell parameters of \( a=10.950, b=21.862, c=10.950 \) and \( Z=19 \) (Anthony et al., 2011).

Bornite is a semi-conductor and its sphalerite type of skeleton is thought to be made of Cu (I) and Fe (III) atoms. Its Gibbs free energy has been determined as \((-715.99 + 0.00339T + \)
9.2550T^{0.5}) \text{ kJ/mol in the temperature between 298-1200 K (Robie et al., 1994).}

Bornite’s distribution for fine crystals include: Australia, Austria, England, Kazakhstan, South Africa, USA and Zimbabwe (Anthony et al., 2011). Traces of bornite have also been reported in the Pilbara region of Western Australia (Anthony et al., 2011).

Figure 5: Bornite rhombohedral structure

1.2.3 Hydrometallurgical Extraction of Copper

Processes that convert copper sulphide ores into high purity electro-refined copper such as from concentration, pyrometallurgy, and electrorefining account for about 80% of primary copper production (Schlesinger et al., 2011). While the remaining 20% of primary copper production comes from hydrometallurgical processing of mainly copper oxide and chalcocite ores (Schlesinger et al., 2011). Modern hydrometallurgical flowsheets all comprise of three essential steps in recovering copper: leaching, followed by solvent extraction and electrowinning. The integration of these three hydrometallurgical processes is illustrated in Figure 6.

Figure 6: Simplified hydrometallurgical flowsheet, showing the acid balance between leaching, solvent extraction (SX) and stripping and the cathodic and anodic reactions during electrowinning (EW) (Sole, 2008). The leaching reaction is shown for bornite. RH is the organic extractant SX.
Enormous research efforts continue to seek better understanding on the mechanism and kinetics of leaching and how the reaction of product and by-products behave.

To break the mineral lattice and release Cu\(^{2+}\) from copper sulphide minerals into solution it requires the use of an acid and an oxidising agent (Figure 7a).

The presence of Fe\(^{3+}\) and O\(_2\) as oxidising agents are required for leaching of all copper sulphides to occur. Fe\(^{3+}\) will oxidised the copper sulphide and the resulting Fe\(^{2+}\) is reoxidised to Fe\(^{3+}\) by O\(_2\) (Schlesinger et al., 2011). The Fe(II)/Fe(III) redox couple acts in a catalytic manner in these bornite reactions (Figure 7b):

\[
\begin{align*}
\text{Bornite:} & \\
(i) & \quad 2\text{Cu}_5\text{Fe}_4\text{S}_4 + 4\text{Fe}_2(\text{SO}_4)_3 \rightarrow 10\text{Cu}^{2+} + 2\text{SO}_4^{2-} + 10\text{FeSO}_4 + 8\text{S} \\
(ii) & \quad 4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \\
(iii) & \quad 2\text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 \\
\text{(Overall)} & \quad 4\text{Cu}_5\text{Fe}_4\text{S}_4 + 33\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow 20\text{Cu}^{2+} + 12\text{SO}_4^{2-} + 2\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4
\end{align*}
\]

\[\text{Figure 7:} \text{ (a) Cu-S-O-H}_2\text{O system showing its pourbaix diagram at 25 °C (House, 1987). Native copper and sulphides requires an oxidising agent and acid to be leached while minerals such as CuO can be leached by lowering the pH. (b) Cu-Fe-S-O-H}_2\text{O system pourbaix diagram at 25 °C (Peters, 1976). The requirement of both an oxidising agent and acidic environment is essential to leach copper as Cu}^{2+} \text{ from most minerals.}\]

1.2.3.1 Leaching Methods of Copper Minerals

The main methods employed for leaching of copper minerals are heap leaching, dump leaching, vat leaching, agitation leaching and pressure oxidation leaching. Table 3 shows a
comparison of the different leaching methods in recovering copper. As shown in Figure 8, the choice of leaching method is dependent on the mineralogy of the copper-bearing ore, copper grade of the ore, and the particle size.

![Figure 8: Copper grade of the ore with different leaching method (Scheffel, 2002).](image)

The geographical location of the ore body including its topography, climatic conditions and prevailing economic conditions may also influence this decision (Scheffel, 2002). Bornite leaching is mainly common using the heap and dump leaching and a less common technology using \textit{in situ} leaching.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textbf{Parameter} & \textbf{Dump} & \textbf{Heap} & \textbf{Vat} & \textbf{Agitation} & \textbf{Agitation} & \textbf{Pressure} \\
\hline
Material treated & ROM, oxide, or secondary sulphide & Oxides, secondary sulphides, tailings, usually milled, acid cured, bacteria-assisted, and agglomerated & Oxides, secondary sulphides leach of tailings, acid cured and agglomerated & Tailings and Oxides & Sulphides & Primary and secondary sulphides, refractory flotation concentrates \\
\hline
Cu grade (%) & 0.1-0.4 & 0.3-2.3 & >0.8 & 0.8-5.0 & >6 & Up to 25 \\
\hline
Particle size (mm) & Up to 1000 & 12-50 & 0.5-2 & 0.1-0.2 & 0.1-0.2 & 0.01-0.75 \\
\hline
Leach time & Years & Months to years & Weeks & Days & Days & Hours \\
\hline
Cu in PLS (g/L) & 0.5-3 & 1.5-8 & 6-40 & 2-30 & 12-25 & 25-80 \\
\hline
Cu recovery (%) & 35-75 & Up to 90% & >90 & 85-100 & 95-98 & >96 \\
\hline
\end{tabular}
\caption{Different leaching methods for hydrometallurgical recovery of copper (Schlesinger et al., 2011).}
\end{table}
1.2.3.2 Heap and Dump Leaching of Copper

Heap leaching and dump leaching involve trickling the $\text{H}_2\text{SO}_4$ lixiviant through large heaps under normal atmospheric conditions (Figure 9). The oxide ores shown in Table 4 and chalcocite are readily leached. While chalcopyrite is not leached to any significant extent under the mild conditions of heap leaching. Covellite, native copper and bornite are leached under biological oxidising conditions.

Table 4: Copper minerals normally found in leach heaps (Schlesinger et al., 2011).

<table>
<thead>
<tr>
<th>Type</th>
<th>Common minerals</th>
<th>Mineral formula</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Secondary minerals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonates</td>
<td>Azurite</td>
<td>$2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$</td>
</tr>
<tr>
<td></td>
<td>Malachite</td>
<td>$\text{CuCO}_3 \cdot \text{CO(OH)}_2$</td>
</tr>
<tr>
<td>Hydroxy-chlorides</td>
<td>Atacamite</td>
<td>$\text{Cu}_2\text{Cl(OH)}_3$</td>
</tr>
<tr>
<td>Hydroxy-silicates</td>
<td>Chrysocolla</td>
<td>$\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Native-copper</td>
<td>Metal</td>
<td>$\text{Cu}^0$</td>
</tr>
<tr>
<td>Oxides</td>
<td>Cuprite</td>
<td>$\text{Cu}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Tenorite</td>
<td>$\text{CuO}$</td>
</tr>
<tr>
<td>Sulphates</td>
<td>Antlerite</td>
<td>$\text{CuSO}_4 \cdot 2\text{Cu(OH)}_2$</td>
</tr>
<tr>
<td></td>
<td>Brochantite</td>
<td>$\text{CuSO}_4 \cdot 3\text{Cu(OH)}_2$</td>
</tr>
<tr>
<td>Supergene sulphides</td>
<td>Chalcocite</td>
<td>$\text{Cu}_2\text{S}$</td>
</tr>
<tr>
<td></td>
<td>Covellite</td>
<td>$\text{CuS}$</td>
</tr>
<tr>
<td></td>
<td>Bornite</td>
<td>$\text{Cu}_6\text{FeS}_4$</td>
</tr>
<tr>
<td><strong>Primary sulphide minerals</strong></td>
<td>Chalcopyrite</td>
<td>$\text{CuFeS}_2$</td>
</tr>
<tr>
<td></td>
<td>Enargite</td>
<td>$\text{Cu}_2\text{AsS}_4$</td>
</tr>
<tr>
<td></td>
<td>Pyrite (source of $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, and $\text{H}_2\text{SO}_4$)</td>
<td>$\text{FeS}_2$</td>
</tr>
</tbody>
</table>

Additionally, heap leaching is also used to recover additional copper from tailings of heap, agitation or vat leaching. The main differences between these methods are the copper grade and particle size of the ore.
Figure 9: Schematic of heap leach process (Smith, 2014).

Chemistry of Heap Leaching and Dump Leaching of Copper

Non-sulphide copper minerals are leached directly by H$_2$SO$_4$ according to equation (10). While leaching of sulphide minerals, requires an oxidising agent as well as H$_2$SO$_4$. The oxidising agent is usually dissolved O$_2$ from air according to equation (11).

\[
\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O} \quad (10)
\]

\[
\text{CuS} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CuS} + \text{CuSO}_4 + \text{H}_2\text{O} \quad (11)
\]

Micro-organisms assists in the heap leaching of sulphides. Naturally occurring bacteria in the ore act as a catalyst for the leaching reaction. These bacteria increase the reaction rate for the time frame of leaching becomes economic for these minerals.

Oxidation by Fe$^{3+}$

According to Schlesinger et al. (2011), the Fe$^{3+}$ is necessary for rapid leaching. Mineral containing iron in the ore such as pyrite are oxidised by Fe$^{3+}$ ions in the presence of sulphur-oxidising bacteria, which releases Fe$^{2+}$ ions. However, the Fe$^{2+}$ ions are rapidly re-oxidised to Fe$^{3+}$ by oxygen and catalysed by ferrous-oxidising bacteria close to the surface of the mineral like pyrite to maintain a high potential. Pyrite provides an important source of acid and copper sulphides (and native copper) are leached by Fe$^{3+}$, which is also assisted by direct bacterial action.

\[
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{SO}_4 \quad (12)
\]

\[
\text{O}_2 + 4\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 2\text{H}_2\text{SO}_4 \rightarrow 4\text{Fe}^{3+} + 6\text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad (13)
\]
\[
\begin{align*}
\text{Cu}_2\text{S} + 10\text{Fe}^{3+} + 15\text{SO}_4^{2-} + 4\text{H}_2\text{O} & \rightarrow 2\text{Cu}^{2+} + 10\text{Fe}^{2+} + 12\text{SO}_4^{2-} + 4\text{H}_2\text{SO}_4 \\
\text{(14)}
\end{align*}
\]

The Fe\(^{3+}\) ions produced by reaction in equation (13) are then reoxidised by the reaction in equation (12) and the process become cyclic. Some direct oxidation may also occur. There is about 1-5 g/L Fe in a PLS from heap leaching (Schlesinger et al., 2011).

**Rates of Leaching of Copper Minerals**

Oxide minerals and chalcocite leach quickly under heap leach conditions. However, covellite and bornite leach much more slowly. This is highly dependent on the heap’s mineralogy and leaching times. While chalcopyrite hardly reacts at all in heap leaching (Miller, 2008).

Heap and dump leaching are never chemical reaction-rate controlled but are diffusion controlled (Schlesinger et al., 2011). The changes in the diffusion rate caused by the geo-technical characteristics of ore, such as the presence of micas, clays and other acicular-shaped particles will result in the long leach times (Miller, 2008).

1.2.3.3 **In situ Copper Leaching**

*In situ* leaching mining is a process in recovering mineral values by circulating solvents, such as dilute sulphuric acid for copper oxide recovery from undisturbed ore in its natural state (Huff et al., 1987). In contrast, conventional mining requires ore breakage and transport to a processing facility.

*In situ* copper mining operation combines subsurface and surface facilities in the following way (Huff et al., 1987):

1. In the surface facility, chemicals are used to dissolve the copper in solution.
2. Solvent is pumped down using a set of injection wells and forced into pores and fractures in the rock by using a pressure that exceeds the hydrostatic pressure in the deposit.
3. As solvent travels through flow channels into pores and fractures in the rock, it dissolves the copper minerals and transport the copper to adjacent production wells.
4. The enriched copper solutions are collected to adjacent production wells and pumped to the surface.
5. Copper is recovered from the copper-enriched solutions in a SX electrowinning plant; the acid is regenerated in the plant for recirculation. The solvent used will get
recirculated through the ore zone before the copper in a given well pattern will be depleted.

These leaching methods, at the fundamental level can be considered to proceed via dissolution and precipitation process, and mineral phase transformations that involves the replacement of one mineral or mineral assemblage by another (Putnis, 2009). Such mineral replacement processes have been very well recognised in Earth sciences, but they are less known to extractive metallurgists, although these same processes prevail in hydrometallurgical processing. Hence, there have only been few previous works studied on mineralogical phase transformations under metallurgical leaching processing conditions (Putnis, 2009). Previous studies have focused mainly on mineral replacement in other sulphide minerals including pyrite, chalcopyrite, pentlandite, pyrrhotite, violarite and marcasite. Mineral replacement reactions produce porous secondary minerals and the pores and their connectivity are important for enhancing mass transfer during leaching (Putnis, 2009). It is therefore important to study the evolutions of mineralogy and porosity during leaching. By understanding the mechanism of mineral replacement of a mineral by another this can provide applications in natural processes and hydrometallurgy, and this has inspired this interdisciplinary research.

