Selective flotation of enargite from copper sulphides in complex ore systems

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Abstract

Recent research has demonstrated promising results showing the possibility of separating arsenic-copper sulphides from other copper minerals by controlling the potential of the flotation pulp. Most of these studies were conducted on single mineral systems, and the selective removal of arsenic-copper minerals in real ore systems is not well understood. In real ore systems, the efficiency of the separation strongly depends on the mineralogical characteristics of the ore samples. This study seeks to understand the effect of ore mineralogy on the floatability of enargite in a complex ore system, under a controlled potential flotation environment.

A composite of several high arsenic-containing drill core intersections for the high arsenic sample (HAS) and a composite of some low arsenic-containing drill core intersections for the low arsenic sample (LAS) were selected from the Tampakan copper-gold deposit in the Philippines, providing a range of arsenic levels. Arsenic in the HAS sample (enargite) was practically twice that for the LAS sample. The non-enargite copper minerals (NECu) were mostly chalcopyrite and bornite in both samples.

Comprehensive size-by-size, chemical and mineralogical analyses were performed on both ore samples. It was observed that the two ore samples had similar mineralogical characteristics in terms of mineral content and liberation distribution, however there are some differences in the proportions of minerals. It was also observed that NECu minerals were mostly distributed to the coarser size fractions, while the proportion of enargite in the finer size fractions was higher than for NECu. The mineral grain size data showed that enargite had the finest grain size distribution compared to other copper minerals.

The selective separation of enargite from NECu minerals in a rougher flotation system under controlled pulp potential was investigated for both samples. It was observed that it is possible to selectively separate enargite from other copper minerals after reducing the pulp potential to about -200 mV SHE at pH 11 in the LAS sample. However, no separation between enargite and NECu minerals was observed at a reducing potential for the HAS sample, and enargite did not float very well for this sample as the Eh was changed.

The Particle Kinetic Model was used to predict the flotation response of enargite and NECu in the HAS sample based on mineral flotation rates derived from the LAS sample and the mineralogy of the HAS sample. It was observed that the predicted values of enargite recoveries were higher in the HAS sample when compared with the results of actual flotation tests. As the mineralogy of the two ore samples was similar in terms of mineralogical and liberation characteristics, the only reason for the
poor prediction of the model for the HAS sample was due to the change in the flotation pulp conditions for the HAS sample. There were two possible reasons for this change in the flotation response of the HAS sample. One was the higher levels of pyrite present in the HAS sample compared to the LAS sample, which could cause galvanic interactions between the sulphide minerals in the flotation pulp. Moreover, the other possible reason was the different amount of the non-sulphide gangue content in the HAS and the LAS sample.

The study of the floatability of non-sulphide gangue minerals in the flotation of the HAS and the LAS samples showed pyrophyllite as a natural gangue mineral, has floated significantly in both samples, which could contribute to the lower recovery of the valuable minerals. However, analysis of the results indicated that there was not sufficient evidence to allow statistically valid conclusions to be drawn on the effect of gangue minerals. Further work is required in terms of surface studies by SEM, XPS, etc.

EDTA extraction and water chemistry tests were performed to evaluate the amount and type of metal ions on the mineral surface and in the process water. It was observed that the copper and arsenic extracted by EDTA were greater in the HAS samples compared to the LAS sample. Based on enargite surface studies by other researchers and the results obtained from the current work, it was concluded that the oxidation of enargite in the HAS sample due to galvanic interactions with pyrite caused its poor floatability and consequently poor selectivity from other copper minerals.

The important outcomes of this work are:

- Enargite tended to be ground more readily than the other copper sulphide minerals.
- It is possible to make a separation between enargite and the other copper minerals in a real ore system using pulp potential control.
- Enargite had the lowest rest potential compared to the other sulphide minerals, which caused strong galvanic interaction between enargite and pyrite.
- A conceptual flowsheet for separating enargite from other copper sulphide minerals was proposed to produce two concentrates: high As-low Cu concentrate and low As-high Cu concentrate.
Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my research higher degree candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

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Publications during candidature

Conference paper


Publications included in this thesis

No publications included.
Contributions by others to the thesis

This research project was discussed with my supervisors, Prof. Emmanuel Manlapig, Dr Elizaveta Forbes, Prof. Dee Bradshaw, and Dr Mansour Edraki. Prof. Emmanuel Manlapig and Dr Elizaveta Forbes prepared ore samples, organised funding, and established the initial project goals. They also regularly reviewed technical outcomes of the work, provided advice on the structure of the thesis, and reviewed the draft of the thesis. Dr Mansour Edraki provided advice in analysing the water chemistry results in Chapter 7. Prof. Dee Bradshaw assisted with the final corrections.

Mr Graeme Heyes provided technical guidance with respect to the flotation experiments, surface chemistry, and data analysis. He also reviewed and edited the final draft of the thesis. Prof. Tim Napier-Munn provided technical revisions during the development of this thesis and assisted in the analysis of the statistical results. Dr Cathy Evans contributed in the modelling part of the thesis. Dr Kym Runge and Dr Francois Vos provided guidance on the mass balancing part and bootstrap techniques. Dr Eugene Louwrens assisted in the editing of the thesis.

Dr Elaine Wightman and Ms Kellie White performed the MLA measurements described in this thesis. ALS-Minerals provided the chemical measurement and Dr David Tilley from United Mineral Services provided the QXRD analysis.

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“Do not feel lonely, the entire universe is inside you”

- Jalaluddin Rumi
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<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>µm</td>
<td>micron</td>
</tr>
<tr>
<td>As</td>
<td>Arsenic</td>
</tr>
<tr>
<td>BSE</td>
<td>Back-Scattered Electron</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic Acid</td>
</tr>
<tr>
<td>Eh</td>
<td>pulp potential</td>
</tr>
<tr>
<td>ENT</td>
<td>degree of entrainment</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>FG</td>
<td>Floatable Gangue minerals</td>
</tr>
<tr>
<td>g/t</td>
<td>gram per tonne</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively Coupled Plasma Atomic Emission Spectrophotometry</td>
</tr>
<tr>
<td>KEX</td>
<td>potassium ethyl xanthate</td>
</tr>
<tr>
<td>L</td>
<td>Litre</td>
</tr>
<tr>
<td>mg/L</td>
<td>milligram per Litre</td>
</tr>
<tr>
<td>mL</td>
<td>millilitres</td>
</tr>
<tr>
<td>MLA</td>
<td>Mineral Liberation Analyser</td>
</tr>
<tr>
<td>NECu</td>
<td>Non-Enargite Copper minerals</td>
</tr>
<tr>
<td>NSG</td>
<td>Non-Sulphide Gangue minerals</td>
</tr>
<tr>
<td>NFG</td>
<td>Non-Floatable Gangue minerals</td>
</tr>
<tr>
<td>pH</td>
<td>measure of the activity of the Hydrogen ion</td>
</tr>
<tr>
<td>ppm</td>
<td>part per million</td>
</tr>
<tr>
<td>Pₘ₀</td>
<td>80% passing size in µm</td>
</tr>
<tr>
<td>QXRD</td>
<td>Quantitative X-Ray Diffraction</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
</tr>
<tr>
<td>ToF -SIMS</td>
<td>Time of Flight Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>wt%</td>
<td>weight percentage</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1

INTRODUCTION

1.1. Background

Copper is an essential industrial metal because of its high ductility, malleability, thermal and electrical conductivity and resistance to corrosion. The U.S. Geological Survey reported that the identified copper resources are 2.1 billion tonnes and estimated the undiscovered copper to be 3.5 billion tonnes in 2013. The global consumption of refined copper increased by 36% from 2004 to 2014 and reached 22.9 million tonnes in 2014, which was greater than the global production by 406,000 tonnes (Brininstool, 2016, Johnson et al., 2014).

As the demand for copper is increasing, the extraction and development of resources including complex deposits with lower grade ores is becoming necessary. These complex deposits often contain high levels of impurities such as arsenic and economic levels of gold and silver (Bruce et al., 2011). Several copper projects are challenged by high levels of arsenic, such as El Indio deposits in Chile (Smith, 1986), Cananea deposit in Mexico (Perez-Segura and Zendejas-Mendivil, 1991), Neves-Corvo deposits in Portugal (Byrne et al., 1995), Tampakan deposit in Philippines (Senior et al., 2006), Northparkes, mine in Australia (Smith and Bruckard, 2007), and Rosebery mine in Australia (Long et al., 2014). More details about the copper deposits containing arsenic-copper bearing minerals are discussed by Long et al. (2012) and Castro (2014).

Arsenic-bearing copper minerals are economically attractive due to the amount of copper, gold, and silver they contain. However, arsenic is not only detrimental to important economic properties of copper metal such as electrical conductivity and ductility (Joseph and Kundig, 1999), it also causes serious environmental problems during the smelting process. Thus, high financial penalties are imposed by smelters to treat copper concentrates containing greater than 0.2% of arsenic and the rejection limit for smelter is 0.5% of arsenic (Wilson and Chanroux, 1993). According to the available references, the arsenic penalties a seller should pay, based on the amount of arsenic present in the concentrate, is US$3 per 0.1% of arsenic (Haque et al., 2012). In 2014, world production of arsenic trioxide was about 36,400 tonnes; China is remaining the world’s biggest producer by producing
approximately 25,000 tonnes of arsenic trioxide followed by Morocco with 8,800 tonnes (Bedinger, 2015).

In the past, this problem was alleviated by selective mining at the mine site or blending with lower grade arsenic ores. However, this practice was not widely used as it was costly and it prevented the capturing of the entire value of the deposit (Mayhew et al., 2011). The pyrometallurgical treatment with the roasting of the copper concentrate before smelting is an economical technique to remove arsenic. There are however serious environmental issues with roasting including potential atmospheric releases of either arsenic trioxide or sulphur dioxide, which limits the usage of this method. On the other hand, the hydrometallurgical methods like leaching are environmentally friendly proven techniques to remove arsenic, however, the final copper product from high-grade copper-arsenic concentrates are limited to about 95 percent due to the arsenic metal compound in the final product. Moreover, disposal of the arsenic-containing raffinate is a challenge (Mayhew et al., 2011, Agorhom et al., 2015).

The current industrial solution is to dilute the high-grade copper-arsenic concentrates with either a concentrate that does not contain arsenic or non-sulphide gangue materials. These techniques require reducing the concentrate grade to ensure that the arsenic grade in the final product is lower than the smelting limit. It is, however, a complicated process as generally the knowledge of the distribution of arsenic through the ore body is incomplete (Long, 2014). Furthermore, for the minerals containing both copper and arsenic, the rejection of arsenic reduces copper recovery, which affects the economic value of the deposit. As a result, it may be more economically beneficial to selectively concentrate arsenic minerals at an earlier stage of the processing (such as froth flotation) and produce a high-arsenic low-copper concentrate and a low-arsenic high-copper concentrate which then can be treated separately (Wilson and Chanroux, 1993, Fornasiero et al., 2001, Guo and Yen, 2005, Smith and Bruckard, 2007, Ma and Bruckard, 2009, Long et al., 2012, Long, 2014).

Recent research studies have been focused on the potential for separation of arsenic-bearing minerals (enargite and tennantite) from other copper/iron sulphides using froth flotation. However, it is challenging to separate them, as the arsenic-bearing minerals are strongly floatable with the conventional collectors. In addition, the standard depressants such as lime, cyanide, sulphide and permanganate are ineffective as the flotation responses of arsenic-bearing minerals are similar to other copper sulphide minerals (Fornasiero et al., 2001, Ma and Bruckard, 2009).

The use of chemical reagents, selective oxidation, or redox agents to selectivity change the surface of the minerals and control electrochemical conditions of the flotation pulp have been studied by many
researchers (Huch and Tucson, 1994, Castro and Honores, 2000, Yen and Tajadod, 2000, Fornasiero et al., 2001, Kantar, 2002, Guo and Yen, 2005, Senior et al., 2006, Smith and Bruckard, 2007, Filippou et al., 2007, Shibayama et al., 2010, Plackowski et al., 2012, Gul et al., 2013). It was found that controlled pulp potential (Eh) flotation is a prospective approach to promote the separation of arsenic-copper minerals from other copper sulphides due to the strong Eh dependence of arsenic mineral flotation (Menacho et al., 1993, Yen and Tajadod, 2000, Kantar, 2002, Guo and Yen, 2005, Senior et al., 2006, Bruckard et al., 2007, Smith and Bruckard, 2007, Bruckard et al., 2010, Haga et al., 2012a, Haga et al., 2012b).

Over the past decades, the effect of pulp potential on the flotation behaviour of many single copper sulphide minerals (Heyes and Trahar, 1977, Heyes and Trahar, 1979, Trahar, 1983, Guy and Trahar, 1984), and enargite (Guo and Yen, 2005, Senior et al., 2006) was determined at various potential (Eh) values. In particular, the study by Senior et al. (2006) demonstrated that the flotation recovery of pure enargite is significantly different from that of other sulphide minerals at a specific pulp Eh range. This information was used to propose a conceptual flowsheet for the selective enargite separation (Senior et al., 2006).

Some work was conducted to test out the new methodology for enargite removal from real ores based on the flotation behaviour of pure minerals, which showed that the separation was possible, but with limited success. It was found that the efficiency of the separation and the selection of the suitable pulp potential region depends on the mineralogy of the ore, the degree of liberation, and the type of the selected reagents, specifically the collector (Smith and Bruckard, 2007). Kappes and Gathje (2010) discussed some of the mineralogical challenges related to the process development to treat arsenic-bearing copper ore. It was concluded that high-quality chemical and mineralogical analysis is required in the development of the project and determination of the processing options, such as the liberation of the sulphide minerals and the gangue minerals, locking of the sulphide minerals with the gangue, and minerals grain size. They also mentioned that the control of the flotation chemistry is essential to achieve a good separation (Kappes and Gathje, 2010).

Based on the previous studies, it has been identified that although pulp potential conditions influence the separability of enargite from other copper minerals, the efficiency of the separation strongly depends on the mineralogical characteristics of the ore samples such as mineral liberation, size distribution, mineral grain size, and mineral association. The lack of fundamental study in this regard has been recognised. Therefore, a detailed study relating to the mineralogical characteristics of the feed and flotation products in a controlled potential flotation environment is necessary to identify the
floatability of arsenic/copper minerals in a complex ore system under oxidising and reducing conditions at a given pH.

1.2. Research objectives

The overall aim of this study is to develop an understanding of the effect of ore mineralogy on the floatability of enargite in complex ore system under controlled pulp potential conditions.