1.2.4 Mineral Replacement Mechanism

Re-equilibration will tend to take place whenever a mineral or mineral assemblage meets a fluid that is out of equilibrium to reduce the free energy of the whole system. These fluid-solid interactions span a range of possible reactions and are responsible for the mineral assemblages that are present in the Earth’s crust. They are commonly controlled by re-precipitation mechanism and interface-coupled dissolution. When a fluid meets an under-saturated mineral, the mineral will begin to dissolve, which usually lead to the formation of an interfacial layer, which can then become supersaturated with respect to a more stable product phase. This can nucleate and grow at the surface of the parent phase as Figure 10-a illustrates. If the precipitation of the product and dissolution of the parent phase are coupled in both space and time, this can lead to the pseudomorphic replacement of the parent phase, the product phase (Figure 10-b, c). Product phases are often observed to evolve both texturally and compositionally until an essentially homogeneous product form (Figure 10-d) (Altree-Williams et al., 2015). Ruiz-Agudo et al. (2014) highlighted several key identifying features of such pseudomorphic replacements or interface coupled dissolution reprecipitation reaction, which Figure 10 demonstrates, including:
Chapter 1 Introduction

i. Close coupling between precipitation and dissolution processes that enables preservation of external morphology;

ii. Sharp interface between the product and parent that exhibits no diffusional profile;

iii. Product phase generates a permeable porosity; and

iv. When an epitaxial relationship exists, there will be a transfer of crystallographic information from parent to product.

Figure 10: Pseudomorphic replacement by interface-coupled dissolution-precipitation reaction. (a) Dissolution of a few monolayers of this parent may result when a solid meets a fluid that is out of equilibrium. (b)-(d) The parent-product continued dissolution and precipitation and results in the generation of interconnected porosity in the product phase allowing the migration of the reaction interface from the surface through the parent phase that pseudomorphically replaced by the product (Ruiz-Agudo et al., 2014).

Replacement reactions are complex reactions controlled by three reaction steps: dissolution, mass transfer and precipitation. The kinetics of replacement reactions is dependent on each of these steps, which may vary as the reaction progresses. The overall reaction rate is dependent on the slowest of these reaction steps. The empirical activation energy is the temperature dependence of the reaction rate. A study by Xia et al. (2009) has shown that when the rate-controlling step is dissolution during mineral replacement reactions, there may be a perfect preservation of the mineral microstructure that is inherited from the parent phase. Dissolution rates depend on the specific area of the mineral that dissolves and the chemistry of the solution. The solutes must be transported to and away from the reaction front. The replacement reactions usually lead to the generation of secondary porosity. This facilitates the total re-equilibration of a crystal without the requirement for volume diffusion. Coupled-dissolution and reprecipitation reactions involve both spatial temporal and spatial coupling between dissolution and precipitation.

Understanding reaction mechanisms is a fundamental step to understand processes in nature and in industry. For example, Janssen and Putnis (2011) demonstrated in their study that
understanding of the reaction mechanism is a fundamental step in optimising the beneficiation process and the purity of the final titanium pigment. Additionally, understanding the mechanism and kinetics of the replacement of a mineral by another mineral is also significant in natural processes and hydrometallurgy. This was demonstrated by Zhao et al. (2010) that the pre-treatment of calaverite to native gold by hydrothermal mineral replacement reactions has been considered as a promising method before cyanide leaching for gold extraction from gold telluride rich-ores. The aqueous fluids in the Earth’s crust are significant for the mineral formation in nature and by understanding of the dissolution, transport and precipitation of minerals through hydrothermal experiments could provide insights into the genesis of hydrothermal deposits. Insights of mineral replacement in the Cu-Fe-S system and porosity in secondary minerals during mineral replacement will give a better understanding on the mechanism of mineral replacement.

1.2.4.1 Mineral Replacement Reactions in the Cu-Fe-S System

From the earliest times, metallic sulphide minerals have been known and valued as sources of metals. The nineteenth century classical mineralogical studies provided systematic data on crystal forms, chemical compositions, mineral associations and elementary properties, such as streak, colour, hardness, specific gravity of these minerals. Most three-component sulphides belong to the Cu-Fe-S system, the relative compositions of some of these minerals are provided in Figure 11 in the Cu-Fe-S ternary diagram. Minerals that belong to this system are often associated with silver, native gold and other economic minerals. Table 5 shows the most common copper minerals.

![Figure 11: Minerals reported within the Cu-Fe-S system (Vaughan and Craig, 1978).](image-url)
There have been many experimental studies on the Cu-Fe-S system to understand the transformations within individual compositions, phase relations, and their common occurrence in different deposits. As reported from Kullerud and Yund (1960), most of the research on Cu-Fe-S system comes from experimental work utilising the classic dry sealed tube and there’s only a few conducted under hydrothermal conditions. As shown in Figure 12, the phase relations of the Cu-Fe-S system in the central portion depicts the relative atomic percent ratio of copper, iron, and sulphur at temperatures of 25 °C, 400 °C and 600 °C. While at higher temperatures, the phase relation in the Cu-Fe-S system are well established and can be easily understood. Temperatures above 400 °C shows that the phase equilibrium in the Cu-Fe-S system consist of three solid solutions: (i) chalcocite-digenite-bornite solid solution, (ii) intermediate or chalcopyrite solid solution (Figure 12 a, b) and (iii) the pyrrhotite solid solution (Cabri, 1973). At 25 °C, as the extent of the solid solution field decreases, the stability of the mineral phases in the Cu-Fe-S system increases (Figure 12 c). In earlier works, the chalcocite-digenite-bornite solid solution was classified as bornite solid solution (Yund and Kullerud, 1966) and as chalcocite solid solution (Merwin and Lombard, 1937). At high temperatures, the intermediate solid solution was classified as chalcopyrite solid solution and as chalcopyrite and cubanite solid solutions below the solvus surface. Brett (1964) studied a wide range of temperatures on the mutual relationship between the so-called solid solutions of chalcopyrite and bornite.

Table 5: Most common copper minerals in order of their copper percentage with its colour, density and hardness (http://webmineral.com/data/).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical Formula</th>
<th>Colour</th>
<th>Cu wt.%</th>
<th>Density (g/cm³)</th>
<th>Mohs Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuprite</td>
<td>Cu₂O</td>
<td>Brown red, Purple red, Red, Black</td>
<td>88.82</td>
<td>6.1</td>
<td>3.5-4</td>
</tr>
<tr>
<td>Tenorite</td>
<td>CuO</td>
<td>Black, steel gray</td>
<td>79.89</td>
<td>6.5</td>
<td>3.5-4</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Cu₃S</td>
<td>Blue black, Gray, Black, Black gray, Steel gray</td>
<td>78.85</td>
<td>5.5-5.8</td>
<td>2.5-3</td>
</tr>
<tr>
<td>Digenite</td>
<td>Cu₉S₅</td>
<td>Blue, Dark blue, Black</td>
<td>78.10</td>
<td>5.6</td>
<td>2.5-3</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>Indigo blue, Light blue, Dark blue, Black</td>
<td>66.46</td>
<td>4.68</td>
<td>1.5-2</td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu₅FeS₄</td>
<td>Copper red, Bronze brown, Purple</td>
<td>63.31</td>
<td>4.9-5.3</td>
<td>3</td>
</tr>
<tr>
<td>Malachite</td>
<td>Cu₂(CO₃)(OH)₂</td>
<td>Green, Dark green, Blackish green</td>
<td>57.48</td>
<td>3.6-4</td>
<td>3.5-4</td>
</tr>
<tr>
<td>Azurite</td>
<td>Cu₃(CO₃)₂(OH)₂</td>
<td>Azure blue, blue, Light blue, Dark blue</td>
<td>55.31</td>
<td>3.77-3.89</td>
<td>3.5-4</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>Brass yellow, Honey yellow</td>
<td>34.63</td>
<td>4.1-4.3</td>
<td>3.5</td>
</tr>
<tr>
<td>Chrysocolla</td>
<td>(Cu,Al)₂H₂Si₂O₅(OH)₄-n(H₂O)</td>
<td>Green, Bluish green, Blackish blue, Brown</td>
<td>33.86</td>
<td>1.9-2.4</td>
<td>2.5-3.5</td>
</tr>
</tbody>
</table>
Amcoff (1988) studied the replacement of chalcopyrite by bornite under 200 °C and 500 °C at different times in sealed glass tubes. Amcoff (1988) aim to gain an insight in the mineral replacement mechanism. From Amcoff’s study, a test was conducted on chalcopyrite with covellite and chalcocite leading to the formation of bornite during the oxidising and reducing conditions, respectively. Amcoff (1988) reported the textural and chemical changes during the solid-state replacement of chalcopyrite by bornite.

![Diagram](image.png)

**Figure 12:** Cu-Fe-S system showing its phase relations in the central portion (a) 600 °C (Cabri, 1973) (b) 400 °C (Craig and Scott, 1974) (c) 25 °C (Vaughan and Craig, 1978).

Minerals in the Cu-Fe-S system occur in deposits that occur under hydrothermal conditions. Therefore, results from classic dry run does not provide an accurate representation of the control during the formation of minerals under hydrothermal conditions. Sugaki et al. (1975) used the thermal gradient transport method to study the phase relations of chalcopyrite, pyrrhotite, bornite and individual phases in intermediate solutions at 300 °C and 350 °C under hydrothermal conditions. A further work of Kojima and Sugaki (1985) studied the phase
relations under hydrothermal conditions between 300 °C to 500 °C in the Cu-Fe-Zn-S quaternary system. The study involved both the thermal gradient transport method and isothermal in situ recrystallisation methods using a gold tube with 5 mL ammonium chloride solution (NH₄Cl, pH = 4.6 at 25 °C and in some cases NH₄Cl acidified by HCl at pH = 0.43 at 25 °C) for the recrystallisation of chalcopyrite, bornite and other sulphides under hydrothermal conditions (Kojima and Sugaki, 1985).

A recent study by Zhao et al. (2014) was conducted under hydrothermal conditions using Cu(I) and hydrosulphide within 200-320 °C at autogenous pressures to show the replacement of chalcopyrite by bornite. The study used powder XRD for the extent of transformations, electron probe microanalysis for determining the chemical compositions of the products and field emission scanning electron microscope for the morphological and textural features of the reacted grain. It was observed that chalcopyrite was replaced by bornite in the experiments. Figure 13 shows the reaction started at the surface of the grain of chalcopyrite and along the cracks to the core of the crystal (Zhao et al., 2014).

Figure 13: Backscattered electron images during replacement of chalcopyrite by bornite (Zhao et al., 2014).

1.2.4.2 Mineral Replacement of Bornite during Leaching

Despite the importance of understanding the mineral replacement of bornite during leaching in the extractive metallurgy of Cu, only a few studies were devoted to understanding its mechanism and/or kinetics (Dutrizac et al., 1970 and 1985; Muszer et al., 2013; Pesic and Olson, 1983 and 1984). Most of these studies have dated back in the 1980s and although these studies have reached a general agreement regarding the kinetics of bornite leaching, there are
still limitations on the detailed reaction mechanisms and kinetics. Due to this lack of study, there have been various literature gaps regarding the mineral replacement of bornite during leaching. It is important to fill these gaps in the literature to give insights into our understanding of the leaching behaviour of bornite.

Various work has studied the oxidative leaching of bornite using different media (Dutrizac et al., 1985; Pesic and Olson, 1984). While Pesic and Olson (1983) shows that leaching of bornite under acidified ferric chloride solution proceeds in two stages. The first stage of bornite leaching was conducted at 40 °C and terminates after 28% copper extraction, which Figure 14 demonstrates. While temperatures above 40 °C, bornite leaching proceeds beyond 28% copper dissolution. As can be seen from Figure 14 and Figure 15 temperatures below 60 °C follow a linear behaviour in the second stage while temperatures above 60 °C shows faster initial rate that diminish with time.

![Figure 14: First stage of leaching of bornite showing the effect of temperature (Pesic and Olson, 1983).](image-url)
From these studies, it was observed that the stage I of leaching rate is directly dependent on temperature but reciprocal on particle size. The leaching rate shows a first order dependence on Fe$^{3+}$ concentration with no dependence on Fe$^{2+}$ and Cu$^{2+}$. The stage I reaction was suggested as:

$$\text{Cu}_5\text{FeS}_4 + 4\text{Fe}^{3+} \rightarrow \text{Cu}_3\text{FeS}_4 + 2\text{Cu}^{2+} + 4\text{Fe}^{2+}$$

(15)

This reaction is suggested that it is diffusion controlled of ferric ions across the boundary layer solution followed by chemical reaction on the bornite surface. The study suggested that the oxidation of Cu$^+$ ions by Fe$^{3+}$ is the mechanism characterising this reaction. According to (Pesic and Olson, 1983), the leaching product is Cu$_3$FeS$_4$ as Figure 16 illustrates.

Stage II has an activation energy of 76.8 kJ/mol, which is significantly higher than stage I. This is the reason why stage II does not proceed at lower temperatures. After 40% copper extraction, it was observed that the activation energy reduced to about 30 kJ/mol. While beyond 40% copper dissolution, the diffusion of species through the sulphur layer during the intermediate stage is believed to have control the rate of reaction.
Figure 16: The X-ray diffraction patterns of leaching products at low temperature. The products converge towards the dotted lines which are the characteristics of CuFeS$_2$ and presumably Cu$_3$FeS$_4$ (Pesic and Olson, 1983).