The specific objectives can be broken down as follows:

- To identify the mineralogical characteristics of two distinct ore samples, termed low arsenic ore (LAS) and high arsenic ore (HAS), within the same deposit in order to delineate the differences between the two in terms of liberation, grain size, and mineral associations.

- To understand the effect of applied potential on the floatability of enargite within these two ores, by characterising the flotation behaviour of both copper and copper-arsenic bearing minerals, and comparing the results to the literature data for pure mineral systems.

- To use the Particle Kinetic Model to predict the recovery of the HAS sample by using HAS mineralogy and floatability data of the LAS sample.

- To identify the causes for the differences in flotation behaviour of the two ores using both the surface chemistry study and the gangue mineralogy of both ores.

- To evaluate the equilibrium water chemistry of the flotation tests and use the results to predict the potential environmental hazards associated with processing arsenic-bearing ores.

- To propose a conceptual flowsheet to improve the separation of enargite from other copper sulphide minerals.
1.3. Thesis methodology

The scope of the research described in this project encompasses two aspects of the enargite separability from other copper sulphide minerals; mineralogical characteristics such as liberation, grain size, and composition of the minerals and the effect of electrochemistry in the flotation response. These aspects are the most important factors in understanding and predicting the separation performance of the ore. In order to achieve the project objectives the following tests have been performed (Figure 1-1):

- Chemical and mineralogical characteristics (such as liberation, grain size, and mineral association) of the two copper-arsenic samples (HAS and LAS) were determined.
- Proof of concept testing on two other arsenic-copper ore samples (A and B) was conducted.
- Flotation tests were performed at several pulp potential values, chosen from literature for two types of ore (HAS and LAS).
- The flotation recoveries were analysed on an unsized, size-by-size, and size-by-liberation basis to determine the floatability of each size and liberation fraction and their effects on flotation behaviour under controlled pulp potential conditions.
- The flotation recoveries of mineral composites from the two copper-arsenic samples (HAS and LAS) were compared with the equivalent floatability of pure minerals in various electrochemical conditions (gained from the literature) as well as maximum theoretical recoveries (calculated from mineralogy study).
- The Particle Kinetic Model was used to predict the final recovery of one ore system (HAS) at different Eh conditions by using the actual flotation data of other sample (LAS).
- The gangue mineralogy and flotation was studied to determine the floatability of different non-sulphide gangue minerals and their effects on the floatability of the valuable minerals.
- EDTA (Ethylenediaminetetraacetic Acid) extraction tests were conducted to determine the extent of oxidation of minerals in the flotation pulps.
- Water chemistry tests were performed to investigate the dissolved species in the flotation pulp. The results were then modelled by PHREEQC version 3 (Parkhurst and Appelo, 1999), using the MINTEQ database.
• The appropriate processing strategies to separate high As-low Cu concentrates from low As-high Cu concentrate were evaluated based on the obtained results of the mineralogy, flotation, and surface chemistry studies.

![Thesis structure diagram](image-url)
1.4. Scope and limitations

The main areas of this thesis are shown in Figure 1-2. The red box shows which methods are included in this thesis, for example flotation was selected from the beneficiation methods and the investigation of other beneficiation techniques was outside the scope of this project.

- Mineralogy:

The focus of this study was on a single deposit, and two levels of arsenic (Low and High). The ore was considered to be a good representation of a wide number of possible ore deposits as it is a typical porphyry-style.

The copper and arsenic-bearing copper sulphide minerals were the focus of this study. Additional minerals such as pyrite were not considered.

The mineralogy was evaluated at a set grind time, with the effects of particle size established through the study of different size fractions. Alternative grind times and grinding mechanisms were not investigated.
• Flotation:

Flotation experiments were performed on the ores only, and not on pure minerals. Flotation performance of the single minerals was gauged from the data available in the literature.

The work used the standard method of measuring and controlling pulp potential as used by other well recognised researchers.

Pulp potential was altered using a set reagent at pH 11. The effect of alternate pulp potential control chemistries was considered.

It should be noted that no reagent optimisation tests were carried out in this study. The suitable types and dosage of the reagents and operating conditions were selected based on the actual confidential reports on those ore samples.

Similarly, the effect of other chemical factors such as saline or seawater used as a flotation medium was not considered.

• Industrial impact:

The goal of the study was to provide an increased understanding of the factors governing the effective separation of arsenic-bearing copper minerals. Suggestions for improvement of current processing methods were made, however, the comprehensive development of a novel treatment strategy for arsenic-rich ores as well as the development of strategies for the treatment and management of concentrated arsenic slurries fall outside of the scope of the study.
1.5. Thesis outline

Chapter 1: Introduction

This chapter presents an overview of the research work, background, objectives, scope and limitations, thesis structure, and statement of sustainability.

Chapter 2: Literature review

This chapter contains a review of the current literature relating to the selective flotation of arsenic-bearing copper ores, the floatability, and surface chemistry of enargite. A brief description of the parameters, affecting the flotation of complex ore is also presented. At the end of this chapter, the gaps in the knowledge are identified, and the hypotheses are presented.

Chapter 3: Experimental methodology and analysis method

This chapter describes the details of the experimental methodology used in this research. It includes the description of the ore samples, crushing and grinding procedure, chemical and mineralogical characteristics methods, and procedure for sieving and cyclosizing. The flotation experiment methodology including reagents, equipment, and procedure is presented. The procedure for examining the surface oxidation by EDTA extraction and the water chemistry tests is described. The experimental error and mass balancing method is also detailed in this chapter.

Chapter 4: Mineralogical and chemical characteristics of the ore samples

This chapter discusses the results of the chemical and the mineralogical characteristics of the ore samples after grinding. Particle and mineral grain size distributions and locking and association characteristics of enargite and other minerals are described on a size-by-size basis. The liberation characteristics of minerals and theoretical grade-recovery curves are also presented. Finally, the key mineralogical attributes are identified.

Chapter 5: Flotation results

This chapter presents the results of the flotation performance of the high arsenic (HAS) and low arsenic (LAS) ores under different pulp potential conditions in unsized, size-by-size, and size-by-liberation basis. The entrainment effect is also detailed. The possibilities of separating the enargite from other copper minerals are discussed, and the results are compared to what was expected from the literature on pure mineral studies.
Chapter 6: Prediction of flotation recovery

This chapter describes the investigation of the applicability of the Particle Kinetic Model to predict the flotation recoveries in different size fractions from the feed mineralogy information. The flotation rates of fully liberated minerals in different size fractions for a 10-minute flotation time for the LAS sample are calculated. The flotation recovery of the HAS sample at different size fraction and Eh conditions is then predicted. At the end, the accuracy of the prediction is evaluated using the real flotation results and the possible reasons for the differences are described.

Chapter 7: EDTA extraction and water chemistry

This chapter includes the EDTA extraction and water chemistry tests results to find out the effect of surface oxidation and water chemistry on the floatability of enargite. It contains the oxidation amount and proportion of surface species in the mill discharge and flotation feed as a function of Eh for both HAS and LAS samples.

Chapter 8: Non-sulphide gangue floatability

This chapter discusses the floatability of different types of non-sulphide gangues under different pulp potential conditions and shows the effect of them on the recoveries, grades, and selective separation of enargite from other copper minerals.

Chapter 9 Process implications and possible flowsheet

This chapter includes the proposed flowsheet for separating enargite from other copper minerals by considering the mineralogical and metallurgical results on the HAS and the LAS samples.

Chapter 10: Conclusions and recommendations

This chapter comprises the summary of the work, the main achievements and includes recommendations for future research.
1.6. Statement of sustainability contribution

- Environment:

Mining activities can disturb the natural cycles of metals in the environment, which cause the release of some potentially toxic material in the food chain. It can affect human, animal, and plant life. For example, arsenic is a naturally occurring element, which is widely distributed in rocks, soil, and natural waters with the average level of 2 ppm. However, the level of arsenic can be increased by mining activities such as arsenic emissions from copper smelting or arsenic leachate from arsenic-bearing ores by cyanide or acid rock drainage. Arsenic is classified as a Group I carcinogen, meaning it is poisonous and causes cancer in humans (Bedinger, 2015, Flora, 2015).

This work seeks to improve industry environmental performance through the development of a method to selectivity separate arsenic mineral from other copper minerals. This method produces two concentrates, a low-arsenic high-copper concentrate and a high-arsenic low-copper concentrate, which can then be treated separately to extract copper. The low-arsenic high-copper concentrate can be sold to smelters without incurring any penalty, and the high-arsenic low-copper concentrate can be processed by other techniques such as low-temperature roasting or hydrometallurgy. The arsenic then can be stored underground or as a stabilised leaching product in the tailings storage facilities.

- Economic:

The smelters have become more restrictive for processing concentrates containing arsenic in recent years. The early removal of arsenic by selective flotation has several economic benefits. First, it makes the undeveloped copper deposits that contain high levels of arsenic possible to exploit. Second, it reduces the penalty costs of the smelters due to the removal of arsenic from the flotation concentrate as well as the costs of hydrometallurgy processes as a lower amount of material will import to this process. Lastly, by providing accurate information about the ore mineralogy and oxidation state of the ore, the implications of different processing strategies can be examined.
Chapter 2

LITERATURE REVIEW

This chapter reviews the literature relating to the mineralogy of arsenic-copper minerals, the selective flotation of arsenic-bearing copper ores, and the floatability, and surface chemistry of enargite.

It begins with a brief review on arsenic mineralogy, arsenic bearing copper minerals, and various deposits with the arsenic problem. A summary on the electrochemistry of copper sulphide minerals is presented. The natural, collectorless, and collector-induced floatability of chalcopyrite, enargite, and pyrite is then discussed. The techniques used to separate arsenic-copper minerals from other copper/iron sulphide minerals in single mineral systems are examined. A brief description of the parameters, affecting the flotation of complex ore is also presented. The chapter finishes with a literature summary, which leads to the identification of gaps in the literature and the thesis hypotheses.
2.1. Factors affecting the flotation performance

“Flotation is a physical-chemical separation process that utilised the difference in surface properties of the valuable minerals and the unwanted gangue minerals” (Wills and Napier-Munn, 2006). Many factors affect the flotation performance, which can be classified into three groups including the operation parameters, the machine variables, and the ore properties. The operation and machine parameters are associated with the physical and chemical nature of the flotation test while the ore properties are associated with the ore physical and chemical characteristics (Figure 2-1). This thesis has focused on ore parameters through controlling the other two components. The only other variable in this study is Eh.

Figure 2-1, Components that affect the overall flotation performance, modified from (Klimpel, 1984)
2.2. Arsenic-bearing minerals

Arsenic can exist in more than 200 minerals including elemental As, arsenides, sulphides, oxides, arsenates, arsenites and sulphosalts. Some of these minerals are not common in the environment, but some are widely distributed in the earth’s crust such as arsenopyrite (FeAsS) which is the most abundant arsenic mineral (Smedley and Kinniburgh, 2002). The major copper-arsenic minerals often occur at various quantities in copper deposits are enargite (Cu₃AsS₄) and tennantite (Cu₁₂As₄S₁₃) (Lattanzi et al., 2008).

Enargite (Cu₃AsS₄) is found in hydrothermal vein deposits formed at moderate temperatures (300-400°C). The lower temperature form of enargite is luzonite (Cu₃AsS₄) (Lattanzi et al., 2008). Enargite replaces pyrite and bornite in porphyry copper deposits (Perez-Segura and Zendejas-Mendivil, 1991). Enargite-bearing massive pyrite deposits are essential parts of the upper volcanic portions of porphyry copper systems, which occurred within zones of advanced argillic alteration (Sillitoe, 1983).

Enargite is a grey-black mineral with a metallic lustre, Moh’s hardness index of 3, and specific gravity of 4.4 g/cm³. Enargite consists of 48.42% Cu, 19.02% As (in the pentavalent state) and 32.56% S and acts as a semiconductor (Lattanzi et al., 2008). It is a complex copper-arsenic sulphide mineral that typically contains significant gold and silver values (Tajadod, 1997). In addition, enargite may contain minor amounts of other elements like Hg and Sb. A summary of the most important properties of enargite is given in Table 2-1.

| Table 2-1, Properties of enargite, from (Anthony, 1990, Magee, 2000, Safarzadeh et al., 2014, Lotter et al., 2016) |
| --- | --- |
| Mineral Property | Description |
| Formula | Cu₃AsS₄ |
| Hardness | 3-3.5 Mohs |
| Specific Gravity | 4.46 g/cm³ |
| Molecular Weight | 393.8 g/mol |
| Copper Percent | 48.4 |
| Crystal Structure | Orthorhombic |
| Colour | Steel gray-black |
| Melting Point | 640-690°C |
| Lustre | Metallic to Dull |
| Electrical Conductivity | Semiconductor, Type P |
2.3. Electrochemical review of sulphide minerals in the flotation system

One of the key factors in sulphide flotation systems is the electrochemical reactions (Woods, 1976). Many researchers have been working on the investigation of the electrochemical reaction mechanism involved in the flotation of sulphide minerals. Since the 1960’s, different electrochemical techniques have been established to explain the interactions in an aqueous solution. Many of these new developments are still in the early stages but have shown promising results to predict the minerals behaviour in the flotation systems, particularly for complex ore (Rao et al., 1992).

The electrochemical study in flotation considers mineral surface species, which have been formed by an anodic oxidation and cathodic reduction (Woods, 2003). The theory of flotation of sulphide minerals can be divided into five parts: natural floatability of sulphide minerals, the sulphide minerals pre-oxidation, the mineral-reagents interactions, the semiconductor property of sulphide minerals, and electrochemical reactions in the grinding stage (Hu et al., 2009). There are two types of electrochemical techniques; a static type which measures the rest potential vs. time and a dynamic type which includes many different methods such as voltammetry, cyclic voltammetry, electrochemical impedance spectroscopy, etc. (Rao et al., 1992, Zoski, 2007).

There are two kinds of electrochemical cells including galvanic cells and electrolyte cells. The reactions in the galvanic cells (i.e. batteries) are spontaneous (\(\Delta G<0\)), whereas the electrolyte cells require the applied potential to run an electrochemical reaction (\(\Delta G>0\)) (Zoski, 2007).

Several types of electrodes are being used in measuring the oxidation-reduction potentials. The main sensing electrodes are noble metal electrodes, ion selective electrodes, and natural mineral electrodes. Noble metal electrodes are made of platinum or gold, which is almost regularly used to measure Eh in laboratory testwork and full-scale processes. Noble electrodes are passive thus chemical or electrochemical reactions do not have an effect on them (Chander, 2003, Woods, 2003).

The potential is measured with reference to Reference Electrodes such as calomel (Hg/Hg\(_2\)Cl\(_2\)) or silver/silver chloride (Ag/AgCl) electrodes. The measured potential is reported on a hydrogen scale by adding 0.2415 V for the calomel electrode or 0.200 V for the silver chloride electrode. The standard hydrogen electrode (SHE) has a potential of zero millivolts at \(T=25^\circ C\) and \(P=1\) atm. (Rao et al., 1992, Chander, 2003, Woods, 2003).

Different kinds of electrochemical potentials are known such as oxidation-reduction potential (redox), rest potential, reversible potential, pulp potential (Eh), and standard potential (E\(^\circ\)) which all refer to chemical reactions (Rao et al., 1992).
Pulp potential is used for measuring the potential across the mineral/solution interface. It is usually measured by submerging the sensing/reference electrode pair in the pulp to measuring the potential of the mineral of interest (Woods, 2010). Pulp potential can be controlled by an external power source (direct control of the potential) or redox reagents. Direct control of the potential means the application of an external energy source on the mineral slurry. Redox reagents method uses the chemical reagents to adjust the pulp potential either through the activity of oxygen in the pulp (by changing the oxygen content of the flotation gas) or by adding suitable oxidising agents and reducing agents (Cheng and Iwasaki, 1992, Rao et al., 1992, Kant, 1997).

The oxidation-reduction potential or redox potential is a measure of the tendency of a solution to be oxidised or reduced. The half-cell reaction can be written as:

\[
\text{Reduced state} = \text{Oxidised state} + n \text{ Electrons}
\]

The relationship between any redox potential \( E \) and the standard potential \( E^\circ \) can he calculated from the Nernst Equation (Rao et al., 1992).

\[
E = E^\circ + \frac{RT}{nF} \ln \left( \frac{a_{\text{Red}}}{a_{\text{Ox}}} \right)
\]

**Equation 2-1**

where: \( n \) is number of electrons transferred in the half reaction, \( R \) is gas constant (8.314 J/mol.K), \( T \) is absolute temperature (°K), \( F \) is Faraday constant (96487 J/V.mol electron), a is chemical activity of species (mol/L), \( a_{\text{Red}} \) is a reducing agent, and \( a_{\text{Ox}} \) is an oxidising agent. \( E \) depends on the concentration of the species in the reactions and the temperature (Rao et al., 1992). It can also be written in the form of \( \log_{10} \) instead of ln. At room temperature, (25°C) \( RT/F \) is equal to 25.693 mV and the equation is:

\[
E = E^\circ + \frac{0.0592}{n} \log \left( \frac{a_{\text{Red}}}{a_{\text{Ox}}} \right)
\]

**Equation 2-2**

There is a close relationship between pH and potential due to the presence of hydrogen ion. Potential decreases with increasing pH according to Nernst equation:

\[
pH = -\log H^+
\]

**Equation 2-3**

Therefore, the Nernst Equation in laboratory measurement is:
\[ Eh = E^\circ - 0.059pH \]  

Equation 2-4

where \( E^\circ \) is 0.85 V in oxygenated acid solutions and 0.95 V in oxygenated alkaline solutions (Chander, 2003).

2.3.1. Eh-pH diagram

The metal ion concentration in solution depends on the oxidation characteristics of the mineral and is a function of pH. It is, therefore, traditional to represent the thermodynamic data of a mineral in the solution in the form of an Eh-pH diagram (Chander, 1999). Eh-pH diagrams have proven to be a standard method for representing the main species involved in the process and have been applied successfully to examine sulphide minerals flotation systems (Rao et al., 1992, Chander, 1999, Hu et al., 2009).

2.3.2. Mixed potential theory

The electrochemical theory assumes that the summation of all the oxidation and reduction reactions in the system should be equal. However, when two (or more) oxidation/reduction couples are present in the system, particularly flotation system, the redox conditions in the system is not characterised by a unique potential value from the Nernst equation, but from a potential called “mixed potential”. It means that the mineral particles accept a particular potential value, which is in between of the reversible reactions (Cheng and Iwasaki, 1992, Rao et al., 1992, Chander, 2003, Woods, 2003, Woods, 2010).
2.4. Natural floatability and collectorless flotation of sulphides

It has been known for many years that a few sulphide minerals, such as molybdenite, orpiment, realgar, and stibnite have shown natural hydrophobicity. The assumption for the natural floatability can be explained by their surface composition and structure; Van der Waal’s bonds between sulphur atoms are naturally hydrophobic and do not interact with water molecules. Therefore, natural floatability of these minerals does not require specific Eh for flotation (Heyes and Trahar, 1979, Hayes and Ralston, 1988, Trahar et al., 1994, Chander, 1999).

On the other hand, some other sulphide minerals such as chalcopyrite become floatable in the absence of collectors. This collectorless floatability of sulphide minerals can happen under a certain range of potentials; an oxidising potential is usually a requirement for collectorless flotation (Heyes and Trahar, 1977, Cheng and Iwasaki, 1992, Chander, 1999, Hu et al., 2009, Woods, 2010).

The influences of pulp potential on the collectorless floatability of sulphide minerals such as chalcopyrite, chalcocite, cuprite, galena, pyrite, pyrrhotite, and sphalerite have been studied by many researchers (Heyes and Trahar, 1977, Heyes and Trahar, 1979, Trahar, 1983, Heyes and Trahar, 1984, Hayes and Ralston, 1988, Cheng and Iwasaki, 1992, Kant, 1997, Fairthorne et al., 1997, Guo and Yen, 2003, Woods, 2003, Guo and Yen, 2005). It was observed that the oxidation of the sulphide minerals produces three forms of sulphur on their surface; metal sulphide ($S^0$), polysulphides ($S_xO_y$), and elemental sulphur ($S_8$); all of which are considered hydrophobic (Leroux et al., 1989, Chander, 1999). Polysulphides are the most prominent in alkaline conditions while elemental sulphur is dominant under acidic conditions.

The oxidation reaction for sulphide minerals in water can be represented by reactions 2-6 and 2-7. In acidic solutions, the metal sulphide undergoes the formation of a metal cation and elemental sulphur:

$$MS \rightarrow Mn^+ + S^0 + ne^-$$

Equation 2-5

In alkaline solutions, it involves the formation of elemental sulphur and metal hydroxide species:

$$MS + nH_2O \rightarrow M(OH)_n + S^0 + nH^+ + ne^-$$

Equation 2-6

where M is metal ion (Rao et al., 1992, Ralston et al., 2005).
Any of these species can cause the mineral surface to become hydrophobic to a certain degree, which is the basis of collectorless flotation (Heyes and Trahar, 1984, Rao et al., 1992). However, under highly oxidative conditions, sulphate or thiosulphate would be formed which causes a lack of hydrophobicity (Rao et al., 1992, Hu et al., 2009).

2.4.1. Collectorless flotation of chalcopyrite

It was observed by Heyes and Trahar (1977) that modest oxidation is required in the flotation of chalcopyrite without collector to oxidise the sulphide to sulphur. It can happen by grinding chalcopyrite in an iron mill followed by aeration which makes the surface of chalcopyrite hydrophobic (Heyes and Trahar, 1977). Hayes and Ralston (1988) found that grinding under reducing conditions would cause the formation of hydrophilic surface coatings while grinding under weakly oxidising conditions produces hydrophobic surface products. These results were confirmed by Gardner and Woods (1979) and Trahar (1983).

Measurements of pulp potential under the conditions required for natural floatability showed a clear correlation between the potential and recovery of chalcopyrite (Figure 2-2) (Heyes and Trahar, 1977). Gardner and Woods (1979) applied a potential directly to the pulp containing chalcopyrite and then floated with nitrogen gas and confirmed that the floatability of chalcopyrite was due to pulp potential rather than oxygen presence. They commented that a certain degree of oxidation is essential for chalcopyrite floatability. The oxidation reaction in alkaline medium was proposed to be:

\[ \text{CuFeS}_2 + 3\text{HO}_2 \rightarrow \text{CuS} + \text{Fe(OH)}_3 + \text{S} + 3\text{H}^+ + 3\text{e}^- \]

Equation 2-7

And in acidic medium:

\[ \text{CuFeS}_2 \rightarrow \text{CuS} + \text{Fe}^{2+} + \text{S} + 2\text{e}^- \]

Equation 2-8

This CuS layer is responsible for the collectorless flotation of chalcopyrite.
The Eh-pH diagram of surface oxidation of chalcopyrite is constructed by combining the above
equations (Figure 2-3) (Hu et al., 2009):

\[ Eh = 0.536 - 0.059pH \]

Equation 2-9

Figure 2-2, Collectorless flotation of chalcopyrite at different Eh conditions at pH 10, modified
from (Heyes and Trahar, 1977)

Figure 2-3, Eh-pH diagram of chalcopyrite in water, modified from (Hu et al., 2009)
2.4.2. Collectorless flotation of pyrite

Heyes and Trahar (1984) and Trahar et al. (1994) investigated the collectorless floatability of pyrite and observed that it did not show self-induced floatability in mildly alkaline solution, and displayed weak floatability in acidic solution. By contrast, pyrite showed strong collectorless floatability in the presence of a second sulphide mineral such as galena or chalcopyrite.

Pyrite oxidation reactions contain the reactions generating hydrophobic species (Ekmekçi and Demirel, 1997):

\[
\text{FeS}_2 \rightarrow \text{Fe}^{2+} + 2\text{S} + 2\text{e}^- \\
\text{FeS}_2 + 3\text{HO}_2 \rightarrow \text{Fe(OH)}_3 + 2\text{S} + 3\text{H}^+ + 3\text{e}^- \\
\text{Equation 2-10}
\]

and, the reactions generating hydrophilic species:

\[
\text{FeS}_2 + 3\text{HO}_2 \rightarrow \text{Fe}^{2+} + \text{S}_2\text{O}_3^{2-} + 6\text{H}^+ + 6\text{e}^- \\
\text{Equation 2-11}
\]

The Eh-pH diagram for pyrite surface oxidation is shown in Figure 2-4. The reactions producing elemental sulphur determine the lower limit potential of flotation. The reactions producing thiosulphate and other hydrophilic species define the upper limit of potential. The collectorless flotation of pyrite is weak in a very strong acidic conditions and very narrow Eh range. Also, pyrite does not show self-induced collectorless floatability in an alkaline environment. It can be due to the presence of Fe(OH)_3 on the surface of pyrite (Trahar et al., 1994, Hu et al., 2009). However, it was observed that in the presence of another sulphide mineral such as chalcopyrite, pyrite can float strongly in the absence of collector (Trahar et al., 1994) even at alkaline pH, when it is expected to be depressed (Rao et al., 1992).
2.4.3. Collectorless flotation of enargite

Kantar (2002) studied the natural floatability of enargite at different Eh conditions using hydrogen peroxide and sodium sulphide to control the potential of the pulp. It was found that enargite natural floatability was strongly depending on pH of the pulp. In the acidic region, enargite displayed natural floatability and was capable of collectorless flotation. The addition of hydrogen peroxide (oxidising agent) enhanced the enargite recovery due to the formation of hydrophobic elemental sulphur on the enargite surface. In contrast, the enargite floatability decreased slowly towards alkaline conditions. Its hydrophobicity decreased with addition of hydrogen peroxide and collectorless flotation was not possible due to the formation of CuO (Kantar, 2002). These observations are in correlation with the findings of Arribas Jr (1995) and Lattanzi et al. (2008). However, Castro and Honores (2000) observed poor floatability of enargite in a wide pH range and reported that enargite does not have natural floatability.

The oxidation reaction in acidic environment was proposed (Kantar, 2002):

\[
Cu_3AsS_4 + 4H_2O \rightarrow 3CuS + H_2AsO_4^- + 6S^0 + 6H^+ + 5e^{-}
\]

Equation 2-12

The oxidation reaction in alkaline environment:

\[
Cu_3AsS_4 + 23H_2O \rightarrow 3CuO + HAsO_4^{2-} + 4SO_4^{2-} + 45H^+ + 35e^{-}
\]

Equation 2-13
Guo and Yen (2005) investigated the collectorless flotation of enargite and chalcopyrite in a pH 10 (Figure 2-5). Chalcopyrite strongly floated in the Eh range from +0.1 V to +0.4 V SHE, while enargite did not show floatability at a potential lower than +0.05 V SHE. Enargite flotation recovery increased sharply when the pulp potential raised from +0.05 to 0.1 V SHE. Its recovery then increased gradually as the pulp potential was increased from +0.1 V to +0.7 V SHE and decreased when the pulp potential was further raised to +0.7 V SHE. The low collectorless floatability of enargite at a potential lower than 0.5 V SHE was due to the lack of S⁰ at enargite surface (Guo and Yen, 2005).

![Figure 2-5](image)

**Figure 2-5, Collectorless floatability of enargite and chalcopyrite at different Eh conditions at pH 10, modified from (Guo and Yen, 2005)**

Bruckard et al. (2007) investigated the natural floatability of metallic arsenic. A metallic arsenic-quartz mixture was used for the test, which was conducted at natural Eh and pH 6 for an 8 min period with polypropylene glycol frother. It was observed that metallic arsenic displays no significant natural floatability (Bruckard et al., 2007).
The Eh-pH diagram for enargite can be divided into three parts, copper/water system, arsenic/water system, and sulphur/water system (Figure 2-6). The Eh-pH diagram of copper/water system suggests that enargite first oxidises to CuS and then the CuS oxidises to CuO in alkaline conditions and Cu$^{2+}$ in acidic conditions under highly oxidising solution.

In Figure 2-6-b, which shows arsenic species in the arsenic/water system, HAsO$_4^{2-}$ becomes dominant in neutral to alkaline conditions, and H$_2$AsO$_4$ and AsO$_4^{2-}$ dominate in acidic conditions.

As for other sulphide minerals, enargite oxidises to elemental sulphur in all pH ranges (Figure 2-6-c). However, it easily converts to SO$_4^{2-}$ due to the instability of elemental sulphur in alkaline conditions (Kantar, 2002).