Another study was carried out by Pesic and Olson (1984) using sulphuric acid with oxygen as oxidant on bornite leaching. Variables such as particle size, temperature and concentration of ferrous, ferric and cupric ions were all investigated. Characterisation of products was conducted using X-ray, microscopic and electron probe micro-analyser. As observed from the study, difference in leaching behaviour are prevalent compared to using hydrochloric acid leaching of bornite. The study observed that iron dissolution produces a bornite species on the surface with iron vacancies precedes Cu$_3$FeS$_4$ formation in the interior and covellite on the surface. The rate of iron depletion controlled the rate of copper dissolution as the iron molecules deplete covellite and idaite were formed. As Figure 17 indicates, the X-ray diffraction of Cu$_3$FeS$_4$ have similar pattern to chalcopyrite or chalcocite. Figure 18 illustrates the schematic
representation during sulphuric leaching of bornite in the presence of oxygen of the mechanism of formation of covellite and $\text{Cu}_3\text{FeS}_4$ on the surface of bornite. In this study by Pesic and Olson (1984), the effect of $\text{Fe}^{3+}$ as oxidant was observed that the reaction rate was at least two orders of magnitude faster compared to using oxygen as oxidant. Therefore, ferrous ion markedly enhanced bornite leaching and $\text{Cu}_3\text{FeS}_4$ was the only residue.

![XRD analysis](image)

**Figure 17**: XRD showing the: (a) initial bornite, (b) 3.5% Cu dissolution (residue), (c) residue from autocatalytic region, (d) residue of the final leaching and (e) residue from initial addition of ferrous sulphate (Pesic and Olson, 1984).

A similar work was conducted by Dutrizac et al. (1985) on the mineralogical changes of bornite leaching using ferric ions and its relevance in the supergene alteration of bornite ores. The experiment from this study used either ferric chloride or ferric sulphate solutions. As observed from the results, the extent of dissolution increases with increasing temperature in
both systems but more vigorous in ferric chloride system. It was reported that the reaction involved a rapid outward diffusion of copper forming a non-stoichiometric covellite, chalcopyrite and bornite. However, the reaction at lower temperatures terminates at the Cu$_3$FeS$_4$ phase but at higher temperatures further dissolution to elemental sulphur was observed and Fe$^{2+}$ and Cu$^{2+}$ were detected. Furthermore, massive bornite was also leached in this study and it was observed that a distinct covellite zone in the Cu$_3$FeS$_4$ phase was prevalent but was not observed in the finely particulate bornite. Figure 19 shows the result from SEM back-scattered electron micrograph showing the covellite zone that chalcopyrite exsolution lamellae rimmed by a copper sulphide. The leaching result of massive bornite appears to be consistent with the mineralogical trends produced by the supergene alteration of bornite ores however Cu$_3$FeS$_4$ is not closely similar to the mineral idaite (Dutrizac et al., 1985).

\[
(Cu_3FeS_4)^{2-} \cdot 2Cu = x(Cu_3Fe_0S_4)^{2-} \cdot 2Cu^+ + (1-x)(Cu_3FeS_4)^{2-} \cdot 2Cu^+ + xFe^{3+} + 3xe
\]

Figure 18: Schematic diagram of the reaction mechanism of covellite and idaite on the surface of bornite leaching using sulphuric acid and oxygen as oxidant (Pesic and Olson, 1984).
Although the various studies above have helped define the phases and the reaction sequences involving oxygen as oxidant and ferric ion leaching of bornite, there are still many uncertainties associated on the effect of various parameters (oxidant type, temperature, particle size, pH) on leaching mechanism and kinetics. The early studies on bornite leaching on these parameters has been very limited, a clear mechanism has not been established. There have been no examination of mineralogy and mineral texture in great detail, but the evolution of mineralogy and texture can provide significant insights into our understanding of the leaching behaviour of bornite. Therefore, a detailed study of textural and mineralogical characterisation of bornite is required to resolve discrepancies in the early studies and to reveal a clearer picture of the mechanism and kinetics of bornite leaching. After all, these parameters are important for heap and in situ leaching.

Figure 19: SEM back-scattered electron micrograph of covellite (medium grey) by synthetic bornite disk that contains abundant exsolved digenite rimmed chalcopyrite (Dutrizac et al., 1985).

A more recent leaching study of Muszer et al. (2013) is about the conversion of copper iron sulphide, chalcopyrite and bornite to chalcocite and covellite. A pressure leaching of copper sulphide in oxygenated sulphuric acid was conducted and it was observed that copper sulphides undergo phase conversion to covellite (Figure 20). Furthermore, permeable open work textures were prevalent in the covellite product during the conversion of copper sulphide (Figure 21).
Chapter 1 Introduction

Figure 20: Grain of primary bornite during conversion stage to chalcocite and to covellite (Muszer et al., 2013).

Figure 21: Final product of phase alteration during pressure leaching. Blue line is an indication of openwork permeable covellite aggregation (Muszer et al., 2013).

From Muszer et al. (2013) microscopic observation of the mineralogical alterations during leaching and its correlation with the leaching kinetics states that the phase transformation of copper sulphides goes through only one mechanism during pressure leaching. Figure 22
Chapter 1 Introduction

presents this in a form of a model of phase conversion containing different copper sulphides for a grain. From this study, it was suggested that control of both the phase conversion and formation work permeable textures leads to an effective optimisation of parameters of pressure leaching of the polymineral sulphide feed.

![Figure 22: Phase conversion model containing different copper sulphides for a grain during pressure leaching. (a, b) The grain consists of chalcopyrite, bornite and chalcocite. (c, d) Specific textures allows the transport of reactants to the leached mineral’s surface. (e, f) The intensive transportation of ions inside the permeable covellite texture, converted both primary and secondary chalcocite grains into openwork and permeable covellite (Muszer et al., 2013).](image)

1.2.5 Summary

Conventional processing of copper involves high temperature smelting and converting but with declining grade of copper and the increasing complexity of mineralogy of ores; leaching
processes is the trend. Heap and *in situ* leaching processes in particular lessens environmental impact and hence are promising technology. Copper iron sulphides are often replaced by secondary minerals. From these changes in mineral assemblages in ores after deposition are a response to the changing physico-chemical conditions typically controllable in hydrometallurgical leaching circuits. Most previous studies focused on chalcopyrite but few studied bornite which is the second most abundant copper sulphides. Furthermore, there are still many uncertainties associated on the effect of various parameters (oxidant type, temperature, particle size, pH) on leaching mechanism and kinetics. There has been a limited examination of mineralogical and textural characterisation, but the evolution of mineralogy and texture can provide significant insights into our understanding of leaching behaviour of bornite. Thus, the careful study of the kinetic results on this work will give the possibility to predict qualitatively the effect of process parameters, including temperature, particle size, and the type of oxidant used on the reaction rates. The information from the mechanism and kinetics study with insights from mineralogical and textural characterisation could serve as a guide in hydrometallurgical processing of bornite and even copper iron sulphide ores. It can be concluded that understanding the behaviour (the mechanism and kinetics) of bornite during heap leaching and *in situ* leaching is significant but have rarely been explored.

1.3 Research Objectives

Based on the limitations of previous work, the principal objective of this project is to get some fundamental insights of the leaching of bornite based on detailed mineralogy and textural characterisation of leached residues from various states of leaching and under various controlled conditions.

The detailed objectives of this project are:

- To understand the mineralogical and textural transformation, at the micrometre scale, of bornite during leaching. Reaction pathways will be proposed for each studied condition.
- To explore the effect of different oxidants including O₂, Fe³⁺, and H₂O₂ on bornite leaching.
- To study the effect of particle size (150-355 µm vs. 38-53 µm) during bornite leaching.
- To discuss the effect of using temperatures of 90 °C and 70 °C on bornite leaching so the research can be complete within a few months rather than years under realistic *in situ* leaching conditions.
1.4 Thesis Organisation

To achieve these objectives, the appropriate experimental methods were employed, which are described in Chapter 2. The results and discussion sections are described in Chapter 3. It presents the study on the effect of different oxidants, particle size, and the specified temperatures. It also incorporates the mineralogical and textural characterisation analysis of the ore and the proposed leaching mechanism. In Chapter 4, the overall conclusions of the investigations and findings of the research will be summarised and some possible suggestions on future research directions will be listed.

The experimental test data are also included (Appendix A) and the other relevant calculations from these data are also added (Appendix B).
Chapter 2

Experimental Methodology
Chapter 2 Experimental Methodology

This chapter includes an introduction to the starting natural mineral, the different apparatus employed, and the analytical methods used in this study. Analytical techniques used in this thesis include solution atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), reflective light optical microscopy, and scanning electron microscopy (SEM). These methods/techniques and the involved instruments are described below.

2.1 Natural Bornite Sample

The natural bornite samples used throughout this thesis is from Moonta mines, South Australia. Crystals were crushed into small fragments using mortar and pestle, ground, and sieved into a -355 + 150 µm fraction and -53 + 38 µm fraction.

2.2 Solution Preparation

Deionised water (DI) was added about halfway to corresponding final volume of the solution in a 500 mL volumetric flask. This was slowly poured into the flask using a funnel. 2.805 mL of 95% sulphuric acid was measured using a 5 mL micropipette and was added into the flask. For best results, the solution was stirred throughout using a magnetic stirrer. The micropipette and the funnel were rinsed with DI water. The stirrer was removed and rinsed with DI water. Then the solution was diluted to the desired 500 mL volume.

2.3 Apparatus and Procedure

Leaching was carried out in a 250 mL Schott bottles as glass reactors (Figure 23) contained 0.08 g of bornite sample and 50 mL of lixiviant (H₂SO₄) solution and leached in the oven. The baseline experimental conditions are described in Table 6. Series of experiments were conducted in which different parameters were investigated (oxidant type, particle size and temperature) and were varied while other baseline conditions remained constant. Different oxidant types were used including O₂, Fe³⁺ ions and H₂O₂. Particle sizes of -355 + 150 µm and -53 + 38 µm and temperatures of 70 °C and 90 °C were studied.
Figure 23: Schott bottles used as glass reactors during the experiment. (a) Schematic diagram representing the glass reactor containing bornite grains in a sulphuric acid solution with oxygen/nitrogen-rich atmosphere. (b) Picture of the different solutions with different oxidants (H\textsubscript{2}O\textsubscript{2}, Fe\textsuperscript{3+}, and O\textsubscript{2}) in glass reactors.

Table 6: Baseline experimental conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite mass</td>
<td>0.08 g</td>
</tr>
<tr>
<td>Solution Volume</td>
<td>50 mL</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4} volume in a 50 mL solution</td>
<td>2.81 mL</td>
</tr>
<tr>
<td>Particle size</td>
<td>150-355 µm or 38-53 µm</td>
</tr>
<tr>
<td>FeCl\textsubscript{3} mass</td>
<td>1.015 g</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2} volume</td>
<td>516 µL</td>
</tr>
<tr>
<td>Temperature</td>
<td>70 °C or 90 °C</td>
</tr>
</tbody>
</table>

Glass reactors are labelled accordingly. The solution was loaded into the glass reactor and the pH was measured. Bornite grains were loaded into the reactors in a glove box filled with either ultra-high purity nitrogen or high purity oxygen and was vacuumed and sealed properly. The glass reactors were then taken out and put in the preheated oven at the desired temperature. According to Figure 24 and due to the fast kinetics of the reactions, preheating is required for short time experiments (< 1 hour) as it takes at least 90 minutes for the solution to reach the desired leaching temperature. After preheating, the reactors were taken out one at a time using heat-proof gloves. Bornite grains and the oxidant were then added into the glass reactor under ultra-high-purity nitrogen atmosphere. These reactors were then immediately put back in the preheated oven at the desired temperature. The time of the reactor outside the oven for sample loading was only a few minutes so the temperature drop was minimal.
Figure 25 and Figure 26 shows the experimental set up for long experiments ($\geq$ 1 hour) under a glovebox and for short experiments ($< 1$ hour) under a funnel-shaped hood, respectively, to ensure the head space is filled entirely with either nitrogen or oxygen. Note that ideally all leaching experiments need preheating the solution, but the fast kinetics was observed only after complete analysis of leaching solution and solid residue of many experiments and due to the time limitation of the project, repeating these long-term experiments is impractical. However, the effect of preheating to the long-term experiments is minimal especially for leaching longer than 4 hours. After leaching, the reactors were taken out accordingly and quenched in a running cold water bath. The cooled final solution was filtered in a conical flask using a funnel and a filter paper. The volume and the pH of the solution were measured using a 100 mL cylinder and a well calibrated temperature-corrected pH-meter with a Ag/AgCl pH probe, respectively.

![Image of heating rate graph](image)

**Figure 24:** Heating rate of a 50 mL solution in a 250 mL glass reactor in the preheated oven at 70°C and 90°C. This was used to determine the minimum time for preheating solution.

Solid residues remaining in the glass reactors were further filtered and rinsed with deionised water. The residue was left to dry and weighed. Following this, the solutions were diluted 200-fold before the concentrations of copper and iron were determined using Agilent 55 AA atomic absorption spectrometer. While solid samples were analysed by XRD and few grains were mounted into resin blocks. A schematic diagram shown in Figure 27 and Figure 28 outlines the overall experimental procedures.
Figure 25: The nitrogen/oxygen-filled glove box used for introducing nitrogen/oxygen-rich atmosphere for long hour (≥ 1 hour) experiments.