![Figure 2-6, Eh-pH diagram for the copper/water (a), arsenic/water (b), and sulphur/water (c) systems with 1 M dissolved species at 25 °C and P=1 bar, from (Kantar, 2002)](image-url)
2.5. Collector-induced flotation of sulphide minerals

Flotation recovery depends on the formation of a hydrophobic film on the mineral surface. This film usually forms through interaction with the collector. It is well known that sulphide minerals are floated very well in the presence of sulphydryl collectors such as xanthate. The mechanism of this collector-induced flotation from the viewpoint of mixed potentials was reviewed by Woods (1984). The electrochemical reactions of the sulphide minerals and collector are assumed to take place via reactions that involve (Rao et al., 1992, Woods, 2010):

- A cathodic reduction of oxygen:

\[
\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- 
\]

Equation 2-14

- An anodic oxidation reaction of collector which collector transfers electron to the mineral in different ways shown in following equations:

The electrochemical adsorption of thio-collector ion:

\[
X^- \rightarrow X_{adsorbed} + e^- 
\]

Equation 2-15

The oxidation of the thio-collector to its dithiolate:

\[
2X^- \rightarrow X_2 + 2e^- 
\]

The overall reactions are:

\[
2X^- + \frac{1}{2}O_2 + H_2O \rightarrow X_2 + 2OH^- 
\]

Equation 2-16

The chemisorption reaction mechanism:

\[
MS + 2X^- \rightarrow MX_2 + S + 2e^- \\
MS + 2X^- + 4H_2O \rightarrow MX_2 + SO_4^{2-} + 8H^+ + 8e^- \\
2MS + 4X^- + 3H_2O \rightarrow 2MX_2 + S_2O_3^{2-} + 6H^+ + 8e^- 
\]

Equation 2-17
where $X^-$ represents a thio ion and MS accounts for a sulphide mineral.

### 2.5.1. Flotation of enargite with collector

Kantar (2002) investigated the flotation of enargite in the presence of $5 \times 10^{-3}$ M sodium ethyl xanthate (NaEX) solution at pH 10.5 at different Eh conditions. It was observed that the enargite floatability is strongly dependent on the Eh of the flotation solution. No floatability observed at Eh below +0.07 V SHE, it increased sharply to a maximum value of circa 100% at potentials between 0.15 and 0.27 V SHE, and decreased suddenly towards higher potentials. It was concluded that the formation of dixanthogen was the essential reason for the flotation of enargite in alkaline solutions. However, the presence of additional oxygen at potential higher than 0.35 V SHE, enhanced oxidation of the enargite surface and accumulated the amounts of hydrophilic oxidation products, which caused decreasing enargite recovery (Kantar, 2002). Pauporte and Schuhmann (1996) confirmed the formation of copper xanthate and dixanthogen on the enargite surface by using a voltammetric study of the enargite-ethylxanthate system. Kantar (2002) suggested the following reaction for the formation of CuX on the enargite surface (Kantar, 2002):

$$
	ext{Cu}_3\text{AsS}_4 + 3X^- + 20\text{H}_2\text{O} \rightarrow 3\text{CuX} + \text{HAsO}_4^{2-} + 4\text{SO}_4^{2-} + 39\text{H}^+ + 32e^-
$$

Equation 2-18

![Figure 2-7](image_url)

**Figure 2-7, Floatability of enargite with NaEX collector at different Eh conditions at pH 10.5, from (Kantar, 2002)**

Castro et al. (2003a) observed good floatability of enargite with different types of thiol collector over a wide pH range (Figure 2-8).
Single mineral flotation of synthetic enargite and natural chalcopyrite in a $7 \times 10^{-5}$ M PAX solution at pH 10 was conducted by Guo and Yen (2005) (Figure 2-9). It was observed that the floatability of enargite and chalcopyrite showed a similar trend in the Eh range between -0.2 to +0.4 V SHE. However, the floatability of chalcopyrite decreased sharply when the Eh was increased from +0.4 V to +0.5 V SHE. In contrast, enargite exhibited good floatability even when the pulp potential was higher than +1.65 V SHE. Similar to the collectorless flotation of enargite (Figure 2-5), its recovery was reduced at a potential higher than +0.7 V SHE. Comparing the collectorless flotation of enargite with its collector-induced (Figure 2-5 and Figure 2-9), showed that in single mineral flotation, enargite floated much faster in the presence of collector than in the collectorless. They concluded that it could be due to the fact that the hydrophobic species at the enargite surface in the collectorless environment were $S^0$ and the hydrophobic species at the enargite surface in the collector environment were $S^0 + X^2$ (dixanthogen). The enargite surface with $S^0$ and dixanthogen was more hydrophobic than the surface with only $S^0$ (Guo and Yen, 2005).

Senior et al. (2006) determined the floatability of enargite at various Eh values between -500 and +500 mV SHE at both pH 8 and 11 using 20 g/t potassium ethyl xanthate (KEX) as a collector (Figure 2-10). It was observed that there is a threshold potential for enargite (recovery of enargite reaches 50% in 1-min flotation), which below that it does not float and above that, it does. At pH 8, this was found to be about -75 mV SHE and at pH 11 circa -25 mV SHE.

Bruckard et al. (2007) investigated the floatability of metallic arsenic in the presence of xanthate collector and observed that although metallic arsenic showed no natural floatability, it floats easily over a wide range of pH and Eh with a KEX and a polypropylene glycol frother (Figure 2-11) (Bruckard et al., 2007).
Figure 2-9, Floatability of enargite and chalcopyrite with PAX collector at different Eh conditions at pH 10, modified from (Guo and Yen, 2005)

Figure 2-10, Floatability of enargite at 1 min flotation with KEX collector at different Eh conditions at pH 8 and 11, modified from (Senior et al., 2006)

Figure 2-11, Floatability of arsenic metal at 1 min flotation with KEX collector at different Eh conditions at pH 6 and 10, modified from (Bruckard et al., 2007)
2.6. Selective flotation of arsenic-copper minerals

The possibility of the separation of arsenic-bearing minerals (enargite and tennantite) from other copper/iron sulphides such as; chalcopyrite (CuFeS₂), covellite (CuS), chalcocite (Cu₂S), bornite (Cu₃FeS₄), and pyrite (FeS₂), has been studied by many researchers (Fornasiero et al., 2001, Kantar, 2002, Guo and Yen, 2005, Senior et al., 2006, Smith and Bruckard, 2007, Filippou et al., 2007, Shibayama et al., 2010, Plackowski et al., 2012, Gul et al., 2013). They tried to separate the arsenic-copper minerals from other copper minerals through using chemical reagents as a depressant, selective oxidation, or redox agents to control electrochemical conditions of the flotation. In this section of the thesis, these three methods of separation are discussed.

2.6.1. Selective flotation using depressants

The use of depressants is common for treating complex sulphide ores, especially when separation of different valuable minerals is required, or a selectivity problem is present (Bulatovic, 2007). Some possible electrochemical mechanisms which happen during mineral depression, can be a) oxidation of mineral surface, b) inhibition of collector oxidation, c) inhibition of oxygen reduction, and d) competition for surface metal sites by complexation (Magee, 2000).

Enargite is strongly floatable with thiol-type collectors. Thus, the separation of enargite from other sulphide copper minerals using standard depressants is difficult (Tajadod, 1997). Various depressants have been tested to selectively depress arsenic bearing minerals, such as lime, sodium sulphide, cyanide, and magnesia mixture.

Lime either as CaO or Ca(OH)₂ is added to make a strong alkaline condition for sulphide flotation. The depressive action of lime on mineral is probably due to the adsorption of calcium ions on its surface and the formation of the hydrophilic compound CaSO₄·2H₂O, which act to prevent electron transfer on the mineral surface (Fuerstenau et al., 1985, Fuerstenau and Han, 1993, Bulatovic, 2007).

In the flotation of mixed sulphide minerals, sodium sulphide (Na₂S) or hydrosulphide has been used by xanthate collector, either in bulk or in selective flotation (Fuerstenau et al., 1985). Tajadod and Yen (1997) investigated the effect of sodium sulphide as a depressant on the selective flotation of enargite and chalcopyrite. It was found that sodium sulphide is an effective depressant for chalcopyrite, but it also has some depressive effects on enargite. Thus, less selectivity is achieved by sodium sulphide (Tajadod, 1997).
Sodium cyanide (NaCN) is probably the most commonly used reagent for selective separation of many complex mineral systems with suitable adjustment of conditions, such as pH, concentration, and conditioning time. The most important aspects of cyanide in flotation is its extreme ability to dissolve the oxides, sulphides and xanthate of the transition metals, reduction of the potential of the flotation pulp (Heyes and Trahar, 1977), and the oxidation of xanthate to dixanthogen because of the large consumption of oxygen by cyanide (Wang, 1989). The flotation selectivity was improved in the study of sodium cyanide as a depressant for nickel arsenides by Qun and Heiskanen (1990).

Potassium cyanide (KCN) provided the best selectivity in the depressing of arsenopyrite from Broken Hill lead concentrates in a laboratory study by David and Quast (1991): 75 percent reduction in arsenic recovery was achieved at pH 10 by using potassium cyanide as a depressant while lead recovery was unaffected.

Tajadod and Yen (1997) investigated the surface properties and flotation characteristics of enargite and chalcopyrite in the presence of a xanthate collector using sodium cyanide and potassium permanganate (KMnO₄) as depressants. Depression of enargite from a bulk chalcopyrite-enargite concentrate at pH 9 was achieved with appropriate concentrations of sodium cyanide and potassium permanganate (Tajadod and Yen, 1997). Although it was found that sodium cyanide is a suitable depressant for enargite, which reduces the arsenic content of copper concentrates, high associated copper losses were recognised. Such massive losses are not sustainable in industrial applications. In addition, no consideration is given to achieve a separation in the more complex multi-mineral systems that exist in practice (Tajadod, 1997).

The application of sodium cyanide also has environmental restrictions therefore non-cyanide reagents would be more suitable for depressing enargite. Using a mixture of magnesium chloride, ammonium chloride, and ammonium hydroxide (MAA) as a depressant for enargite resulted in the achievement of the separation of enargite and chalcopyrite. It was demonstrated that a magnesium-ammonium mixture depressed enargite, while it did not have any depressing effect on chalcopyrite flotation, which allows a selective separation of chalcopyrite and enargite from artificial mineral mixtures (Figure 2-12) (Tajadod, 1997, Yen and Tajadod, 2000).
Castro et al. (2003b) used the magnesia mixture as a depressant for a pure enargite sample and reported some results contrary to the findings of Yen and Tajadod (2000); no depression was observed in the pH range 7-9 using 0-11 kg/t magnesia mixture. At pH 10, weak depression of enargite was observed using about 2.5 kg/t MAA. However, when the dosage increased to 7 kg/t, the depression disappeared completely (Figure 2-13).
2.6.2. Selective flotation using selective oxidation

The oxidation of sulphide minerals has a major role in their floatability behaviour. The oxidation can promote the adsorption of collectors on the mineral surface or prevent their adsorption by forming a hydrophilic layer on the mineral surface (Fullston et al., 1999a). Hence, studying the oxidation of arsenic minerals is important in understanding their flotation performance (Ma and Bruckard, 2009).

A number of comprehensive studies have been performed on the separation of enargite and tennantite by selective oxidation (Fullston et al., 1999a, Fullston et al., 1999b, Fullston et al., 1999c, Fornasiero et al., 2001). Fullston et al. (1999a), (1999b) studied the surface oxidation of enargite and tennantite at pH 11 by measuring and monitoring their dissolution, zeta potential, and X-ray photoelectron spectroscopy (XPS) characteristics. It was found that the amount of copper dissolved from the enargite and tennantite was much higher than that of arsenic. The XPS study showed that even with weak oxidants such as dissolved oxygen, two-oxidation layers form on the surface of enargite: a thin layer comprised of copper and arsenic oxide, or hydroxide, and a layer made of metal-deficient sulphide and/or polysulphide. In addition, a small amount of iron, as an impurity, was observed on the mineral’s surface which can cause the galvanic interactions in these samples (Fullston et al., 1999a, Fullston et al., 1999b).

In another study by Fullston et al. (1999c) the zeta potential of the copper sulphide minerals (chalcoctite, covellite, chalcopyrite, bornite, enargite, and tennantite) were investigated and the oxidation rate compared. It was stated that the oxidation rate of the copper sulphide minerals at pH 11 follows the order: chalcocite > tennantite > enargite > bornite> covellite > chalcopyrite. It means that the separation of tennantite and enargite from the other copper sulphide minerals is possible if the ore does not contain chalcocite (Fullston et al., 1999c). The oxidation order of the non-arsenic copper minerals is in agreement with that of their rest potential value (Fornasiero et al., 2000).

Fornasiero et al. (2001) examined the separation of enargite and tennantite from other copper sulphide minerals (chalcoctite, covellite, and chalcopyrite) by flotation in mixed mineral systems. They observed that separation was difficult in the absent of H₂O₂ at pH 5. However, they showed separation at pH 11. The better separation happened after oxidation of the minerals surfaces by H₂O₂ at pH 5, or at pH 11 followed by EDTA addition, before collector addition. The XPS results confirmed that the surface of the arsenic minerals was more oxidised than the non-arsenic minerals (Figure 2-14 and Figure 2-15) (Fornasiero et al., 2001).
Figure 2-14, Flotation recoveries of the chalcocite-enargite, covellite-enargite, chalcopyrite-enargite, chalcocite-tennantite, covellite-tennantite and chalcopyrite-tennantite mixed mineral systems at 1, 2, 4 and 8 min at pH 5, modified from (Fornasiero et al., 2000).

Figure 2-15, Flotation recoveries of the chalcocite-enargite, covellite-enargite, chalcopyrite-enargite, chalcocite-tennantite, covellite-tennantite and chalcopyrite-tennantite mixed mineral systems at 1, 2, 4 and 8 min at pH 11, modified from (Fornasiero et al., 2000).
Filippou et al. (2007) mentioned enargite is generally characterised as a “refractory mineral,” as it cannot be easily digested in aqueous media. Even in alkaline solutions, enargite is not dissolved easily and is the last in the order by which copper sulphides dissolve in ammonia solutions: chalcocite > covellite > bornite > chalcopyrite > enargite (Filippou et al., 2007).