Figure 26: Schematic diagram of the experimental set-up used for introducing nitrogen-rich atmosphere for short time (< 1 hour) experiments.
Chapter 2 Experimental Methodology

**Figure 27:** Schematic of the thesis project for long hours (≥ 1 hour) experiments.
Chapter 2 Experimental Methodology

Figure 28: Schematic of the thesis project for short hours (< 1 hour) experiments.
2.4 Sample Preparation for Microscopy

A few coarse-grained solid residues were mounted on a FixiForm stub with an EpoFix resin and hardener. Resin blocks are embedded and impregnated using a vacuum to remove the trapped air from the mounting material and eliminate any gaps between the grains and resin. The blocks are cut about one cm thick using Struers Discoplan-TS. Polished blocks are then ground using Struers LaboForce-100 with a 1200 grit SiC paper at a speed of 300 rpm and a force of 35 N per specimen for 2 minutes. This was further polished using MD-Dac DiaPro 3 \( \mu \)m at 150 rpm speed and 30 N force per specimen for 5 minutes. Furthermore, a MD-Nap DiaPro 1 \( \mu \)m was used to further polished the resin blocks at 150 rpm speed and 25 N force per specimen for 1 minute. Figure 29 shows the equipment used for cutting and polishing resin blocks. Optical images were captured from polished blocks using a reflective optical light microscope. Polished blocks were further characterised using scanning electron microscope.

![Figure 29: Equipment used for refinement of polished blocks for SEM analysis. (Left) Struers Discoplan-TS for cutting resin blocks. (Right) Struers LaboForce-100 for grinding and polishing the resin blocks.](image)

2.5 Analytical Measurements

All instruments listed below are used for the sample analysis and are carried out at the School of Engineering and Information Technology, Murdoch University.

2.5.1 Flame Atomic Absorption Spectroscopy (AAS)

AAS was used to determine the total metal ion (Cu or Fe) concentration. The instrument employed was Agilent 55B AA Spectrometer at Murdoch University (Figure 30). Calibration of Cu using standard solutions were 0.5, 2.5, 5, 7.5 and 10 ppm while for Fe were 1, 2.5, 5, 10 and 15 ppm (Figure 31). The leach liquor samples were diluted 25 times for Fe and 200 times for Cu to get the concentrations within the linear calibration range.
Chapter 2 Experimental Methodology

Figure 30: The 55 AA Atomic Absorption Spectrometer for solution analysis.

Figure 31: Standard calibration curves for Fe and Cu used in AAS.

The hollow cathode lamp (HCL) for either Fe or Cu was inserted. The AAS machine was switched on and the default parameters of the element being tested was loaded. The default was ensured in integration mode. The measurement parameters were set to pre-read delay of 3 seconds, read time to 3 seconds and replicates to 3. The HCL was optimised by turning the two
lamp adjustment knobs until there is a maximum signal on the bar graph. “Signal” was selected and the acetylene gas at the wall mounted regulator was turned on. The flame was lit up and when the flame has stabilised, blank DI water was aspirated for instrument zero. A standard was then aspirated to give an absorbance of at least 0.2. The “Calibrate” page was selected, and the standard concentrations were entered. The re-slope standard was set to the median of the standard concentrations of 5 ppm for either Cu or Fe. The standard solutions were then aspirated and “Read” was pressed. The samples were then aspirated next and “Read” was then pressed to obtain results. AAS data were obtained for Cu from solutions using oxygen, ferric (III) sulphate and hydrogen peroxide as oxidants and Fe using oxygen, and hydrogen peroxide as oxidants. The iron extraction using ferric (III) sulphate was not recorded as most ferric ions in solution are from the oxidant.

2.5.2 X-ray Diffraction (XRD)

XRD patterns of the samples were collected using an Enhanced Mini-Materials Analyser (eMMA) at Murdoch University, Western Australia (Figure 32). The X-ray is generated by a cathode ray tube, filtered to produce monochromatic radiation at 35 kV and 28 mA. In a typical experiment about 5 mg of sample was finely ground and homogenised in an agate mortar. The fine powder was mixed with ethanol and homogeneously spread onto a silicon-based sample holder. After drying, the silicon-based sample holder was mounted into the sample loader. The XRD machine was then checked that the power switches on the wall was connected to the Water Cooler and the XRD was turned on. The ‘Control Power On’ was switched on the Spellman DF3 generator panel. The water cooler was then switched on and the temperature should be 18-20 degrees with 60 Pa pressures. Appropriate slits of D1, R0.2, and S1 were inserted in the XRD machine. The generator was then switched on by pressing the ‘X Ray On’ and the voltage was started up to 20 kV while the current was at 10 mA. The power settings were left at their initial values for 10 minutes, then it was slowly raised the voltage to the operating value of 35 kV and 28 mA currents. This should give a tube power of about 1 kW.

The software in the computer used for XRD analysis are reset with the following measurement settings:

- 2θ: 20-65°
- Step size: 0.02°
- Speed: 0.5°/min
Based on the settings, each sample was approximately exposed to 120 minutes of X-ray. At the end of each tests, each sample produced different XRD patterns. The phase characterisations for these peaks were performed using the program called Match!

**Figure 32:** Picture of the Enhanced Mini-Materials Analyser (εMMA) at Murdoch University. This X-ray diffractometer consist of three basic elements: an X-ray tube, a sample holder and an X-ray detector. The X-rays are generated by a cathode ray tube, and then filtered producing monochromatic radiation, collimated to concentrate, and directed toward the sample.

### 2.5.3 Reflective Light Optical Microscopy

Microscopic identification, analyses and characterisation of residue mounted in polished blocks was firstly analysed using Nikon Eclipse E200 optical light microscopy in Murdoch University (Figure 33). Images from 10X, 20X, 50X and 100X magnification were directly captured in a software called TCapture.
Figure 33: Nikon Eclipse E200 optical microscope at Murdoch University.

2.5.4 Scanning Electron Microscopy (SEM)

Selected samples were carbon film coated by SPI Supplies Sputter Coater with Carbon Coater Module™ at Murdoch University (Figure 34). The vacuum in glass chamber was firstly released by turning the Vacuum Release Valve anticlockwise. The Carbon Coater Head was carefully removed from the glass chamber and a 3.5 cm carbon fibre string was installed into the Carbon Coater Head. Glass chamber was removed carefully. The sample and a clean SEM sample mount of similar height was then placed onto the sample holder. The sample holder height was either lowered or increased so that the height from the bottom of the chamber to the top of the sample was 4 cm. The glass chamber was returned and ensured that it fits neatly with the O-ring. The Carbon Coater head was placed on top of the glass chamber and the two leads were placed back into the sockets at the top of the Carbon Coater Head. The chamber was then sealed by turning the Vacuum Release Valve clockwise. The argon valve was opened and set to approximately 5 psi. The Gas Leak Valve was rotated clockwise to ensure that it is closed at the Control Module. The Control Module was turned on and allow the vacuum pump to pump down the chamber. When the vacuum has maximised the Gas Leak Valve was released, and the chamber was purged for 15 sec. The valve was then closed, and the vacuuming was repeated two more times. At the Carbon Coater Module, the voltage was ensured at “0” and the rocker switch was switched off. The Carbon Coater Module was switched on and “CONT” was
selected on the rocker switch. The voltage was gradually increased until small current is observed up to 2.1 volts. After 10 seconds the voltage was returned to zero. The “PULSE” was selected on the rocker switch and the voltage control was turned to 9 volts. The “PULSE” button was pressed until the SEM sample mount becomes “brassy” in colour. Once finished, voltage control was turned to “0” and the rocker switched was switch to “OFF”. Carbon Coater Module and the Control Module was then switched off. The argon gas was shut and the lead sockets from the top were taken out. The Vacuum was then released, and the sample was taken out.

![Image of SPI Supplies Sputter Coater with Carbon Coater Module™ at Murdoch University.]

The carbon coated sample was then loaded into a SEM sample holder to be examined. Scanning electron microscopic analyses were carried out on JEOL JCM-6000 at Murdoch University (Figure 35). The microscope was equipped with backscattered electron imaging (BEI) and secondary electron imaging (SEI). The BEI and SEI were used to obtain backscattered and secondary micrographs, respectively. All carbon coated resin blocks were examined under BSE while SE was used on unpolished particles. Both types follow the same procedures where the aperture knob was firstly ensured that it is in the “12 o’clock” position. The SEM was pressed “ON/OFF” and was vented to stop the vacuum pump and fill the SEM chamber with air. The carbon coated prepared sample in a SEM sample holder was placed securely into the SEM sample stage. The stage was centred, and the door was slowly slide closed. Once the SEM chamber has fully evacuated the software was allowed to run to full
auto-adjustment. Depending on sample charging and magnification, the accelerating voltage for the SEI was maintained at 5, 10 or 15 kV while for BEI was at 15 kV.

Figure 35: JEOL JCM-6000 scanning electron microscope at Murdoch University.
Chapter 3

Results and Discussion
Chapter 3 Results and Discussion

Altogether, 89 leaching experiments were carried out to study the effect of temperature, oxidant type, particle size and time. All solution samples were analysed by AAS, and all solid samples were analysed by XRD, reflective light optical microscope, and selected samples were also examined by SEM. Results from experiments are discussed in this section. Individual leaching behaviour is compared against existing information and possible mechanisms are explored. Individual leaching results for mineral textures and solutions are evaluated with reference to results.

3.1 Starting Bornite

3.1.1 Chemical Composition of Bornite

A portion of the initial sample was digested using aqua regia and the solution with Cu and Fe composition was analysed using AAS. Assuming the dissolved solid is 100% bornite; the sulphur composition was determined through mass balance and revealed that the initial sample consisted of 63.3% Cu, 11.1% Fe and 25.6% S with a chemical composition of \( \text{Cu}_{4.95}\text{Fe}_{1.07}\text{S}_{3.98} \) (Table 7). This composition was used for the calculation of copper extraction in the leaching experiments.

Table 7: Chemical composition data of the digested sample using aqua regia of the starting bornite.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (ppm)</th>
<th>Elemental Weight (g)</th>
<th>Elemental Weight (%)</th>
<th>wt% of Ideal Bornite ( \text{Cu}_4\text{Fe}_1\text{S}_4 )</th>
<th>Number of Element in Bornite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1182.00</td>
<td>0.59</td>
<td>62.72%</td>
<td>63.31%</td>
<td>4.95</td>
</tr>
<tr>
<td>Fe</td>
<td>223.60</td>
<td>0.11</td>
<td>11.86%</td>
<td>11.13%</td>
<td>1.07</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>0.24</td>
<td>25.42%</td>
<td>25.56%</td>
<td>3.98</td>
</tr>
</tbody>
</table>

Notes: a. 1 g of sample was added into aqua regia. After dissolution, 0.0577 g of undissolved solid residue (silicate impurities) remained; b. the weight of sulphur was calculated based on mass balance: 1-0.0577-0.11-0.59 = 0.24 g.

3.1.2 XRD of Starting Bornite

Figure 36 displays the synchrotron X-ray diffraction showing the patterns at different intensity of the starting bornite sample at 5 to 40 degrees. This data was analysed using Match! and demonstrates an orthorhombic crystal lattice of bornite. Furthermore, this bornite sample has a space group belonging to Pbca with unit cell parameters of \( a=10.950 \) Å, \( b=21.862 \) Å, and \( c=10.950 \) Å.
3.2 Leaching at 90 °C

Leaching of bornite in a sulphuric acid solution with oxygen, ferric (III) sulphate and hydrogen peroxide as oxidant were investigated using the parameters: temperature, particle size and time. The pH of the solution before leaching were around 0.97-1.22. It was found that after leaching at 90 °C, the pH does not change much and pH values were around 0.87-1.27. Results of bornite leaching at 90 °C are presented below identifying the different phase formation, mineralogical and textural characterisation, and leaching kinetics.

3.2.1 Leaching Kinetics

The effect of varying the oxidants is investigated to better understand the kinetics of bornite leaching. Figure 37 shows the weight loss percent of the sample as a function of leaching time at 90 °C. Figure 38 and Figure 39 summarised the leaching results on the amount of Cu and Fe extracted, respectively, at different leaching time intervals of using oxygen, iron (III) sulphate and hydrogen peroxide as oxidants at 90 °C. The weight loss and the Cu extraction follows a similar pattern, but the inconsistency in values between the percent weight loss and the percent Cu extracted is may be due to the sample undissolved solid residue (silicate minerals) remained (not 100% bornite) as found during acid digestion. It may also due to the large error when trying to measure few milligrams of sample.
The results indicate that the rate of dissolution and level of copper and iron extracted increased with increasing time. The overall trend for copper and iron extraction for all oxidants shows that there is a rapid dissolution of bornite mineral within the first 1-2 hours of leaching and copper and iron extraction started to asymptote as further leaching occurred.

At 24 hours of leaching, using ferric ions as oxidant, extracted 93.0% copper while using oxygen and hydrogen peroxide as oxidant only achieved 20.3% and 35.8% copper extraction, respectively. After 192 hours of leaching, using ferric ions as oxidants extracted 100% leaching while using oxygen extracted 97.2% copper within 768 hours of leaching. Additionally, a 39.6% copper extraction was achieved after 192 hours of leaching using hydrogen peroxide. These results show that using ferric (III) sulphate as an oxidant produced the fastest kinetics of leaching of bornite at 90 °C. While using hydrogen peroxide achieved a faster kinetics than using oxygen within shorter leaching up to 24 hours but as leaching time increases after 24 hours, the kinetics using oxygen as oxidant becomes faster than using hydrogen peroxide at 90 °C.

Figure 39 shows a similar pattern as the extraction of copper and found that using iron (III) sulphate gives the fastest kinetics on Fe extraction within shorter leaching time and slowed down as leaching time increases. Using oxygen as oxidant seems to have a faster kinetics than using hydrogen peroxide and both asymptote as leaching time increases at 90 °C. Longer leaching times for all three oxidants seems to slow down and asymptote. This may be due to the formation of a passivation layer for temperatures above certain temperature resulting in the slowdown of the reaction. This is evident due to the colour difference representing the phase difference from the obtained photomicrographs.

Figure 37: Sample weight loss at different leaching time using different oxidants at 90 °C.
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Figure 38: Effect of different oxidants at 90 °C on copper extraction from bornite at different time.

Figure 39: Effect of different oxidants at 90 °C on iron extraction from bornite at different time.

The experiments using oxygen and ferric ions as oxidants achieved close to 100% extraction at 90 °C. Although a maximum dissolution was not achieved after 192 hours using hydrogen peroxide at 90 °C, the results suggest that the sample will continue to react slowly beyond 192 hours. It can be observed from the results that the absence of ferric ions; the leaching rate was significantly lower. From the literature, experiment conducted using oxygen as oxidant, the leaching of bornite is known to experience an induction that can last over two hours before the rate increases considerably (Pesic and Olson, 1983). The results agree with the literature that at over six hours leaching of bornite using oxygen as oxidant increases the rate significantly.
The rate of leaching experiments at 90 °C revealed several facts that may be important in industrial heap leaching. The data shows that the kinetics are parabolic; where the rate of copper dissolution decreases steadily with time. This agrees well with the findings from the literature. This advantageous practice could be achieved by using large heaps as it retains the heat of reaction.

### 3.2.2 Mineralogical Transformation During Bornite Leaching

The progress of bornite leaching was followed by phase identification of crushed grains samples using room temperature powder XRD. Figure 40, Figure 41 and Figure 42 presents the X-ray diffraction patterns of the feed material and of leaching residues using oxygen, ferric (III) sulphate and hydrogen peroxide as oxidants at 90 °C, respectively. The pattern for the feed material shows characteristics peaks mainly of bornite prevalent at 2θ = 47. The peaks at 2θ = 38 and 44 is due to the aluminium disc used during the XRD and not part of the mineralogical transformation during bornite leaching.

Figure 40 illustrates the XRD data using oxygen as oxidant and shows that as time progresses to 6, 12 and 24 hours, another type of bornite with a different crystal structure is evident at 2θ = 47.5. Using the software Match!, this peak was identified to have a cubic crystal system belonging to F-43m space group with unit cell parameter of a=10.70 Å (Ding et al., 2005). This is in agreement with the observation of Pesic and Olson (1984) who has identified this secondary bornite as a non-stoichiometric bornite. Covellite also starts to peak on 2θ = 32 and chalcopyrite of a higher intensity at 2θ = 29 and 33 starting at 6 hours. Furthermore, the intensity of covellite and chalcopyrite peaks increased as leaching time increases up to 768 hours. The increasing intensity means that the proportion of these minerals are also increasing.

Figure 41 illustrates the XRD data using ferric (III) sulphate as oxidant. It can be seen at only 5 minutes; secondary bornite has started forming. Rapid mineralogical transformation from primary bornite to secondary bornite has occurred within relatively short period of time (5 minutes to 1 hour). After 2 hours of leaching, chalcopyrite peaks are evident at 2θ = 38 and 48. Then just within 4 hours of leaching sulphur peak is evident at 2θ = 23. This peak intensity started to increase as further leaching time increases. While chalcopyrite intensity at 2θ = 29 and 48 started to decrease from 16 hours to 192 hours of leaching.

Figure 42 illustrates the XRD data using hydrogen peroxide as oxidant. As can be seen in the overall trend, mineral transformation from the starting bornite to 192 hours there is a slow reaction compared to using oxygen or ferric (III) sulphate. Secondary bornite is evident after 5 minutes to 1 hour of leaching. After two hours of leaching this phase have transformed into
chalcopyrite at 2θ = 39 and 48. From the XRD data, bornite is no longer oxidise further by H₂O₂ and there is no sulphur formation.

Mineralogical transformations during bornite leaching for all three oxidants illustrates that the peaks become broader and shift to a higher angle, towards the right of the XRD graph. According to Scherrer equation, the broader peaks mean decreasing in crystallite size at the nanometre scale, and according to Bragg’s law, the peaks shifting means it is decreasing in unit size.

**Figure 40:** Phase identification using oxygen as oxidant during bornite leaching at 90 °C. The leaching products converge towards the dotted line, which are characteristics of minerals shown on the graph. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; Cv = covellite; and Al = Aluminium.
Figure 41: Phase identification using ferric (III) sulphate as oxidant during bornite leaching at 90 °C. The leaching products converge towards dotted line, which are characteristics of minerals shown on the graph. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; S = sulfur; and Al = Aluminium.
Figure 42: Phase identification using hydrogen peroxide as oxidant during bornite leaching at 90 °C. The leaching products converge towards dotted line, which are characteristics of minerals shown on the graph. Bn = bornite; Bn_\text{c} = secondary bornite; Ccp = chalcopyrite; Cv = covellite; and Al = Aluminium.
3.2.3 Textural Evolution During Bornite Leaching

Figure 43, Figure 44 and Figure 45 illustrates photomicrographs of polished specimens and unpolished grains of bornite that had been leached. All photomicrographs are for -355 + 150 µm fraction leached at 90 °C.

Figure 43 in particular, demonstrates the textural evolution of bornite using oxygen as oxidant at 90 °C. After 6 hours of leaching, optical and scanning electron images revealed the formation of covellite on the other surface layer of the grain (Figure 43 a-b). As leaching time increased to 12 h and 24 h, the secondary, cubic bornite and chalcopyrite exsolution lamellae matrix are seen to be gradually replaced by copper sulphide (covellite) along the rim of the grain (Figure 43 c-d). As leaching time further increased to 48, 96, and 216 h, covellite and chalcopyrite zone increased in size reinforcing the increased in intensity from the XRD graphs (Figure 40) (Figure 43 e-l). Crystal size also decreased in size as leaching time increased. For experiment conducted after 768 leaching-time, it was observed with the SEM that secondary bornite, covellite and chalcopyrite have been completely converted to sulphur, thereby leading to the formation of a highly porous replaced material. It was also observed from the SEM that the pores are oriented perpendicular to the cleavage directions. It was suggested from this experiment that the porosity generated must have been formed due to the loss of some Cu²⁺ and Fe²⁺ into the solution (Figure 43 n-o).

Figure 44 demonstrates the textural evolution of bornite using ferric sulphate as oxidant at 90 °C. As can be observed, there is a fast-textural evolution from 20 minutes to 192 hours. Within the first 20 minutes to 2 hours, there are evident of covellite and chalcopyrite formation (Figure 44 a-g). Scanning electron images shows evident of sulphur just within 8 hours of leaching (Figure 44 i-k). After 16 and 24 hours of leaching, backscattered electron micrograph shows covellite and sulphur with porous texture formation (Figure 44 l-p). As leaching time increased further, the grains became more porous. This can be clearly seen at 192 hours where optical micrographs shows a sulphur texture (Figure 44 r-t). As grain’s size decreases with increasing leaching time, the sulphur area is also growing with time. This data supports the XRD analysis that as time progresses; grains decreases in crystal size and shift toward the right side of the XRD graph.

Figure 45 demonstrates the textural evolution of bornite using hydrogen peroxide as oxidant at 90 °C. From the obtained micrographs, using hydrogen peroxide provides a slower textural evolution compared to using ferric (III) sulphate or oxygen at longer hours. Initial bornite transformed into secondary bornite within 1 hour of leaching (Figure 45 a-i). Chalcopyrite
formation started to appear within 24 hours of leaching. This can be clearly seen from the optical micrograph given at 24 hours of leaching (Figure 45 j). However, micrographs at 72, 144, and 192 hours of leaching only indicate little amount of covellite and chalcopyrite formation are present (Figure 45 k-o).

From all three conditions, the photomicrographs show development within the bornite particles of initial homogeneous subcrystallites. As leaching time increased, the subcrystallites change little in general size or shape, but the interstices between particles enlarge. Furthermore, after 30% extraction the formerly hard mineral particles become friable, as evident from the photomicrographs. The sample texture of the leached residue also showed typical features of mineral replacement reactions, including the reaction from the surface to the interior of the grains, with a shape reaction front (the phase boundary between primary to product phases) moving towards the core, generating significant porosities within the product phases. In extractive metallurgy, these are called shrinking core reactions, but the fundamental mechanism behind these phenomenon is actually interface-coupled dissolution-precipitation mineral replacement reactions (Putnis, 2009). The produced texture is similar to other mineral replacement reactions to metal sulphides, such as chalcopyrite to bornite (Zhao et al., 2014), pentlandite to violarite (Xia et al., 2009), pyrrhotite to pyrite (Qian et al., 2011).
Figure 43: Scanning electron photomicrographs and optical photomicrographs of the textural evolution during bornite leaching at 90 °C using oxygen as oxidant at various stages of leaching for (a,b) 6 h, (c) 12 h, (d) 24 h, (e) 48 h, (f) 96 h (g-l) 216 h, (m-o) 768 h. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; and Cv = covellite.
Figure 44: Scanning electron photomicrographs and optical photomicrographs of the textural evolution during bornite leaching at 90 °C using ferric (III) sulphate as oxidant at various stages of leaching for (a-c) 20 min, (d) 1 h, (e-g) 2 h, (h) 4 h, (i-k) 8 h (l,m) 16 h, (n-p) 24 h, (q) = 48 h, (r-t) = 192 h. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; and S = sulfur.
Figure 45: Scanning electron photomicrographs and optical photomicrographs of the textural evolution during bornite leaching at 90 °C using hydrogen peroxide as oxidant at various stages of leaching for (a-e) 5 min, (f-i) 1 h, (g) 24 h, (k) 72 h, (l) 144 h, (m-o) 192 h. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; and Cv = covellite.
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3.3 Leaching at 70 °C

It was found that after leaching at 70 °C, the pH does not change much as well and pH values were around 0.88-1.27. Results of bornite leaching at 70 °C are presented below identifying the different phase formation, mineralogical and textural characterisation, and leaching kinetics.

3.3.1 Leaching Kinetics

The effect of varying the oxidants at 70 °C is also investigated to better understand the kinetics of bornite leaching at a different temperature. Figure 46 shows the weight loss percent of the sample as a function of leaching time at 70 °C. Figure 47 and Figure 48 summarised the leaching results on the amount of Cu and Fe extracted, respectively, at different leaching time intervals of using oxygen, iron (III) sulphate and hydrogen peroxide as oxidants at 70 °C.

The results indicate that the rate of leaching has a slower kinetics at 70 °C than at 90 °C for all three oxidants. From Figure 47 dissolution and level of copper and iron extracted at 70 °C are rapid within the first 48 hours and starts to slow down with further leaching. For example, 95.0% Cu and 43.68% Fe extracted at 70 °C while at 90 °C, 97.2% Cu and 48.0% Fe are extracted. The use of ferric (III) sulphate as oxidant shows a faster kinetics than using oxygen and hydrogen peroxide. A Cu extraction of more than 90% has already been achieved just within 48 hours of leaching compared to using oxygen at 31.7% Cu extracted. While using hydrogen peroxide at 70 °C illustrates the slowest kinetics out of all the conditions. This can be observed when only 41.6% Cu and 12.7% Fe extracted at 384 hours.

![Figure 46: Sample weight loss at different leaching time using different oxidants at 70 °C.](image-url)
Figure 47: Effect of different oxidants at 70 °C on copper extraction from bornite at different time.

Figure 48: Effect of different oxidants at 70 °C on iron extraction from bornite at different time.

From these results of leaching of bornite at two different temperatures indicates that the leaching rate is faster and extracted more copper and iron at 90 °C. The rate of leaching seems to be improving with time for 70 and 90 °C. Under established conditions, both 70 and 90 °C using ferric ions as oxidants achieved more than 99% dissolution with a 192-h time difference to maximum dissolution between the two temperatures. This means that a slight increase in temperature has a strong effect on the reaction kinetics. This behaviour may be an indicator of the reaction mechanism because for small changes in temperature the chemical-reaction-controlled processes exhibit large differences (Dreisinger and Abed, 2002). Additionally, high
temperature leaching at 70 and 90 °C of bornite follows the expected behaviour in which the sharp initial rate starts to fall off with time after 50% copper extraction. Temperature in this case is enough to overcome the higher activation energy required by the intermediate and second stage. For example, in the presence of ferric ions has a very rapid initial rate but starts to slow down around 40% copper extraction then the rate went up rapidly again after 50% extraction but slows down at 80% copper extraction and continues at this slowed rate. The formation of a passivation layer at longer duration, which slows down the reaction, may be the reason for this. Slowing down on the leaching rate may be due to the formation of elemental sulphur based on the optimal microscopy and SEM’s images. This is noticeable due to the colour difference representing the phase difference reinforcing the mineralogical transformation on the grains. Limited leaching is due to less unreacted bornite readily available. This finding is significant as there are no publications available on the leaching of bornite at these longer hours. Furthermore, the kinetics data showing that ferric (III) sulphate as a faster oxidant is verified by the study from various literature. For example, Pesic and Olson (1983) studied the leaching of bornite using FeCl₃ and found that the reaction was about two order of magnitude more rapid than found in the study of Pesic and Olson (1984) using oxygen as oxidant within 10 hours of leaching. In their ferric chloride study, they observed two distinct stages of reaction and a transition period between these stages. The first stage involves the rapid and terminated at 28% copper extraction. While in this study oxygen as oxidant the reaction is two orders of magnitude slower than using ferric (III) sulphate as oxidant. This is in agreement with the literature that using oxygen as oxidant is two orders slower but with ferric chloride, or other ferric ion solutions, which Fe³⁺ is the oxidant (Pesic and Olson, 1984).