Lattanzi et al. (2008) focused on the oxidative reactions of enargite and claimed that the oxidation of enargite in solution at low pH is moderately slower than the oxidation rate at higher pH. They mentioned that for oxidation in acidic solutions, potentials greater than 0.5 V SHE are required. They noted that oxidation-dissolution of enargite could be an acid-generating process:

\[
\text{Cu}_3\text{AsS}_4 + 8.75\text{O}_2 + 2.5\text{H}_2\text{O} \rightarrow 3\text{Cu}^{2+} + \text{AsO}_4^{3-} + 4\text{SO}_4^{2-} + 5\text{H}^+ \\
\text{Equation 2-19}
\]

In the presence of ferric ion:

\[
\text{Cu}_3\text{AsS}_4 + 35\text{Fe}^{3+} + 20\text{H}_2\text{O} \rightarrow 3\text{Cu}^{2+} + \text{HAsO}_4^{2-} + 4\text{SO}_4^{2-} + 39\text{H}^+ + 35\text{Fe}^{2+} \\
\text{Equation 2-20}
\]

At alkaline conditions, the oxidation of enargite is fast with the formation of a copper-depleted layer and Cu-O species on its surface. It is also possible that cupric arsenate is formed. An XPS study of the enargite surface at alkaline pH also indicated the presence of cupric oxide and arsenic oxide on the enargite surface (Lattanzi et al., 2008). It was noted that most of the laboratory experiment are conducted on polished surfaces of enargite, which may not be representative of an untreated surface or a mixed mineral system.

In another detailed study of the electrochemical behaviour of enargite, a passivation layer was found to form over a broad potential range (-660 to +1070 mV SHE). The main oxidation product found on the mineral surface was copper hydroxide (\(\text{Cu(OH)}_2\)) (Guo and Yen, 2014).
2.6.3. Selective flotation using pulp potential (Eh) control


The difference in the floatability of sulphide minerals at different pulp potentials, as shown in Figure 2-16 (Richardson and Walker, 1985) could provide an opportunity to selectively separate them by differential flotation (Chander, 1999). Some research laboratories in Australia, Canada, USA, China, Russia, and Finland have attempted to use the pulp potential control to improve flotation selectivity at industrial mineral process plants (Woods, 2000).

![Figure 2-16, Flotation recovery of different sulphide minerals as a function of Eh, modified from (Richardson and Walker, 1985)](image)
Flotation separation of arsenic-bearing copper sulphides from other copper sulphides has also been studied since these minerals have similar flotation properties to copper sulphide minerals. Research on separation of arsenic-bearing copper sulphides from other copper sulphides, by flotation, indicated that Eh control has shown promising results for eliminating arsenic from other copper sulphides, due to the strong Eh dependence of arsenic mineral flotation (Menacho et al., 1993, Yen and Tajadod, 2000, Kantar, 2002, Guo and Yen, 2005, Senior et al., 2006, Bruckard et al., 2007, Smith and Bruckard, 2007, Bruckard et al., 2010, Haga et al., 2012a, Haga et al., 2012b, Ruiz et al., 2013, Long et al., 2014).

Menacho et al. (1993) were the first to demonstrate that the separation of enargite from chalcopyrite-enargite ore is possible by pulp potential control. They observed only slight oxidation of enargite after a pre-oxidation procedure using sodium hypochlorite at pH 11.5 in a synthetic mixture of enargite and chalcopyrite. This resistance to oxidation demonstrated by enargite has been used to separate it from chalcopyrite in flotation (80% of enargite recovered while only 40% of chalcopyrite recovered). They attributed this separation to differences in the semiconducting properties between the two minerals (Menacho et al., 1993).

In parallel, Byrne et al. (1995) found that tetrahedrite and tennantite could be depressed selectively by pulp potential control by adding H2O2 at pH 10.0 with isoamyl dithiophosphate collector. However, the addition of H2O2 also enhanced the floatability of pyrite; therefore, it was recommended that selective oxidation is used only on a final concentrate stream where pyrite has already been removed (Byrne et al., 1995).

Yen and Tajadod (2000) applied pulp potential control to separate enargite from chalcopyrite by flotation with amyl xanthate at pH 9.0. It was observed that at a potential of -10 mV SHE using sodium sulphide, enargite could be separated from chalcopyrite by flotation; enargite floated and chalcopyrite remained depressed (Yen and Tajadod, 2000).

Kantar (2002) investigated the flotation characteristics of enargite using hydrogen peroxide and sodium sulphide to control the potential of the system. It was found that in the presence of xanthate floatability was strongly dependent on the pulp potential with maximum enargite recovery at Eh between +150 and +270 mV SHE, and decreasing sharply above or below this range (Kantar, 2002).

Guo and Yen (2005) studied the separation of enargite from chalcopyrite using pulp potential control by micro-flotation tests in a modified Hallimond tube, using a 1 g sample. They successfully achieved the selective flotation of enargite from chalcopyrite at highly oxidation conditions, where enargite floated well and chalcopyrite was completely depressed (Figure 2-9).
A single mineral flotation study was undertaken by Senior et al. (2006) on an enargite sample from Tampakan ore, Philippines, to investigate the floatability of enargite as a function of pulp potential and pH. They performed the flotation tests in a 3 L modified stainless steel Denver cell and demonstrated that the flotation recovery of pure enargite is significantly different from that of other sulphide minerals at a specific pulp Eh range, as shown in Figure 2-17. It indicates that the pulp potential dependence of enargite flotation is different from that of chalcocite, chalcopyrite, cuprite, and pyrite. The transition from non-floatability to strongly floatability of enargite happen over a range of about -150 to -50 mV SHE at pH 8.0. This transition is in reasonable agreement to that reported by Guo and Yen (2005) in the range of about -150 to +100 mV SHE at pH 10.0.

Figure 2-17 demonstrates that the recovery of chalcopyrite, chalcocite, pyrite, and enargite show little or no floatability under strongly reducing conditions (Eh) below -300 mV SHE. The recovery of chalcocite gradually increases in the Eh ranges between -200 to -100 mV SHE, while the other minerals still show no floatability. This region could then potentially be used to separate chalcocite from enargite. Enargite could be selectively floated from chalcopyrite in the Eh range between -100 and 0 mV SHE as enargite recovery begins to rise around -100 mV SHE while the recovery of chalcopyrite remains low until the potential reaches 0 mV SHE. In addition enargite could be separated from chalcocite and pyrite in the oxidative Eh range above 300 mV SHE as the recovery of chalcocite and pyrite decline sharply while enargite floatability remain constant in highly oxidising conditions. The information regarding the flotation behaviour of sulphide minerals at potentials above +400 mV SHE is scarce (Guo and Yen, 2005, Senior et al., 2006). Furthermore, it is doubtful whether such highly oxidative conditions are practically achievable in an industrial setting.
This information was used to propose a conceptual flowsheet for separating enargite from other copper minerals (Figure 2-18) from the Tampakan ore-Philippines, which involves the following steps (Senior et al., 2006):

1. Floating chalcocite and cuprite at pH 11 under a reducing condition (-125 mV SHE).

2. Floating enargite from copper-iron sulphides such as chalcopyrite at pH 8 or 11 after raising the potential to about 0 mV SHE, the tails will be rich in chalcopyrite.

3. Floating enargite from copper sulphides such as chalcocite and copper oxide such as cuprite products (from stage 1 and stage 2) at pH 11 after setting the potential to about +290mV SHE. The enargite will float and leave a chalcocite-cuprite rich tail and would pass to an arsenic removal stage (Senior et al., 2006).
Some work was performed to test out the new methodology on real ores, which showed that the separations were possible, but with limited success. Smith and Bruckard (2007) have worked on the separation of tennantite from chalcopyrite and bornite by using controlled potential flotation on a sample from a high-arsenic section of the Northparkes orebody.
A bulk copper-arsenic flotation concentrate was produced using standard flotation conditions, and then the concentrate was reground and became the feed to the arsenic rejection step. The separation was made in the arsenic rejection stage at pH 12 after reducing the pulp potential to about -150 mV SHE and floating the tennantite from the other copper sulphide minerals. The pulp potential dependence of tennantite appears to be similar to that of enargite (Figure 2-19). (Smith and Bruckard, 2007).

Based on the results obtained, Smith and Bruckard (2007) proposed a new flowsheet (Figure 2-20) to treat tennantite in the Northparkes ore, which involves the following steps:

1. Floating copper minerals using standard flotation conditions.
2. Regrinding the copper-arsenic concentrate.
3. Floating tennantite from copper-iron sulphides such as chalcopyrite and bornite at pH 12 with lime and nitrogen after reducing the potential to -150 mV SHE, the tails will be rich in chalcopyrite and bornite. The froth product is termed the high-arsenic low-copper concentrate.
4. Floating copper-iron sulphides (chalcopyrite and bornite) at pH 12 after raising the pulp potential to the air-set potential by changing the flotation gas to air. The froth product is termed the low-arsenic high-copper concentrate and can be sent straight to a smelter to produce copper metal (Smith and Bruckard, 2007).
Haque et al. (2010) evaluated the net value of the new early removal process proposed by Smith and Bruckard (2007) to treat high-arsenic copper ores and found that there is a net benefit.

Figure 2-20, Conceptual flowsheet for the treatment of a high-arsenic copper ore from the Northparkes ore, from (Smith and Bruckard, 2007)
Bruckard et al. (2010) introduced a new flowsheet for the treatment of arsenic-bearing copper ores based on the early elimination of arsenic at the flotation concentrator. The proposed flowsheet includes three key steps:

In the first stage, controlled-potential flotation is used to separate arsenic and copper minerals to produce a high-arsenic low-copper concentrate and a low-arsenic high-copper concentrate.

In the second stage, low-temperature roasting will be used to treat the high-arsenic low-copper concentrate, so that the arsenic is selectively fumed off leaving a high-copper calcine, which can be smelted without penalty.

The final stage is a stabilisation stage where the high-arsenic fume is treated to produce a stable low-volume stream that can safely be disposed of arsenic. A hydrometallurgical step is an alternative option to the roasting step in the initial arsenic removal process. In this case, the high-arsenic low-copper concentrate is leached with alkaline sulphide (a mixture of NaOH and Na₂S) to dissolve the arsenic selectively leaving a copper-rich leach residue (Figure 2-21).

Figure 2-21, Early arsenic removal flowsheet for treatment of high-arsenic copper ores (roasting and leaching scenarios), modified from (Haque et al., 2012)
The flowsheet has been sequentially tested in the laboratory at small scale (Bruckard et al., 2010). The techno-economic analysis of the new flowsheet showed that a net economic benefit can be achieved which is encouraging to further development of the new flow sheet (Haque et al., 2012).

Smith et al. (2012) reported some case studies by using pulp potential control to separate copper and arsenic. At first, a rougher-scavenger concentrate was produced and then pulp potential control was used during a cleaner flotation stage on that concentrate to make a copper-arsenic separation. In one instance, a composite of some high-arsenic drill core intersections from a high-arsenic section of a copper ore body was collected and ground to P$_{80}$ of 90 µm. It was observed that tennantite was floated from the other non-tennantite copper minerals (bornite and chalcopyrite) between -200 and -130 mV SHE.

In another case reported by Smith et al. (2012) a composite of several drill core intersections from a copper ore body was received and ground to 150 µm. It was observed that there was the little recovery of either arsenic (tetrahedrite/tennantite) or non-arsenic copper (chalcopyrite) mineral at reducing potentials. There was, however, a window at +400 mV to separate arsenic and non-arsenic copper minerals (Figure 2-22). It was found that the efficiency of the separation and the selection of the suitable pulp potential region depended on the mineralogy of the ore, the degree of liberation, and the reagent selection specifically the collector type (Smith et al., 2012).

Figure 2-22, Recovery of NTCu and As (at 4 minutes) from Ore B as a function of pulp potential, from (Smith et al., 2012)
2.7. Flotation of complex ore

It is well understood that the sulphide minerals in a complex ore systems behave differently from that predicted by single mineral studies. The main reasons for this difference in floatability can be due to the liberation of valuable minerals, particle size distribution, galvanic interaction, gangue mineralogy, surface oxidation, and water chemistry. In this section, each parameter is briefly discussed.

2.7.1. Mineralogy of the ore

The mineralogy and the texture of ore are the important factors affecting the flotation performance. An understanding of these factors can be used to improve the flotation response. The key mineralogical factors that influence the recovery of valuable minerals to the flotation concentrate are the modal mineralogy, the mineral associations, and the grain size distribution of the valuable minerals (Cropp et al., 2013).

- Modal mineralogy: the weight percent of minerals present in the ore sample, which can be determined by point counting using optical microscopy methods (Sylvester, 2012).

- Mineral associations: the lengths of boundary shared between minerals.

- Grain size distribution: the sizes of mineral grains in the ore sample.

- Elemental deportment: the proportion of the element present in minerals (Butcher, 2010).

- Mineral locking: an indication if mineral of interest is liberated or occur associated with only one other mineral (binary), or with more than one mineral (ternary) (Figueroa et al., 2011)

Several MLA measurement methods exist to measure different mineralogical information for different sample types including back-scattered electrons (BSE) liberation analysis, extended BSE liberation analysis (XBSE), sparse phase liberation (SPL) analysis, particle X-ray mapping (PXMAP) analysis, selected particle X-ray mapping (SXMAP) analysis, X-ray modal (XMOD) analysis, and rare phase search (RPS) methods. The BSE is the most basic liberation analysis method in which a series of images are taken on-line and then processed off-line to produce liberation data (Gu, 2003).

In a study by Kappes and Gathje (2010), some of the mineralogical challenges related to the process development of arsenic-bearing copper ore in Newmont Mining Corporation was discussed. It was concluded that high-quality chemical and mineralogical analyses were needed in the development of the project and the determination of the processing options, such as the liberation of the sulphide and
the gangue minerals, the locking of the sulphide minerals with the gangue, and the minerals grain size
(Kappes and Gathje, 2010).

2.7.2. Liberation

High recovery and grade are the ultimate goals for all mineral processing plants and are strongly
determined by the liberation of minerals of interest in the ground ore samples (Evans, 2010, Zhou et
al.). Hence, the main purpose of comminution particles in the processing of most ores is to liberate
the valuable minerals from gangue minerals (Figure 2-23). If the valuable mineral is not sufficiently
liberated from the gangue minerals, they cannot be concentrated Mineral liberation is, therefore,
essential to the metallurgical performance of any separation process (Evans, 2002). In the flotation
process, liberation has a direct effect on the interactions between minerals and reagents (Vianna,
2004).

Even though it is important, very little research has been carried out in this field, especially in the
study of the separation of arsenic-copper minerals from other copper minerals, which the poor
liberation of arsenic-copper minerals makes their selectivity difficult (Agorhom et al., 2015).

Kappes et al. (2007) investigated the mineralogy characteristics of the Newmont gold-copper deposit
containing elevated levels of tennantite group minerals. The sample was fine ground to approximately
20 µm, to liberate tennantite and chalcopyrite. Flotation tests resulted in 62-80% of the arsenic
reporting to cleaner tails, along with 7.4-14.1% of the liberated copper. It was concluded that although
chalcopyrite and tennantite were successfully liberated by the fine grinding; a major portion of very

![Figure 2-23, Particle size reduction to liberate minerals in a complex ore, from (Butcher, 2010)](image)
Fine chalcopyrite was produced, which caused lower copper recoveries in the cleaner stage (Kappes et al., 2007).