From the leaching kinetics results, it is clear that at 90 °C produced a higher recovery than at 70 °C. The extent of kinetics at 90 °C, however, are not that huge of a difference than at 70 °C. For example, after 768 hours of leaching, there is only a difference of 2.17% Cu extracted using oxygen as oxidants between both temperatures. Furthermore, after 192 hours of leaching using ferric (III) sulphate and hydrogen peroxide there are only differences of 0.85% and 2.03% Cu extracted, respectively, between two temperatures. From a mineral processing perspective, leaching at 70 °C may be economically desirable than leaching at 90 °C. It is therefore recommended from these results that bornite leaching at 70 °C may be beneficial to save more money as leaching to higher temperatures requires a lot of energy.
3.3.2 Mineralogical Transformation During Bornite Leaching

Phase identification of crushed grains samples using room temperature powder XRD for 70 °C using oxygen, ferric (III) sulphate and hydrogen peroxide are also presented in Figure 49, Figure 50 and Figure 51, respectively.

Figure 49 illustrates that the mineralogical transformation of using oxygen at 70 °C follows the same patterns as using oxygen as oxidant at 90 °C but in a much slower phase. Secondary bornite formation is evident at 2θ = 47.5 within 6 to 24 hours of leaching. Chalcopyrite peaks started to increase in intensity and decrease in size as leaching time increases. Sulphur formation is evident starting at 385 hours and started to increase in intensity at 768 and 1536 hours of leaching. While chalcopyrite peaks have completely transformed into sulphur at 768 hours of leaching.

Figure 50 illustrates the mineralogical transformation using ferric (III) sulphate and follows the same patterns as 90 °C leaching that rapid mineralogical transformation from primary bornite to secondary bornite has occurred within relatively short period of time (5 minutes to 2 hours). After 4 hours of leaching chalcopyrite peaks are evident at 2θ = 38° and 48°. After 24 hours of leaching, sulphur peak is evident at 2θ = 23°. This peak intensity started to increase as further leaching time increases. While chalcopyrite intensity at 2θ = 29 and 48 started to decrease after 24 hours of leaching. After 24 hours of leaching, sulphur peaks started to emerge at 2θ = 23°, 26°, 27°, 28° and 31.5°.

Figure 51 illustrates the mineralogical transformation using hydrogen peroxide as oxidant. Mineral transformation from the starting bornite to 192 hours shows that there is a slow reaction compared to using oxygen and ferric (III) sulphate and using a 90 °C temperature. Secondary bornite is evident after 5 minutes to 24 hours of leaching. Within 24 hours, covellite and chalcopyrite peaks started forming. There is no sulphur formation using hydrogen peroxide as oxidant within 384 hours of leaching.
Figure 49: Phase identification using oxygen as oxidant during bornite leaching at 70 °C. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; Cv = covellite; and Al = aluminium.
Figure 50: Phase identification using ferric (III) sulphate as oxidant during bornite leaching at 70 °C. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; and S = sulfur.
Figure 51: Phase identification using hydrogen peroxide as oxidant during bornite leaching at 70 °C. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; and Al = aluminium.

The identified secondary, cubic bornite was observed under all leaching conditions studied in this project. For the purpose of a more fundamental understanding of this rapid phase transition, the leached residues at 70 °C using Fe$^{3+}$ as oxidant was taken as an example, and determined the evolution of chemical composition and unit cell parameters of the secondary bornite phase (Figure 52). The chemical composition was determined by the acid digestion and AAS method, and the unit cell was refined by the Topas software. In this case, the conservation
of S was assumed and set to $S=4$ in the bornite formula. As Figure 52 illustrates, the depletion of Cu and Fe in the bornite structure increased with increasing leaching time. The depletion of Cu is much faster than Fe, indicating Cu diffusion is faster in the bornite structure. As a consequence, the unit cell became smaller with increasing leaching time.

**Figure 52:** Evolution of chemical composition and unit cell parameters of the secondary bornite phase at various leaching time from the experiments using ferric (III) sulphate as the oxidant. 0.03 g of sample was added into aqua regia and the conservation of sulphur was set to $S=4$ in the bornite formula. Unit cell was calculated using Topas.
3.3.3 Textural Evolution During Bornite Leaching

The textural evolution during bornite leaching at 70 °C are presented below. Figure 53 demonstrates the textural evolution of bornite using oxygen as oxidant at 70 °C. After 6 to 12 hours of leaching optical and scanning electron images revealed the evolution of covellite and chalcopyrite on the other surface layer of the bornite grain (Figure 53 a-f). Furthermore, evolution of covellite and chalcopyrite zone increases in size as leaching time increased further to 12, 96, 385 hours (Figure 53 g-k). Crystal sizes are also noticeably decreasing in size and the formation of the porous sulphur layer increases as leaching time increased particularly at 1536 hours (Figure 53 l-o). Based on the optical and scanning electron photomicrographs obtained, there is a textural evolution from smooth surface bornite into a more porous sulphur layers. Additionally, the size of the domain decreases with time producing a one-core structure. Figure 54 demonstrates the textural evolution of bornite using ferric sulphate as oxidant at 70 °C. As can be observed, there is a fast-textural evolution from 5 minutes to 40 minutes, where chalcopyrite lamellae started forming (Figure 54 a-d). Within 8 hours of leaching, chalcopyrite layer started to increase in surface area (Figure 54 e-f). At 192 hours, the grains core shell structure has shrunk in size and completely turned porous mainly made up of sulphur (Figure 54 g-i). This data supports the XRD analysis that as time progresses; grains decreases in size as it shifts towards the right side of the XRD graph (Figure 50).

Figure 55 demonstrates the textural evolution of bornite using hydrogen peroxide as oxidant at 70 °C. From the obtained micrographs, using hydrogen peroxide provides a slower textural evolution compared to using oxygen or ferric (III) sulphate as oxidants. Small amount of textural evolution can be seen throughout the leaching times from 5 minutes to 384 hours using hydrogen peroxide at 70 °C (Figure 55 a-f). Small amount of chalcopyrite formation is evident from the obtained photomicrographs started forming at 10 minutes of leaching (Figure 55 c). It was found that the secondary cubic bornite crystal structure from hydrogen peroxide or oxygen as oxidants that the unit cell size has gradually decreased in size with increasing distance from the original bornite towards the covellite and chalcopyrite layer. This suggests a gradual withdrawal of material from the bornite with a resulting slight contraction of the unit cell. This supports the work of Dutrizac et al. (1970) when they studied the kinetics dissolution of bornite and found that the bornite pellets were leached for longer periods, the chalcopyrite-plus-sulfur layer was covered by an additional layer of sulphur that arose from decomposition of the CuFeS₂. The non-stoichiometric bornite was still present between bornite and chalcopyrite when the sulphur layer formed.
Figure 53: Scanning electron photomicrographs and optical photomicrographs of the textural evolution during bornite leaching at 70 °C using oxygen as oxidant at various stages of leaching for (a-e) 6 h, (f) 12 h, (g,h) 96 h, (i-l) 385 h, (m-o) 1536 h. Bn = bornite; Bn_c = secondary bornite; S = sulfur; and Cv = covellite.
Figure 54: Scanning electron photomicrographs and optical photomicrographs of the textural evolution during bornite leaching at 70 °C using ferric (III) sulphate as oxidant at various stages of leaching for (a,b) 5 min, (c,d) 40 min, (e,f) 8 h, (g-i) 192 h. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; S = sulfur.
Figure 55: Scanning electron photomicrographs and optical photomicrographs of the textural evolution during bornite leaching at 70 °C using hydrogen peroxide as oxidant at various stages of leaching for (a,b) 5 min, (c) 10 min, (d) 4 h, (e,f) 384 h. Bn = bornite; Bn_c = secondary bornite; Ccp = chalcopyrite; and S = sulfur.

The reaction products formed during the leaching of bornite using oxygen, ferric (III) sulphate and hydrogen peroxide as oxidants depend on the leaching conditions as well as the particle size of the bornite. The extent of dissolution is always more vigorous in the ferric (III) sulphate system and increased with increasing temperature as can be observed from the obtained photomicrographs. The reaction initially involves the rapid outward diffusion of copper to form slightly non-stoichiometric bornite, chalcopyrite and covellite. The non-stoichiometric bornite is progressively converted to covellite. The reaction at 90 °C proceeds initially at the covellite phase and as time progresses results in further dissolution to elemental sulphur and soluble Cu^{2+} and Fe^{2+}. The leaching of bornite at -355 + 150 µm fraction illustrates the complexities of the leaching reaction more clearly than is observed for the 38-53 µm fraction. Additionally, chalcopyrite exsolution lamellae rimmed by a copper sulphide appear in the covellite zone and in the non-stoichiometric bornite. The experimental leaching results involving the -355 + 150 µm fraction are generally consistent with the mineralogical trends during the supergene alteration of bornite ores. Pesic and Olson (1984) studied the dissolution of bornite in sulphuric acid using oxygen as oxidant, and they found that Cu_3FeS_4 and covellite were the main intermediates species. Additionally, their study showed that copper dissolution
rate was controlled by the iron dissolution rate, and the initial preferential iron dissolution has caused the iron-deficient bornite formation, which was further transformed to \( \text{Cu}_3\text{FeS}_4 \) and CuS from the diffusion and depletion of labile Cu\(^+\) ions.

### 3.4 Effect of Particle Size

Two different particle size ranges at \(-355 + 150 \) and \(-53 + 38 \) \( \mu \)m for 70 and 90 °C were examined (Figure 56). From the experiments conducted, the result shows that copper extraction was highly dependent on grain size. The difference in the size fraction affected the kinetics of bornite leaching. For example, using oxygen as the oxidant for 48 h at 70 °C recovered 31.59% and 37.51% and at 90 °C recovered 24.48% and 42.25% from respective particle size ranges of \(-355 + 150 \) and \(-53 + 38 \) \( \mu \)m. Additionally, using ferric ions as the oxidant for 8 h at 70 °C recovered 40.47% and 55.28% and at 90 °C recovered 48.37% and 63.38% from respective particle size ranges of \(-355 + 150 \) and \(-53 + 38 \) \( \mu \)m. Furthermore, using hydrogen peroxide as the oxidant for 8 h at 70 °C recovered 25.67% and 29.62% and at 90 °C recovered 28.87% and 31.98% from respective particle size ranges of \(-355 + 150 \) and \(-53 + 38 \) \( \mu \)m. Smaller particle size has greater surface area, which increases the chance of bornite particles to be in contact with the oxidant and pull molecules away from the bulk crystal more efficiently. While the larger particle size ranges of \(-355 + 150 \) has smaller surface area to volume ratio, where particles have more mass to dissolve than smaller particles. The leaching rate is therefore not linearly dependent on particle size (or specific surface area). This means that higher percent extractions that are observed at \(-53 + 38 \) \( \mu \)m than at \(-355 + 150 \) \( \mu \)m could indicate that leaching is not controlled by surface chemical reactions. It also highly dependent on the mineralogical phase transformation processes within the grains. This is also supported from the calculated unit cell edge that leaching rate is not linearly dependent on particle size (Figure 52). This is most likely that the formation of secondary bornite make the initially non-porous bornite porous, due to shrinkage of unit cell. The created porosity provided pathways for the penetration of leaching solution into the mineral grains, and hence promoted leaching for large particle size bornite. This is supported by the micrographs where you can see a lot of cracks within the grains (e.g. Figure 44 i; Figure 45 g; Figure 53 g, h, l, j; Figure 54 d; Figure 55 f).

Although the data shows that at smaller particle size range of \(-53 + 38 \) \( \mu \)m produced a higher recovery than \(-355 + 150 \) \( \mu \)m, the difference in the recoveries are not that huge. For example, the difference in copper extraction using oxygen, ferric (III) sulphate, and hydrogen peroxide as oxidants at 70 °C are 5.93%, 14.84%, and 3.96% (Figure 56 a-f) and at 90 °C are 6.73%, 15.04%, and 3.12% (Figure 56 g-l), respectively. While the difference in iron extraction using
oxygen, and hydrogen peroxide as oxidants for the two particle size ranges at 70 °C are 1.49%, 8.46% (Figure 56 m-p) and at 90 °C are 5.95% and 18.08% (Figure 56 q-t), respectively. It is clear from the results that the differences in extraction between -53 + 38 µm and -355 + 150 µm have not much improvement and it is therefore recommended in the mineral processing industries that using -355 + 150 µm are more economically desirable. This is because grinding to finer sizes in the comminution circuit is becoming an increasingly common unit operation in mineral processing. While further grinding can liberate ores into smaller particle size, it can entail high costs in terms of energy consumption and media use. These costs can be minimised by selecting appropriate operating conditions. Thus, grinding at coarse particle sizes of -355 + 150 µm than at -53 + 38 µm is recommended and may be beneficial to reduce both operating costs and the environmental footprint of the comminution circuit.