Long et al. (2014) studied the separation of tennantite and arsenopyrite from copper sulphides at the Rosebery concentrator (Figure 2-24). Mineralogy characterisation of the feed sample indicated that arsenopyrite brought the majority of arsenic into the copper circuit; while tennantite contributed the majority of arsenic to copper concentrate. Arsenopyrite was appropriately depressed in the rougher stage however the high arsenic content of the final copper concentrate was mainly tennantite due to its similar floatability to the other copper sulphide minerals. Regrinding the copper rougher concentrate was therefore investigated as a means of rejecting tennantite in cleaner flotation. It was observed that although finer grinding increased the mass fraction in the ultrafine fraction, the increase in tennantite liberation was minor. Flotation tests determined that the greatest selectivity between copper and arsenic happen in a P80 of 10 μm, but it also reduced copper recovery.

![Figure 2-24, Separation of tennantite from chalcopyrite and bornite in the Rosebery copper concentrator, modified from (Long, 2014)](image)
2.7.3. Particle size

It is well known that particle size is an important factor affecting the recovery of valuable minerals. In fact, the floatability of valuable mineral particles follows the general pattern where the maximum recovery is typically happening in the intermediate size region (Figure 2-25).

The low recovery of fine particles can be due to a) small particle mass that can cause entrainment, b) high specific surface area that leads to increase reagent adsorption, high pulp viscosity, and the coating of the valuable particles by ultrafine gangue particles (i.e. slime coatings), and c) high specific surface energy which causes the undesirable adsorption of reagents (Trahar and Warren, 1976, Trahar, 1981, Moudgil et al., 1988, Feng and Aldrich, 1999).

In contrast, the main reason that coarse particles are difficult to float is the detachment of particle from bubbles because of turbulence within the pulp (Trahar, 1981, Feng and Aldrich, 1999, Wills and Napier-Munn, 2006).

![Figure 2-25, Mineral recovery as a function of particle size, modified from (Trahar, 1981)]
2.7.4. Gangue mineralogy

Non-sulphide gangue minerals mainly consist of silicate minerals, which are made up of oxygen and silicon (tetrahedral unit) and are classified according to the various way that these tetrahedra are linked together, such as a phyllosilicate group, which consists of sheets of tetrahedra or tectosilicate group containing a three-dimensional framework of tetrahedra (Brindley, 1951, Burdukova et al., 2008). Figure 2-26 shows the classification of silicate minerals with a focus on phyllosilicates (Brindley, 1951).

The phyllosilicate group consist of different types of minerals that are formed based upon the way that the silica tetrahedral (T-layer) bonds to the octahedral sheet (O-layer). The 1:1 phyllosilicate minerals are formed by bonding of one tetrahedral and one octahedral sheet, while 2:1 phyllosilicate minerals are formed by bonding of two tetrahedral and one octahedral sheet. Phyllosilicate minerals have several types of surfaces, external basal (planar) and edge surfaces, and internal (interlayer) surfaces. The faces and edges of phyllosilicates carry different electrical charges. The faces (or basal planes) tend to be negatively charged, while the edges are either positive or negative depending on the pH (Brigatti et al., 2006). Three different aggregate structures of clay minerals are the edge-face (EF), face-face (FF) and edge-edge (EE).
The presence of gangue minerals, in particular clay minerals, has various undesirable effects on both the recovery of the sulphides and the separation efficiency. A good understanding of the deportment of these undesirable minerals is needed to control the grade and recovery of valuable minerals.

### 2.7.4.1. Slime coating

One of the effects of very fine clay particles on flotation is slime coating that occurs through the electrostatic attraction. In this phenomenon, the anisotropic charges on edges and basal surfaces allow hydrophilic clay slimes to coat the surface of valuable coarse particles. Thus these particles become hydrophilic and prevent collector adsorption (Gaudin, 1957, Trahar, 1981, Arnold and Aplan, 1986, Peng and Zhao, 2011, Forbes et al., 2014).

### 2.7.4.2. Pulp rheology

Pulp rheology also plays a critical role in the selective separation of valuable minerals. There should be an optimum viscosity in the flotation pulp in order to increase the probability of particle/bubble attachment and decrease their detachment. The presence of phyllosilicate can increase the viscosity.
and the rheology of the flotation pulp due to particle aggregation (Burdukova et al., 2008, Patra et al., 2010, Ndlovu et al., 2011, Cruz et al., 2013, Forbes et al., 2014, Zhang and Peng, 2015)

2.7.4.3. Froth stability

Froth stability, which can be defined as a measure of the lifetime of froth, or the persistence of the froth (Subrahmanyam and Forssberg, 1988), is known to play a significant role in determining the mineral grade and recovery achieved from a flotation operation. Harris (1982) defined two types of froth, unstable, and ‘metastable’ or persistent froths. Unstable froth continuously breaks down due to drainage of liquid from the plateau borders, while ‘metastable’ froths are more persistent, and have a longer lifetime in the absence of disturbances. When the froth is not sufficiently stable, the mineralized bubbles rupture before they can be transferred to the concentrate launder, and in this way mineral particles already collected become detached and settle back into pulp. On the other hand, a too stable froth could entrain a significant amount of gangue, and a concentrate of high recovery and low grade would result (Subrahmanyam and Forssberg, 1988, Tao et al., 2000, Zanin et al., 2009).

The presence of clay minerals in the flotation process can dramatically affect the froth stability. Jorjani et al. (2011) observed that reducing the pulp density from 29% to 24% decreased the Al₂O₃ and SiO₂ grade and recovery while increasing the Cu and Mo grade and recovery.

When clay minerals are present as individual particles, they may adsorb a significant amount of frother due to their large surface area, and thereby decreasing the froth stability. On the other hand, the clay aggregates can also interact with the hydrophobic valuable minerals resulting in high froth stability.

2.7.4.4. Entrainment

Entrainment is the primary mechanism for the unselective recovery of mineral particles below 20 µm in size (Trahar, 1981, Savassi, 1998). It is a non-selective mechanism whereby both valuable and gangue mineral particles can be recovered. Hence, it has an adverse effect on the selectivity of the process. The recovery of particles by entrainment is strongly controlled by the recovery of water into the froth, the particle properties (e.g. size, shape, density), and the rheological properties of the pulp (Smith and Warren, 1989, Neethling and Cilliers, 2002, Vianna, 2004, Johnson, 2005b, Zheng et al., 2006), with higher water recoveries being indicative of a greater degree of entrainment.
2.7.5. Galvanic interactions

In order to achieve effective flotation grade and recovery, the grinding of the ore is essential for the liberation of the sulphide minerals. However, it can have a detrimental effect on flotation. One of the important influences of the grinding stage on the floatability of sulphide minerals is the galvanic interactions among different sulphide minerals or between the grinding media and various minerals. The galvanic cell is set up when the minerals or the iron in the grinding medium have different rest potentials. The higher rest potential mineral acts as a cathode while that of lower potential is the anode. Pyrite has the highest rest potential among all the sulphide minerals (Table 2-2) (Guy and Trahar, 1984, Rao et al., 1992, Cheng and Iwasaki, 1992, Hu et al., 2009).

Pauprote and Schuhmann (1996) investigated the electrochemical characteristics of natural enargite under alkaline conditions and determined the rest potential of enargite of 0.28 V SHE in the presence of bubbling oxygen without xanthate and 0.21 V SHE in the presence of xanthate.

Table 2-2, Galvanic series of some sulphide minerals, from (Rao et al., 1992, Hu et al., 2009)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Rest potential (V SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>0.66</td>
</tr>
<tr>
<td>Marcasite</td>
<td>0.63</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.56</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>0.46</td>
</tr>
<tr>
<td>Covellite</td>
<td>0.45</td>
</tr>
<tr>
<td>Bornite</td>
<td>0.42</td>
</tr>
<tr>
<td>Galena</td>
<td>0.40</td>
</tr>
<tr>
<td>Argentite</td>
<td>0.28</td>
</tr>
<tr>
<td>Stibnite</td>
<td>0.12</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Galvanic interactions can reduce the selectivity in sulphide minerals in flotation. In the case of mineral-mineral interactions, a mineral with higher potential acts as a cathode, while a mineral with lower potential serves as an anode. For example pyrite/chalcopyrite interactions, chalcopyrite oxidises and loses electrons while pyrite accepts the electrons. These electrons transfer to oxygen of the water, forming OH⁻ ions. The formation of hydrophilic OH⁻ ion and reduced potential consequently depress the sulphide minerals flotation (Martin et al., 1989, Cheng and Iwasaki, 1992).

For a multiple minerals/grinding media system, the galvanic interactions are more complex. Pyrite acts as a cathode (the highest rest potential), whereas the grinding media undergoes anodic dissolution. The other sulphide minerals like chalcopyrite, with higher rest potential than the grinding medium and lower rest potential than pyrite, act as an anode (Figure 2-28) (Rao et al., 1992).
The following electrochemical reactions may occur on sulphide minerals and grinding media surface (Ekmekçi and Demirel, 1997, Azizi et al., 2013):

At the cathodic mineral surface:

\[
\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-
\]

Equation 2-21

At the anodic mineral surface:

\[MS \rightarrow M^{2+} + S + 2e^-\]

Equation 2-22

Oxidation of the steel media (Anodic reaction):

\[Fe \rightarrow Fe^{2+} + 2e^-\]

Equation 2-23

Precipitation:

\[M^{2+} + 2OH^- \rightarrow M(OH)_2\]

\[Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\]

Equation 2-24

Figure 2-28, Model of galvanic interactions among two minerals and grinding media, modified from (Cheng and Iwasaki, 1992)
The deposition of iron hydroxides on a mineral surface may have an activating or depressing effect on flotation. While studies have indicated that pure chalcopyrite samples floated strongly without collector (Heyes and Trahar, 1977), its natural floatability reduced sharply in the presence of other sulphide minerals (Hayes and Ralston, 1988). In addition, it was found that the floatability of chalcopyrite is higher after grinding with stainless-steel balls than with high-carbon steel balls (Cheng and Iwasaki, 1992).

By increasing the pH or removing the oxygen from the slurry (nitrogen aeration), or using stainless-steel grinding media, the galvanic interactions would be minimised. By grinding the ore under nitrogen (i.e. removing the oxygen), the pulp potential can be reduced and pyrite, for example, would be depressed. However, grinding under oxygen and floating under nitrogen, could even promote pyrite floatability (Martin et al., 1989, Rao et al., 1992).

2.7.6. Effect of other metal ions

It was recognised by many researchers that when more than one sulphide mineral is present in a flotation system, the separation efficiency might change (Bruckard et al., 2011, Owusu et al., 2014, Yang et al., 2016). One of the factors limiting the selectivity of sulphide minerals is the presence of metal ions such as Fe$^{3+}$, Cu$^{2+}$, SO$_3^{2-}$, S$^{2-}$, etc. These metal ions are the result of surface oxidation of sulphide minerals and grinding media, the presence of semi-soluble minerals, the interactions among the different minerals, and the use of recycling water. They can either depress the valuable minerals or activate the unwanted minerals (Zhang et al., 1997).
2.7.7. Surface oxidation

Sulphide minerals readily oxidise in the presence of aerated aqueous conditions due to the electrochemical interactions that occur between sulphide minerals and solution species (Fullston et al., 1999c, Peng and Zhao, 2011, Jacques et al., 2016). The oxidation reaction for sulphide minerals in water can be represented by following equations:

- In acidic solutions, the dissociation of the metal sulphide includes the formation of a metal cation and elemental sulphur:

  \[ MS \rightarrow M^+ + S^0 + e^- \]  
  \[ \text{Equation 2-25} \]

- In alkaline solutions, this dissociation involves the formation of elemental sulphur and metal hydroxide species:

  \[ MS + 2H_2O \rightarrow M(OH)_2 + S^0 + 2H^+ + 2e^- \]  
  \[ \text{Equation 2-26} \]

  \[ MS + 2O_2 + H_2O \rightarrow M(OH)_2 + M^+ + S_2O_3^- \]  
  \[ \text{Equation 2-27} \]

where M is metal ion (Ralston et al., 2005).

Although mild surface oxidation can increase the floatability of sulphide minerals by forming elemental sulphur or polysulphides, high surface oxidation usually reduces the flotation recovery and selectivity (Senior and Trahar, 1991). The oxidation products, which include reactive and hydrophilic precipitated metal species, have generally been termed “metal hydroxides”. The depressant effects of metal hydroxides on sulphide hydrophobicity have been recognised by many researchers (Senior and Trahar, 1991, Kant et al., 1994, Clarke et al., 1995, Rumball and Richmond, 1996, Greet and Smart, 2002).

The pulp solution may contain metal ions originating from grinding media or minerals present in the ore, or reagent addition. With increasing pH, these metal ions may adsorb or precipitate on the mineral surface (Ralston et al., 2005).
EDTA (Ethylenediaminetetraacetic acid) (Figure 2-29) has been used to determine the extent of oxidation of minerals in the flotation pulps. It has the ability to extract the precipitated metal ions from the surfaces of minerals (Rao and Leja, 2004).

![EDTA Structure](image)

**Figure 2-29, EDTA structure, from (Grano, 2010)**

Previous researchers have mentioned the ability of EDTA to solubilise surface oxidised products, such as oxides/hydroxides, sulphates, and carbonates, but not the metal sulphide (Kant et al., 1994, Rumball and Richmond, 1996, Greet and Smart, 2002).

Shannon and Trahar (1986) found that the removal of surface species by EDTA increased the floatability of chalcopyrite. Senior and Trahar (1991) studied the effect of the addition of EDTA on the interactions of lead and zinc hydroxide with chalcopyrite in the absence and presence of xanthate. They showed that the precipitated metal hydroxides on the surface of chalcopyrite prevented its collectorless flotation and reduced its recovery in collector-induced flotation. They also observed that the effect of xanthate on the floatability of chalcopyrite depends on the type of metal hydroxide.

Rumball and Richmond (1996) studied the selective leaching of the oxidation of galena, sphalerite, and pyrite by EDTA in the Hellyer circuit. They suggested that chalcopyrite released iron but not copper (Rumball and Richmond, 1996). Kant et al. (1994) used the EDTA extraction technique in a study of sulphide mineral surfaces and found also that EDTA did not extract copper from chalcopyrite.
2.7.8. Water chemistry

Water quality is an essential aspect of froth flotation, as it may have a strong effect on the efficiency of the processes, hence an understanding of the effects of water quality on the metallurgical performance is necessary.

It is important to measure the elements and ionic species such as Ca, Mg, Na, Cl, K, $\text{SO}_4^{2-}$, $\text{S}_2\text{O}_3^{2-}$ (e.g. thiosulfate) which could not be measured by the EDTA extraction technique, as well as the total dissolved solids (TDS), the heavy metal cations, carbonate, and total organic carbon (TOC), which may be a measure of residual reagents in solution (Grano, 2010).

Bicak et al. (2012) investigated the effects of dissolved ions on the flotation performance of a Cu-Zn complex sulphide ore and discovered that the dissolved metal ions and sulphide ions, mainly in the form of $\text{SO}_4^{2-}$ and $\text{S}_2\text{O}_3^{2-}$, influenced both the froth stability and surface chemistry. The stability of the froth was increased by increasing the dissolved ion concentration due to the increased stability of the water layer between air bubbles.

Smith and Heyes (2012) investigated the effect of water quality on the flotation of chalcopyrite and bornite in the absence of collector. They observed that the water quality had no effect on the collectorless flotation recovery of chalcopyrite at pH 8. However, the collectorless flotation of bornite at pH 8 was depressed when floated in hypersaline water.

Furthermore, the significant role of water chemistry in tailings management is known. Since tailings water is a continuum of process water, understanding the chemical composition of process water helps predict the potential environmental hazards including the quality of tailings seepage (Huynh and Edraki, 2013). As suggested by Edraki et al. (2014) an integrated approach is required to follow the geochemical pathways of arsenic from the concentrator to the tailings storage facility (Edraki et al., 2014).
2.8. Flotation modelling based on particle composition

Most of the flotation models have been based on this fact that flotation is a kinetic process. The flotation rate can be measured from many chemical, physical, and operation parameters that define the flotation environment (King, 2001). A few researchers have attempted to investigate the possibility of developing a predictive flotation model based on particle composition distribution and flotation rate (Schaap, 1979, Gong et al., 1992, Luitjens, 2006, Evans, 2010). The developed models by Schaap (1979) and Gong et al. (1992) were not successful to predict the flotation response of the ores. More details about these models are discussed by Evans (2010).

Luitjens (2006) has proposed a simple modelling approach which uses particle surface composition data from MLA analyses and flotation kinetic data for each mineral to predict the flotation response of each particle in a flotation feed.

In this method, the flotation rate of a composite particle is estimated from the rates of the individual minerals grains in the particle. For this purpose, the MLA data on particle surface composition and the flotation kinetic data for each mineral are being used to predict the flotation response of each particle in a flotation feed. The general form of the Luitjens (2006) model is shown in Equation 2-28:

$$K_P = \frac{\sum_i K_i \times L_i}{\sum_i L_i}$$

Equation 2-28

where $K_P$ is the flotation rate constant for a particle, $K_i$ is the flotation rate constants for mineral $i$, $L_i$ is the proportion of the particle perimeter occupied by minerals $i$, and for each individual particle $\sum_i L_i = 1$.

An example of a composite particle with three different mineral grains is presented in Figure 2-30, and the combined flotation rate of the particle is calculated by Equation 2-29.

$$k_P = \frac{k_a L_a + k_b L_b + k_c L_c}{L_a + L_b + L_c}$$

Equation 2-29
where $k_a$, $k_b$ and $k_c$ are the individual mineral flotation rates and $L_a$, $L_b$, and $L_c$ is the length of the exposed perimeter of each mineral (Wightman et al., 2010b).

The recovery of each particle ($R_P$) is then estimated by the first order rate Equation 2-30:

$$R_P = (1 - e^{-K_Pt})$$

\textbf{Equation 2-30}

where $R_P$ is the recovery of the particle, $K_P$ is the flotation rate of the particle (min$^{-1}$), and $t$ is the flotation time (min). The recoveries of all particles with varying composition in each size fraction will then be summed, and the total recovery for each mineral will be finally calculated (Evans, 2010). For this model, it is required to provide a flotation rate constant for each mineral of interest and in each size fraction. This value must be obtained from a physical flotation test, and the flotation response predicted by the model is only valid as long as the flotation conditions remain unchanged from the original test (Evans, 2010). An estimate of the flotation rate of each mineral can be obtained from the recovery data for the 99-100% liberated surface composition class of that mineral. The flotation rate is calculated using Equation 2-31:

$$K_{i,j} = -\frac{\ln(1 - R_{i,j})}{t}$$

\textbf{Equation 2-31}

where $K_{i,j}$ is the flotation rate of mineral in size class $i$, surface composition class $j$ (min$^{-1}$), $R_{i,j}$ is the recovery of mineral in size class $i$, surface composition class $j$ at time $t$, and $t$ is the flotation time (min) (Evans, 2010).
2.9. Summary of the literature review and identified gaps

The aim of this chapter was to discuss the previous research relevant to this study and determine the lack of knowledge in this area. The significant findings from the literature are as follows:

- Collectorless and collector-induced floatability of enargite were studied by some researchers, which showed that in the single mineral system, enargite floated much faster in the presence of collector than in the collectorless. It was also discussed that the enargite floatability is strongly dependent on the Eh of the flotation solution.

- The selective flotation has seemed a promising method, which provides sufficient selectivity between arsenic-copper minerals and other copper minerals, is desirable. Three main selective flotation mechanisms for achieving enargite selectivity are the use of selective flotation using depressants, selective oxidation, and pulp potential control.
  
  - Selective flotation using depressants: conditioning with depressants such as sodium cyanide and sodium sulphide has shown limited success, with generally poor separation efficiency and high copper losses. The use of MAA to depress enargite has shown mixed results, with some authors reporting good selectivity while other studies fail to give the same results.

  - Selective flotation using selective oxidation: selective oxidation of the mineral surface to influence collector adsorption using a pre-conditioning step has been shown to be effective in separating enargite from non-arsenic copper sulphides by using oxidising reagents and pulp aeration with air or oxygen gas.

  - Selective flotation using pulp potential control has been found as a prospective approach for achieving selective flotation of arsenic-copper minerals due to the strong Eh dependence of arsenic mineral flotation. Single mineral studies by using pulp potential control showed that there is a threshold potential for separation of enargite from other copper minerals. Some researchers have reported successful results on the separation of arsenic minerals from copper concentrates by using pulp potential controlled flotation and some flowsheets have been proposed. However, there is no data available on the successful application of any of the proposed flowsheets in this review and reported results were not consistent for different ore types.
• The poor liberation between the arsenic-copper minerals and the copper sulphide minerals (i.e. chalcopyrite, bornite, chalcocite, etc.) has found to make the selectivity difficult during copper sulphide flotation.

• A few researchers used fine grinding to liberate the arsenic-copper minerals from other copper sulphide minerals, which achieved significant improvement in arsenic separation. However, lower copper recovery was obtained due to excessive regrinding, which produced more fines.

• Mineralogical and liberation characteristics of the ore, surface oxidation, pulp chemistry and water chemistry analysis, together with the gangue mineralogy have been found the important factors which influence the floatability of the sulphide mineral in the flotation of a complex ore system.

• A comprehensive study must be done to understand the fundamental mechanisms of the floatability of enargite in the presence of other copper sulphide and gangue minerals to further develop a process more readily applicable to industrial separation.
The following gaps were identified in the literature review:

- The vast majority of the studies on enargite separation was performed on pure mineral systems. However, there is no comprehensive study on the selective flotation of arsenic-bearing copper minerals from a real complex ore.

- No detailed study was found on the investigation of the effect of ore mineralogy on the separation of enargite from other copper minerals.

- Although previous studies have identified some strategies that can be applied to separate arsenic-bearing copper minerals, there is no reliable framework to overcome the arsenic challenge.

- Compared to the well-developed method of pulp potential control, there is no detailed study on enargite surface oxidation in the presence of other minerals.

- The flotation recovery of enargite on size-by-size and size-by-liberation basis is not reported in the available literature.

- The lack of EDTA extraction technique as a function of pulp potential for enargite was identified.

- No previous study has considered the effect of gangue mineralogy on the selectivity of separation of enargite from other copper minerals.
2.10. Research hypotheses

The main hypothesis is:

The flotation behaviour of arsenic-bearing minerals within complex ores differs significantly from that of pure mineral systems due to the effects of mineralogical composition, the degree of liberation, and the surface oxidation. The understanding and manipulation of these effects can lead to improvements in the selective flotation recovery of arsenic-bearing species from complex ore systems.

The main hypothesis can be broken down into components:

- The two ore samples (HAS and LAS) will be characterised by largely similar base metal sulphide components, with the mineralogical differences residing within the gangue mineral phase.

- The high-arsenic ore sample (HAS) is expected to be characterised by higher enargite floatability than the low-arsenic ore sample (LAS), due to the greater proportion of the enargite mineral within its feed composition.

- The flotation behaviour of the HAS ore can be estimated using a predictive particle kinetic model, which uses the ore mineralogical composition of the HAS ore and the flotation responses of the LAS ore, as inputs.

- The degree of oxidation of the enargite mineral surfaces has a significant influence on enargite flotation behaviour.

- Appropriate control of flotation pulp potential enables an effective separation of enargite from other copper sulphide minerals within a complex ore system.
Chapter 3

EXPERIMENTAL METHODOLOGY

AND ANALYSIS METHOD

This chapter consists of two sections; the first section explains the experimental approach employed to provide the data necessary for investigating of the hypotheses of the thesis and the second section presents the analysis method, which was used to calculate the data and the errors.

In the experimental section, the ore samples, sample preparation, and method of chemical and mineralogical analysis are described. The detailed description of the batch flotation reagents and equipment used for the study is given. The experimental procedure adopted to obtain different types of minerals floatability is presented. Finally, the procedure for the EDTA extraction test and the water chemistry experiment is discussed.

In the analysis section, the equations used for the calculation of the recovery in unsized, size-by-size, and size-by-liberation basis, as well as water recovery, the degree of entrainment, and the recovery by entrainment are given. At the end of this section, the errors associated with the experimental data and the mass balancing is presented.
3.1. Experimental methodology

The experimental procedure used in this thesis to study the HAS and the LAS sample is shown in Figure 3-1, which demonstrates the phases that were used for conducting the testwork. In this section, the details of each phase are explained.

Figure 3-1, Schematic block diagram of the experimental approach
3.1.1. Materials

The ore samples used in this research were supplied from the Tampakan copper-gold deposit located in the SE part of Mindanao in the Philippines. This porphyry copper deposit is estimated to be 1340 million tonnes of ore with an average grade of 0.66% Cu and 0.27 g/t Au. It has significant levels of arsenic as Enargite (Cu₃AsS₄) (Rohrlach et al., 1999, Senior et al., 2006).

A composite of several high arsenic-containing drill core intersections for the high arsenic sample (HAS) and a composite of some low arsenic-containing drill core intersections for the low arsenic sample (LAS), were selected to provide a range of arsenic levels. The drill core samples were kept in a freezer.

3.1.2. Sample preparation

The sample preparation was performed in two steps, Figure 3-2 (Appendix A):

- **Crushing**

  Approximately 100 kg of drill core intersections of the HAS and the LAS (50 kg each) from the Tampakan deposit were received at JKMRC.

  The drill core samples had been kept in the freezer for a long period of time, resulting in significant surface oxidation. When received, the drill core samples were dried at 65 ºC in an oven. To remove the fines, which account for the major portion of the oxidised surface, the drill core samples were sieved at 500 µm. Assays indicated that there was very little difference, chemically, between the coarse fraction and the fine fraction. Further study on the -500 µm size fraction fell out of scope of this project. When the +500 µm fraction is ground to flotation feed size, calculation shows that about 99% of the ground surface is newly fractured, thus giving confidence in the test data.

  A Rocklabs laboratory jaw crusher followed by a roll crusher in closed circuit with a sieve were used for crushing the samples to 100% finer than 1.7 mm.

- **Blending and samples splitting**

  The HAS and the LAS samples were blended separately and homogenised using a Retsch PT100 rotary splitter. Each composite was then divided into replicate samples of approximately 500 g mass and stored in a dry cupboard to prevent further oxidation. The size distribution of the samples after crushing is presented in Figure 3-3.
Figure 3-2, Schematic of the sample preparation procedure

Figure 3-3, Size distribution of the HAS and the LAS samples after crushing
Sub-samples of the HAS and the LAS ores were taken for chemical analysis using Inductively Coupled Plasma (ICP) Atomic Emission Spectrophotometry (AES) to determine the distribution of Cu, As, Fe, and S in the ore samples.

The head assays of the samples are shown in Table 3-1. The data show that the arsenic in the HAS sample (at 230 ppm) is practically twice that for the LAS. While the copper assay is slightly higher in the HAS sample, the non-enargite copper assay (NECu) which indicates the amount of copper in other copper sulphide minerals except enargite, is similar in both samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu(%)</th>
<th>As(ppm)</th>
<th>S(%)</th>
<th>Fe(%)</th>
<th>NECu(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAS</td>
<td>0.64</td>
<td>233</td>
<td>2.96</td>
<td>2.91</td>
<td>0.58</td>
</tr>
<tr>
<td>LAS</td>
<td>0.57</td>
<td>114</td>
<td>1.91</td>
<td>2.29</td>
<td>0.54</td>
</tr>
</tbody>
</table>

The specific gravity of the HAS and the LAS samples (g/cm³) were measured using Micromeritics, AccuPyc 111340, Gas Pycnometer (Unit 1 SN1477 100 cm³). The results showed the specific gravity of the HAS sample is slightly higher than LAS sample, Table 3-2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Density g/cm³</th>
<th>Std Dev g/cm³</th>
<th>Weight g</th>
</tr>
</thead>
<tbody>
<tr>
<td>High As</td>
<td>2.85</td>
<td>0.0007</td>
<td>8.65</td>
</tr>
<tr>
<td>Low As</td>
<td>2.79</td>
<td>0.0009</td>
<td>9.69</td>
</tr>
</tbody>
</table>

Sub-samples of the HAS and the LAS samples were analysed by Quantitative X-Ray Diffraction (QXRD) to identify the major minerals of the ore samples. The results of the QXRD mineral analysis are shown in Table 3-3 and Figure 3-4.