![Figure 56: The percent extraction of Cu and Fe using oxygen, ferric (III) sulphate, and hydrogen peroxide for -355 + 150 and -53 + 38 µm at 70 °C and 90°C, and at various stages of leaching for oxygen at (a, b, g, h, m, n, q, r) 48 h and for ferric (III) sulphate and hydrogen peroxide at (c, d, e, f, i, j, k, l, o, p, s, t) 8 h.](image-url)
3.5 Proposed Leaching Mechanism

Residue samples were studied by qualitative XRD, optical microscope and SEM and the reaction mechanisms of bornite leaching from the given oxidants were revealed by the evolution of the product phases. These data clearly show the progressive transformation from pure bornite to reaction products including chalcopyrite, covellite, and sulphur. The results for all three oxidants suggested a stepwise mechanism of bornite leaching.

3.5.1 Leaching Using Oxygen as Oxidant

From the quantitative phase evolution, a schematic representation of the mineral transformation is given in Figure 57. Based on the mineralogical evolution, the proposed dominant chemical reactions are provided in equations 16-20. In step 1, the transformation of the original bornite to secondary bornite is very “rapid”. Quantitative analysis shows that secondary bornite is a type of bornite with a cubic crystal structure and a space group of F-43m. In step 2, the continued “quick” depletion of Cu and Fe leads to the formation of covellite on the outer area of the grains. Step 3 commences on the formation of chalcopyrite lamellae at a slightly slower phase compare to the initial reactions. Step 4 is the further depletion of Cu and Fe and the start of the formation of sulphur. This process is extremely sluggish and is expected as the slow transformation may be due to the armouring of copper iron sulphide layer.

**Figure 57:** Reaction schematic of bornite leaching using oxygen as oxidant.

Step 1:

$$\text{Cu}_5\text{FeS}_4 + 2\text{H}^+ + 0.5\text{O}_2(\text{aq}) \rightarrow \text{Cu}_4\text{FeS}_4 + \text{Cu}^{2+} + \text{H}_2\text{O}$$  \hspace{1cm} (16)

Step 2:

$$\text{Cu}_4\text{FeS}_4 + 3\text{H}^+ + 0.75\text{O}_2(\text{aq}) \rightarrow 4\text{CuS} + \text{Fe}^{3+} + 1.5\text{H}_2\text{O}$$  \hspace{1cm} (17)

Step 3:

$$\text{Cu}_4\text{FeS}_4 + 2\text{H}^+ + 0.5\text{O}_2(\text{aq}) \rightarrow \text{CuFeS}_2 + 2\text{CuS} + \text{Cu}^{2+} + \text{H}_2\text{O}$$  \hspace{1cm} (18)

Step 4:

$$\text{CuFeS}_2 + 1.25\text{O}_2(\text{aq}) + 5\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2\text{S} + 2.5\text{H}_2\text{O}$$  \hspace{1cm} (19)
Cu$^+$ + 0.5O$_2$(aq) + 2H$^+$ → Cu$^{2+}$ + S + H$_2$O \hspace{1cm} (20)

### 3.5.2 Leaching Using Ferric (III) Sulphate as Oxidant

A schematic representation of the mineral transformation using ferric (III) sulphate is given in Figure 58. Based on the mineralogical evolution, the proposed dominant chemical reactions using ferric (III) sulphate as oxidants are provided in equations 21-23. The stepwise mechanism can be viewed based on the evolution of the Cu and Fe species. The pathway is the bornite evolution from primary to secondary cubic crystal structure bornite, and then the rapid formation of chalcopyrite lamellae, and finally the transformation into smaller, more porous sulphur. These take place in the core of the grain and are achieved by stepwise depletion of Cu and Fe.

**Figure 58:** Reaction schematic of bornite leaching using ferric (III) sulphate as oxidant.

Step 1:

$$\text{Cu}_5\text{Fe}_4\text{S}_4 + 2\text{Fe}^{3+} \rightarrow \text{Cu}_4\text{Fe}_4\text{S}_4 + \text{Cu}^{2+} + 2\text{Fe}^{2+}$$ \hspace{1cm} (21)

Step 2:

$$\text{Cu}_4\text{Fe}_4\text{S}_4 + 6\text{Fe}^{3+} \rightarrow \text{CuFe}_2 + 3\text{Cu}^{2+} + 6\text{Fe}^{2+} + 2\text{S}$$ \hspace{1cm} (22)

Step 3:

$$\text{CuFe}_2 + 4\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}$$ \hspace{1cm} (23)

### 3.5.3 Leaching Using Hydrogen Peroxide as Oxidant

Figure 59 illustrates a schematic representation of the mineral transformation using hydrogen peroxide. Based on the mineralogical evolution, the proposed dominant chemical reactions using hydrogen peroxide as oxidants are provided in equations 24-26. The stepwise mechanism can be also viewed based on the evolution of the Cu and Fe species. The pathway is the evolution of initial bornite to a secondary cubic crystal structure bornite, and then the slow formation of the covellite zone, and finally the slow formation of chalcopyrite exsolution lamellae. These also take place in the core of the grain and are achieved by stepwise depletion of Cu and Fe.
Figure 59: Reaction schematic of bornite leaching using hydrogen peroxide as oxidant.

Step 1:

\[ \text{Cu}_5\text{FeS}_4 + 2\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}_4\text{FeS}_4 + \text{Cu}^{2+} + 2\text{H}_2\text{O} \]  \hspace{1cm} (24)

Step 2:

\[ \text{Cu}_4\text{FeS}_4 + 3\text{H}^+ + 1.5\text{H}_2\text{O}_2 \rightarrow 4\text{CuS} + \text{Fe}^{3+} + 3\text{H}_2\text{O} \]  \hspace{1cm} (25)

Step 3:

\[ \text{Cu}_4\text{FeS}_4 + 6\text{H}^+ + 3\text{H}_2\text{O}_2 \rightarrow \text{CuFeS}_2 + 3\text{Cu}^{2+} + 2\text{S} + 6\text{H}_2\text{O} \]  \hspace{1cm} (26)
Chapter 4

Conclusions
Chapter 4 Conclusions

The major contribution of this thesis is that it advances our knowledge and understanding on the mechanism of bornite leaching: insights from mineralogical and textural characterisation. This chapter draws brief conclusions, brings out the contribution of the project, and highlights the possible investigation of future research.

4.1 Summary

There has been a selection of leaching conditions that are evaluated on bornite leaching in the presence of sulphuric acid. These conditions were studied to understand the mineralogical and textural characterisation, at the micro level, of the mechanism of leaching on bornite. The effects of multiple independent variables were tested, including types of oxidant, particle size and temperature at different leaching times. The solutions were mixed in a glass reactor under the designed experimental conditions. The leached solutions and residues were analysed using AAS, XRD, optical light microscope and SEM. Based on the quantitative and qualitative analysis of the results, the objectives have been met and it is found that:

- Using ferric (III) sulphate on bornite leaching as oxidant produced the fastest kinetics and led to the highest recovery at a given time. Using hydrogen peroxide as oxidant produced a faster kinetics than using oxygen at shorter leaching times (<24 hours). But at longer leaching times (≥24 hours) oxygen produced faster kinetics than using hydrogen peroxide;
- The design under each condition one experiment using small particle size (-53 + 38 µm) produced a higher recovery of copper and iron than using a larger particle size (-355 + 150 µm) for all conditions; and
- Using temperature of 90 ºC produced higher recovery and faster kinetics than 70 ºC temperature for all conditions.

Furthermore, a mechanism has been proposed for the reactions taking place during the leaching of bornite. For oxygen as oxidant, transformation of the original bornite to secondary bornite, then to covellite and chalcopyrite and finally to sulphur has been proposed. For ferric (III) sulphate as oxidant, the bornite evolution from primary to secondary, and then the formation of chalcopyrite lamellae, and finally the transformation into sulphur has been proposed. For hydrogen peroxide as oxidant, mineral transformation is the evolution of initial bornite to a secondary bornite, and then the formation of the covellite, and finally the slow formation of chalcopyrite exsolution lamellae has been proposed.
4.2 Future Work

This work reveals the mechanism of bornite leaching at the given parameters, but there are several interesting questions related to aspects of study that could not be explored in this thesis. Thus, some relevant work is listed below as future investigations. These are discussed in the following.

1. The reactions in this study were monitored ex situ, therefore the observed reaction texture may not be the same as that under the reaction conditions. For example, the cooling process when glass reactors were taken out of the oven may induce some of the observed cracks. In situ study can reveal the real mechanism of mineral replacement during bornite leaching, thus will give a better picture on the reactions under hydrothermal conditions. Therefore, future and better tests need to use in situ monitoring studies, such as using flow-through reactors.

2. In this study, reactions are conducted in closed systems, in which fluid composition keep changing with time and reaction may respond differently with time as well. It is therefore important to keep the solution in steady state for critical quantitative kinetic studies. Future work on this may involve equipment such as open mixed flow-through reactors, where the effect of fluid flow to the mechanism and kinetics on replacement reactions of bornite can be studied.

3. This work confirms the mechanisms by kinetics, mineralogical and textural study, but using sulphuric acid as the only lixiviant to reveal the mechanism as it is a more popular technique in the literature. Thus, a further study of the mechanism of bornite leaching can be carried out by using different lixiviants, such as hydrochloric acid and nitric acid.

4. Phase characterisations of this work was determined using software such as Match! and TOPAS, but due to equipment breakdown within the timeframe of this thesis; energy dispersive spectroscopy (EDS) was not used to better confirm the quantitative and qualitative results. Alternatively, using other equipment such as X-ray fluorescence to analyse residues may give better understanding of the solid contents as EDS only focuses its rays on the centre and not the whole residue sample.

5. The initial plan for this study is the use of glovebox for longer leaching times of more than 6 hours, but the rapid mineralogical transformations revealed by the XRD results showed that the leaching at shorter times are needed. Therefore, a new methodology of leaching that involves the preheating of solution was introduced. The inconsistency of
different methods may introduce errors, such as the test that was conducted took 45-50 minutes for the solution to reached the desired temperature. This clearly shows that the first test at 1 hour without preheating was only leaching for 10-15 minutes at the desired temperature. Future tests on consistent, better design methodologies that include a preheated solution without the presence of air that will affect the reactions is recommended.

6. This work reveals the mineralogical and textural evolution during bornite leaching and the distribution of porosity and cracks and their origin in the product phase is very important to the replacement reactions as it control the behaviour of fluid flows. However, there is not much study known about porosity or cracks evolution during mineral replacement. Future work on porosity studies is recommended. This can be achieve using neutron scattering technique, small angle neutron scattering or small angle X-ray scattering to study the evolution of porosity.
References


Lowe, D.F., 1970. The kinetics of the dissolution reactions of copper and copper-iron-sulfide minerals using ferric-sulfate solutions


References


Sole, K.C., 2008. Solvent extraction in the hydrometallurgical processing and purification of metals: process design and selected applications, Solvent extraction and liquid membranes. CRC Press, pp. 159-218.
References


Appendices

Appendix A – Testwork Data

Table 8: Leaching data showing the extraction of Cu and Fe from AAS using oxygen as oxidant at 90 °C.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Sample Label</th>
<th>Concentration (ppm)</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>Fe</td>
</tr>
<tr>
<td>6</td>
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<td>132.75</td>
<td>56.25</td>
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<td>24</td>
<td>BL90O201_24h</td>
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</tr>
<tr>
<td>48</td>
<td>BL90O201_48h</td>
<td>360.00</td>
<td>116.50</td>
</tr>
<tr>
<td>96</td>
<td>BL90O201_96h</td>
<td>390.00</td>
<td>151.25</td>
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<tr>
<td>216</td>
<td>BL90O201_216h</td>
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<td>162.50</td>
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<td>384</td>
<td>BL90O201_384h</td>
<td>642.00</td>
<td>177.75</td>
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<td>BL90O201_768h</td>
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<td>197.75</td>
</tr>
<tr>
<td>48</td>
<td>BL90O202_48h</td>
<td>428.00</td>
<td>141.00</td>
</tr>
</tbody>
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Note: BL90O201_6h to BL90O201_768h used the particle size range of -355 + 150 μm while BL90O202_48h used the particle size range of -53 + 38 μm.
Table 9: Leaching data showing the extraction of Cu and Fe from AAS using ferric (III) sulphate as oxidant at 90 °C.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Sample Label</th>
<th>Concentration (ppm)</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>Cu</td>
<td>Fe</td>
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<td>BL90Fe01_5min</td>
<td>151.75</td>
<td>4440</td>
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<tr>
<td>0.17</td>
<td>BL90Fe01_10min</td>
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<td>0.33</td>
<td>BL90Fe01_20min</td>
<td>201.00</td>
<td>4752</td>
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<tr>
<td>0.50</td>
<td>BL90Fe01_30min</td>
<td>212.00</td>
<td>4884</td>
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<tr>
<td>0.67</td>
<td>BL90Fe01_40min</td>
<td>258.00</td>
<td>4944</td>
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<td>274.00</td>
<td>5088</td>
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<tr>
<td>2</td>
<td>BL90Fe01_2h</td>
<td>364.00</td>
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<tr>
<td>4</td>
<td>BL90Fe01_4h</td>
<td>448.00</td>
<td>5280</td>
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<td>BL90Fe01_8h</td>
<td>490.00</td>
<td>5424</td>
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<td>BL90Fe01_16h</td>
<td>510.00</td>
<td>5652</td>
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<td>BL90Fe01_24h</td>
<td>940.00</td>
<td>5724</td>
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<td>BL90Fe01_48h</td>
<td>980.00</td>
<td>5748</td>
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<td>BL90Fe01_72h</td>
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<td>5844</td>
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<td>BL90Fe01_96h</td>
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<td>144</td>
<td>BL90Fe01_144h</td>
<td>1002.00</td>
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<td>192</td>
<td>BL90Fe01_192h</td>
<td>1012.00</td>
<td>6012</td>
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<td>8</td>
<td>BL90Fe02_8h</td>
<td>642.00</td>
<td>5892</td>
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Note: BL90Fe01_5min to BL90Fe01_192h used the particle size range of -355 + 150 µm while BL90Fe02_8h used the particle size range of -53 + 38 µm.
Table 10: Leaching data showing the extraction of Cu and Fe from AAS using hydrogen peroxide as oxidant at 90 °C.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Sample Label</th>
<th>Concentration (ppm)</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td>Cu</td>
<td>Fe</td>
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<td>0.08</td>
<td>BL90H2O201_5min</td>
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<td>0.17</td>
<td>BL90H2O201_10min</td>
<td>148.50</td>
<td>6.86</td>
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<td>0.33</td>
<td>BL90H2O201_20min</td>
<td>157.50</td>
<td>7.20</td>
</tr>
<tr>
<td>0.50</td>
<td>BL90H2O201_30min</td>
<td>169.50</td>
<td>7.66</td>
</tr>
<tr>
<td>0.67</td>
<td>BL90H2O201_40min</td>
<td>181.75</td>
<td>8.38</td>
</tr>
<tr>
<td>1</td>
<td>BL90H2O201_1h</td>
<td>280.00</td>
<td>12.66</td>
</tr>
<tr>
<td>2</td>
<td>BL90H2O201_2h</td>
<td>289.50</td>
<td>12.30</td>
</tr>
<tr>
<td>4</td>
<td>BL90H2O201_4h</td>
<td>291.00</td>
<td>18.22</td>
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<tr>
<td>8</td>
<td>BL90H2O201_8h</td>
<td>292.50</td>
<td>15.48</td>
</tr>
<tr>
<td>16</td>
<td>BL90H2O201_16h</td>
<td>352.50</td>
<td>24.24</td>
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<tr>
<td>24</td>
<td>BL90H2O201_24h</td>
<td>361.50</td>
<td>24.36</td>
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<tr>
<td>48</td>
<td>BL90H2O201_48h</td>
<td>369.00</td>
<td>92.00</td>
</tr>
<tr>
<td>72</td>
<td>BL90H2O201_72h</td>
<td>394.50</td>
<td>105.00</td>
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<td>99</td>
<td>BL90H2O201_99h</td>
<td>396.00</td>
<td>107.75</td>
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<td>109.50</td>
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<td>192</td>
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<td>400.50</td>
<td>124.50</td>
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<td>8</td>
<td>BL90H2O202_8h</td>
<td>324.00</td>
<td>90.00</td>
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</table>

Note: BL90H2O201_5min to BL90H2O201_192h used the particle size range of -355 + 150 µm while BL90H2O202_8h used the particle size range of -53 + 38 µm.
Table 11: Leaching data showing the extraction of Cu and Fe from AAS using oxygen as oxidant at 70 °C.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Sample Label</th>
<th>Concentration (ppm)</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>Fe</td>
</tr>
<tr>
<td>6</td>
<td>BL70O201_6h</td>
<td>40.00</td>
<td>4.12</td>
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<td>12</td>
<td>BL70O201_12h</td>
<td>132.50</td>
<td>8.24</td>
</tr>
<tr>
<td>24</td>
<td>BL70O201_24h</td>
<td>205.00</td>
<td>11.60</td>
</tr>
<tr>
<td>48</td>
<td>BL70O201_48h</td>
<td>320.00</td>
<td>14.36</td>
</tr>
<tr>
<td>96</td>
<td>BL70O201_96h</td>
<td>380.00</td>
<td>18.38</td>
</tr>
<tr>
<td>192</td>
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<td>384</td>
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<td>620.00</td>
<td>90.00</td>
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<td>768</td>
<td>BL70O201_768h</td>
<td>960.00</td>
<td>180.00</td>
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<td>1536</td>
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<td>190.75</td>
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<td>48</td>
<td>BL70O202_48h</td>
<td>380.00</td>
<td>20.48</td>
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</table>

Note: BL70Fe01_6h to BL70O201_1536h used the particle size range of -355 + 150 µm while BL70O202_48h used the particle size range of -53 + 38 µm.
### Table 12: Leaching data showing the extraction of Cu and Fe from AAS using ferric (III) sulphate as oxidant at 70 °C.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Sample Label</th>
<th>Concentration (ppm)</th>
<th>Extraction (%)</th>
</tr>
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<tbody>
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<td>0.17</td>
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</tr>
<tr>
<td>0.33</td>
<td>BL70Fe01_20min</td>
<td>200.00</td>
<td>19.79</td>
</tr>
<tr>
<td>0.50</td>
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</tr>
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<td>0.67</td>
<td>BL70Fe01_40min</td>
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<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>BL70Fe01_2h</td>
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<td>31.67</td>
</tr>
<tr>
<td>4</td>
<td>BL70Fe01_4h</td>
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<td>35.62</td>
</tr>
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<td>40.57</td>
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<td>83.12</td>
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<td>BL70Fe01_48h</td>
<td>960.00</td>
<td>95.00</td>
</tr>
<tr>
<td>72</td>
<td>BL70Fe01_72h</td>
<td>980.00</td>
<td>96.97</td>
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<tr>
<td>96</td>
<td>BL70Fe01_96h</td>
<td>990.00</td>
<td>97.96</td>
</tr>
<tr>
<td>144</td>
<td>BL70Fe01_144h</td>
<td>1000.00</td>
<td>98.95</td>
</tr>
<tr>
<td>192</td>
<td>BL70Fe01_192h</td>
<td>1002.00</td>
<td>99.15</td>
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<tr>
<td>384</td>
<td>BL70Fe01_384h</td>
<td>1002.00</td>
<td>99.15</td>
</tr>
<tr>
<td>8</td>
<td>BL70Fe02_8h</td>
<td>560.00</td>
<td>55.41</td>
</tr>
</tbody>
</table>

Note: BL70Fe01_5min to BL70Fe01_384h used the particle size range of -355 + 150 µm while BL70Fe02_8h used the particle size range of -53 + 38 µm.
Table 13: Leaching data showing the extraction of Cu and Fe from AAS using hydrogen peroxide as oxidant at 70 °C.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Sample Label</th>
<th>Concentration (ppm)</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>BL70H2O201_5min</td>
<td>Cu: 70.00 Fe: 4.50</td>
<td>Cu 6.93 Fe 1.09</td>
</tr>
<tr>
<td>0.17</td>
<td>BL70H2O201_10min</td>
<td>Cu: 117.50 Fe: 4.54</td>
<td>Cu 11.63 Fe 1.10</td>
</tr>
<tr>
<td>0.33</td>
<td>BL70H2O201_20min</td>
<td>Cu: 177.50 Fe: 6.02</td>
<td>Cu 17.56 Fe 1.46</td>
</tr>
<tr>
<td>0.50</td>
<td>BL70H2O201_30min</td>
<td>Cu: 200.00 Fe: 6.50</td>
<td>Cu 19.79 Fe 1.58</td>
</tr>
<tr>
<td>0.67</td>
<td>BL70H2O201_40min</td>
<td>Cu: 205.00 Fe: 6.52</td>
<td>Cu 20.29 Fe 1.58</td>
</tr>
<tr>
<td>1</td>
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<td>Cu: 217.50 Fe: 6.72</td>
<td>Cu 21.52 Fe 1.63</td>
</tr>
<tr>
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<td>BL70H2O201_2h</td>
<td>Cu: 220.00 Fe: 6.92</td>
<td>Cu 21.77 Fe 1.68</td>
</tr>
<tr>
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<td>BL70H2O201_4h</td>
<td>Cu: 240.00 Fe: 10.00</td>
<td>Cu 23.75 Fe 2.43</td>
</tr>
<tr>
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<td>BL70H2O201_8h</td>
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<td>Cu 25.73 Fe 2.46</td>
</tr>
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<td>BL70H2O201_16h</td>
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</tr>
<tr>
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<td>Cu: 280.00 Fe: 11.78</td>
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<tr>
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<td>Cu: 300.00 Fe: 14.46</td>
<td>Cu 29.69 Fe 3.51</td>
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<tr>
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<td>Cu: 308.00 Fe: 18.48</td>
<td>Cu 30.48 Fe 4.48</td>
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<tr>
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<td>Cu: 320.00 Fe: 19.56</td>
<td>Cu 31.67 Fe 4.75</td>
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<td>144</td>
<td>BL70H2O201_144h</td>
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<td>Cu 35.62 Fe 5.31</td>
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<td>BL70H2O201_192h</td>
<td>Cu: 380.00 Fe: 22.20</td>
<td>Cu 37.60 Fe 5.39</td>
</tr>
<tr>
<td>384</td>
<td>BL70H2O201_384h</td>
<td>Cu: 420.00 Fe: 52.50</td>
<td>Cu 41.56 Fe 12.74</td>
</tr>
<tr>
<td>8</td>
<td>BL70H2O202_8h</td>
<td>Cu: 300.00 Fe: 45.00</td>
<td>Cu 29.69 Fe 10.92</td>
</tr>
</tbody>
</table>

Note: BL70H2O201_5min to BL70H2O201_384h used the particle size range of -355 + 150 µm while BL70H2O202_8h used the particle size range of -53 + 38 µm.
Appendix B – Calculations

Finding the volume of sulphuric acid needed in a 50 mL dilution:

- Concentration\(_{\text{H}_2\text{SO}_4,\text{needed}}\) = 0.1 M
- Volume\(_{\text{needed}}\) = 500 mL
- Molar mass\(_{\text{H}_2\text{SO}_4} = 98.07 \frac{g}{\text{mol}}\)
- \(\rho_{\text{H}_2\text{SO}_4} = 1.84 \frac{\text{kg}}{\text{L}}\)
- 95% Sulphuric acid
- Bornite sample chemical composition: \(\text{Cu}_{4.95}\text{Fe}_{1.07}\text{S}_{3.98}\)

Calculating mass:

\[
M = \frac{\text{moles}}{\text{L}} = 0.1 \text{ M} = 0.1 \frac{\text{moles}}{\text{L}}
\]

\[
n = 0.1 \frac{\text{moles}}{\text{L}} \times 0.5 \text{ L} = 0.05 \text{ moles}
\]

\[
\therefore m = 0.05 \times 98.07 = 4.9035 \text{ g}
\]

Calculating volume of \(\text{H}_2\text{SO}_4\) needed in a 500 mL solution:

\[
V = \frac{4.9035 \text{ g}}{1.84 \frac{\text{kg}}{\text{L}}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{100}{95} = 0.00280521 \text{ L} = 2.805 \text{ mL}
\]

Finding the amount of copper in solution:

- \(m_{\text{Cu}_{4.95}\text{Fe}_{1.07}\text{S}_{3.98}} = 0.08 \text{ g} = 80 \text{ mg}\)
- Cu wt\% = \(\frac{4.95 \times 63.546 \frac{\text{g}}{\text{mol}} + 100}{(4.95 \times 63.546 + 55.845 + 32.065 + 3.98) \frac{\text{g}}{\text{mol}}} \times 100 = \frac{314.5527}{498.0164} \times 100 = 63.16\%\)

Calculating the mass of Cu in bornite:

\[
m_{\text{Cu}} = 80 \text{ mg} \times 63.16\% = 50.53 \text{ mg}
\]

Calculating the concentration of Cu in 50 mL solution:

\[
c = \frac{m}{V} = \frac{50.53 \text{ mg}}{0.05 \text{ L}} = 1010.58 \text{ ppm}
\]

Finding the amount of iron in solution:

- \(m_{\text{Cu}_{4.95}\text{Fe}_{1.07}\text{S}_{3.98}} = 0.08 \text{ g} = 80 \text{ mg}\)
• Fe wt% = \frac{4 \times 32.065 \text{ g mol}^-1}{(4.95 + 63.546 + 55.845 + 32.065 + 3.98) \text{ g mol}^-1} \times 100 = \frac{128.26}{498.0164} \times 100 = 25.75\%

Calculating the mass of Fe in bornite:
\[ m_{Cu} = 80 \text{ mg} \times 25.75\% = 20.60 \text{ mg} \]

Calculating the concentration of Fe in 50 mL solution:
\[ c = \frac{m}{V} = \frac{20.60 \text{ mg}}{0.05 \text{ L}} = 412.07 \text{ ppm} \]