The gangue minerals identified were quartz, illite, kaolin, pyrophyllite, diaspora, and alunite in both samples. The results showed that the total amount of phyllosilicates which include illite, kaolin, and pyrophyllite in the LAS sample is higher than those in the HAS sample, 29.8 vs. 23.1 wt% respectively. However, the amount of quartz and diaspora in the HAS with 50.8 wt% is higher than that in the LAS sample with 36.2 wt%.
XRD relies on the structure of the minerals to be crystalline to obtain a diffraction pattern, so if the material is non-crystalline or extremely fine-grained, i.e. nanoscopic, then a diffraction pattern is absent, and the material is termed “amorphous” or “poorly diffracting material”. The amorphous material could be composed of a variety of materials such as amorphous silica, extremely fine clay, or oxidised sulphide minerals that could consist of amorphous iron oxides and oxyhydroxides. In addition, if the copper minerals in the samples are less than 1 wt% they would report to the “amorphous material” category (although they may not be amorphous, but could be well-crystalline). Amorphous materials represent 20.6% and 31% of the head samples of the HAS and the LAS respectively.

Table 3-3, Quantitative XRD Mineral Analysis Results (wt%)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Indicative Formula*</th>
<th>LS1524-10%ZnO-01 HAS-Head sample</th>
<th>LS1524-10%ZnO-02 LAS-Head sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>Undefined</td>
<td>20.6</td>
<td>31</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>36</td>
<td>28.2</td>
</tr>
<tr>
<td>Diaspore</td>
<td>a-AlO(OH)</td>
<td>14.8</td>
<td>8</td>
</tr>
<tr>
<td>Illite</td>
<td>K₁.₅₁₋₁.₀Al₁<a href="OH">Si₆.₇₋₇.₀Al₁₁.₅₋₁.₀O₂₀</a>₄</td>
<td>2.6</td>
<td>18.7</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>Al₁₁<a href="OH">Si₆O₂₀</a>₄</td>
<td>12.3</td>
<td>10.1</td>
</tr>
<tr>
<td>Kaolin</td>
<td>A₁₂<a href="OH">Si₃O₁₀</a>₈</td>
<td>8.2</td>
<td>1</td>
</tr>
<tr>
<td>Alunite</td>
<td>(Na,K)Al₃(SO₄)₂(OH)₆</td>
<td>2.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>3.2</td>
<td>1.7</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>


Figure 3-4, Quantitative XRD Mineral Analysis Results (wt%)
3.1.3. Grinding curve determination

Several different grinding times tests were conducted on the HAS and the LAS ores to determine the grinding times required to obtain a particle size of 80% passing 90 µm.

Several HAS and LAS samples weighing 500 g were ground in an iron ball mill 250 mm(H) × 250 mm(D) at a solid-liquid ratio of 2:1 i.e. 67% solids by weight, using Brisbane tap water. The ore samples were ground at natural pH of 6.1. The mill was cleaned by grinding a sample of quartz for 10 minutes prior to each test series.

The HAS ore samples were ground using 55 stainless steel 316 balls i.e. 30×25mm and 25×31.75mm, the total weight of 4.435kg, while 35×25mm stainless steel 316 balls with a total weight of 2.334kg were used for the LAS ore samples. The different ball charges were used because of the various amounts of clay present in the samples, thus enabling grind times more than 10 minutes.

The size analyses of the ground product were done using wet and dry sieve sizing, and the grinding curves were established which indicated that the HAS sample needed 10 minutes grinding whereas 13.5 min grinding time was required for the LAS sample to achieve the P 80 of 90 µm. These grind times were used for all the rougher flotation tests.

3.1.4. Mill products analysis

Sub-samples of the HAS and the LAS with P80 of 90 µm were sized using a combination of wet and dry sieving and cyclosizing. One of the biggest concerns for the MLA image analysis was the agglomeration of the particles during sample sizing, as it would introduce bias in the measurements. In order to avoid these circumstances a sizing procedure was developed and samples were sized for 12 size fractions, as follows (where C represents a cyclosizer fraction): +150 µm, +106 µm, +75 µm, +53 µm, +38 µm, CS1, CS2, CS3, CS4, CS5, CS6, and -CS6; the sieve series selected was a standard root 2 series. The sizing procedure is shown in Figure 3-5, and the details are explained in the Appendix B.

Sieving followed by cyclosizing was used in the separation of samples in different size ranges. The cyclosizing method was chosen for this project over micro-sieving due to the limited time available and the amount of material required for product analyses. It represented a change from determining size as a geometric property to determining size as a function of settling rate. Therefore, the separation of particles in the cyclosizer is carried out based on the diameter and the density of particles. It is the only instrument available to accurately separate particles with a diameter smaller than 40µm,
Figure 3-6 and still provide the significant mass required for product analyses. The procedure for using the Warman Cyclosizer is presented in the Appendix B (Warman, 1997). The results of sieve sizing and cyclosizing are shown in Figure 3-7.

Figure 3-5, Schematic of the sizing procedure

Figure 3-6, CSIRO cyclosizer
Figure 3-7, Size distribution of the HAS and the LAS samples after grinding

The similarity of the shape of the flotation feed particle size distribution curves shows that the ore grinding was similar for the HAS and the LAS samples, indicating that ore breakage in grinding was independent of their mineralogy. However, the differences in the grinding times required to get the P<sub>80</sub> of 90 µm suggest that there is a difference in the hardness of the ores, with the HAS sample being harder than the LAS sample.

Representative sub-samples of the +106 µm, -106+75 µm, -75+ 53 µm, -53+38 µm, -38+32 µm, -32+23 µm, -23+15 µm, -15+11 µm, -11+6 µm, and -6 µm size fractions were submitted for chemical analysis using ICP-AES and Mineral Liberation Analyser (MLA) to identify the deportment of minerals of interest and quantify their degree of liberation.

The MLA system comprised of a sophisticated Scanning Electron Microscope (SEM) coupled with an X-ray analyser. Liberation analysis was carried out using the extended BSE method (XBSE). In this approach, mineral grain boundaries were delineated from the Back Scattered Electron (BSE) image and then identified by an X-ray scan of the area (Welsby, 2009).
3.1.5. Flotation testwork

The special flotation cell used for this study, and the auxiliary equipment needed to operate it, were transferred from the CSIRO laboratories in Melbourne and set up in the QCAT laboratories in Brisbane.

3.1.5.1. Equipment

The flotation tests were conducted in a modified laboratory 3 dm³ stainless steel Denver cell (Guy, 1992) in which the impeller is driven from below and is fitted with an adjustable speed drive. This allows scraping the surface of the froth at a constant depth and at constant time intervals (Senior et al., 2006). The flotation cell was fitted with a sight tube, rubber diaphragm, and an electronic sensor for automatic detection and control of the pulp surface level. A Precision Bore Flowrate Tube FP1/4-25-G-5/81 was used to measure the volume of supply gas. With this cell design, no external gas entered during conditioning and flotation and gas only entered the pulp when the gas on/off control was turned on. That allowed rigorous control of the pulp redox environment. The pH was measured with a Radiometer glass electrode and calibrated using standard pH 7 and pH 10 buffer solutions before each test. The system included a Radiometer Copenhagen® TTT60 Titrator that is an automatic titration control unit for adding acid or alkali to a set point where the amount of titrant necessary to reach certain fixed end-point must be accurately measured. It was connected to a Radiometer Copenhagen® PHM82 Standard pH meter, which is a digital precision laboratory instrument for measuring the pH. The pulp potential was measured with a high impedance differential voltmeter using a polished platinum electrode and an Ag/AgCl reference electrode and was checked using a standard ferric-ferrous solution (Light, 1972). By using this equipment, it was possible to continuously monitor and control the pH and pulp potential (Eh). Measured potentials were converted to the standard hydrogen electrode (SHE) scale by the addition of 200 mV. Frother was added continually using an Oxford Automatic Dispenser with variable speed control (Senior et al., 2006). A photo of the CSIRO flotation cell and the controllers is shown in Figure 3-8.

3.1.5.2. Reagents

A fresh sample of potassium ethyl xanthate (KEX) as 0.1% w/w solution in distilled water was made up daily and used as the collector in all the flotation tests. This sample of xanthate was prepared and purified by CSIRO. The frother was a commercial quality polypropylene glycol (Aerofroth 65) which prepared as a 0.25 %w/w solution with distilled water. The flotation gas was bulk air for the flotation tests conducted at the Eh +200 and +400 mV SHE or high purity bottled nitrogen for tests carried out
at Eh -200 and 0 mV SHE. Nitrogen gas was used to maintain the Eh at levels below air set value. Dilute solutions (2.5% w/w) of sodium hypochlorite (NaClO) as an oxidising agent and sodium dithionite (D.T) (Na₂S₂O₄) as a reducing agent were used to set and maintain the potential of the flotation pulp during each test. A 2.5 % w/w solution of sodium hydroxide (NaOH) and nitric acid (HNO₃) were added to the pulp to set and maintain the pulp pH at 11. Makeup water used in the flotation tests was Brisbane tap water.

3.1.5.3. Procedures

Based on the single mineral studies by Senior et al. (2006) and CSIRO confidential reports, four different pulp potential values of -200, 0, +200, and +400 mV SHE were selected for this study and flotation tests were conducted at these Eh values for both the HAS and the LAS samples.

After the ground slurry was transferred to the flotation cell, water was added to reach the target level, and the pH adjusted to 11 using NaOH. Automatic titrators were used to deliver dilute solutions of sodium hypochlorite or sodium dithionite to set and maintain the Eh at the test value. The pulp was conditioned for 5 minutes. The sequence of addition of the oxidising and reducing reagents depended on the test being performed. 30 g/t of the collector was then added, and the pulp was conditioned for a further 2 minutes.

The strategy used to control the water recovery was to decrease the frother addition and the scraping rate as the test progressed. Hence, the froth was sufficiently active but not too high that water recoveries were excessive. Frother was added 1 minute before flotation commenced continually at 2ml/min for the first minute and 1ml/min for the rest of the flotation. The gas was turned on 15 seconds prior to the concentrate collection. Flotation concentrates were collected at 0.5, 1, 2, 4, and 10 minutes by hand scraping rates of once every 5-second for the first minute and once every 10-second for the rest of the test. For both the conditioning and the flotation, the impeller speed was 1200 rpm and the gas flow rate was 8 dm³min⁻¹. For the tests that were conducted at Eh -200 or 0 mV SHE, nitrogen gas was used, and the pulp was deoxygenized by bubbling the nitrogen through the pulp.

Flotation products were weighed wet to calculate water recovery and dried. Flotation tests were repeated several times at each Eh condition to establish reproducibility and in order to have enough material for subsequent analysis. Further, some of the tests were selected, and their concentrates were mixed to provide enough products for further analysis.

For the test conducted at Eh +400 mV SHE, no frother was needed.
Figure 3-8, CSIRO instrumented flotation unit
3.1.6. Chemical and mineralogical analysis of the flotation products

As mentioned before, five concentrates and a tail were collected in each flotation test. Four flotation tests at each Eh condition, which had the most similar results, were chosen and their products were then combined to form a combined RC1, RC2, RC3, RC4, RC5, and RT. These five combined concentrates and the tail for each condition (in total 48 samples; 2 samples × 4 Eh ranges × 6 concentrates and tail) were assayed for arsenic, copper, sulphur, and iron using the ICP-AES method to calculate the recovery and the kinetic parameters.

In addition, the five collected concentrates of each condition were mixed and blended to represent a rougher concentrate. The individual combined concentrate was prepared by first splitting the individual concentrates in the quarter, retaining one-quarter for reserve and combining the rest with the other four concentrates, which were prepared in the same way. The combined concentrate and the tail were then sized using a combination of wet and dry sieving and cyclolosizing in 11 size fractions for the feed sample. Due to time and cost restrictions, a significant number of fractions (2 samples × 4 Eh ranges × 11 size fractions × 2 (Conc and tail) = 176 samples) could not all be sent for MLA analysis. In addition, some of the size intervals in the concentrate lacked sufficient material to be assayed (minimum one gram each required for assay and MLA). These limitations required that the size fractions be combined to minimise the number of analyses. These issues were solved by combining size fractions so that there was a sufficient amount of sample available in a combined class and the smaller number MLA analyses were required. That resulted in the initial 11 size fractions being reduced to five, as follows: +106 µm, -106+53 µm, -53 µm +CS2, -CS2+CS5, and -CS5. Individual samples were sub-sampled for assay and MLA using a micro-rotary splitter to ensure reproducibility. The schematic of the flotation test procedure is illustrated in Figure 3-9.

Figure 3-9, Schematic of the flotation test procedure
3.1.7. EDTA extraction and water chemistry tests

Ethylenediaminetetraacetic acid tri-sodium salt (Na$_3$EDTA) as an AnalaR product was used to solubilise metal sulphide oxidation products from the surface of particles and to determine the type and amount of oxidation species from the minerals surface.

Two sets of EDTA extraction tests were conducted. The schematic of the experimental procedure is shown in Figure 3-10:

- The first set of tests was conducted on the HAS and the LAS samples, which were ground to $P_{80}$ of 90 µm (Mill discharge).
- The second set of tests was performed on the conditioning stage of the flotation tests (Flotation feed).

Extensive studies in the CSIRO laboratories showed that, for a range of non-ferrous ores, EDTA extractions were complete in less than 10 minutes. Thus in order to minimise unnecessary test work the CSIRO procedure of using 10 minutes was copied.

For the first set of tests, after grinding the sample of the HAS or the LAS to $P_{80}$ of 90 µm, the sample was weighed and leached by 5 % solution Na$_3$EDTA for 10 min using an electrical stirrer. The slurry was filtered using a Whatman number 40 filter paper and again was fine filtered using a 0.45µm Millipore filter. The solubilised metals were determined by Inductively Coupled Plasma (ICP) Atomic Emission Spectrophotometry (AES).

For the second set of tests, similar to the flotation tests which were described in pervious paper, four different pulp potential (Eh) values of -200, 0, +200, and +400 mV SHE were selected and the experiments were conducted at these Eh values for both the HAS and the LAS samples in a 3 dm$^3$ modified laboratory stainless steel Denver cell. The cell was fitted with pulp level control, an automatic titration control unit for control and monitoring pH and pulp potential, and a gas on/ off control. The pH was measured with a Radiometer glass electrode, and calibrated using standard pH 7 and pH 10 buffer solutions before each test. The pulp potential was measured with a high impedance differential voltmeter using polished platinum electrode and an Ag/AgCl reference electrode, and was checked using a standard ferric-ferrous solution. Measured potentials were converted to the standard hydrogen electrode (SHE) scale by the addition of 0.2 V. By using this equipment; it was possible to continuously monitor and control the pH and Eh.
After the ground slurry (P80 of 90 µm) was transferred to the flotation cell, water was added to reach the target level, and pH adjusted to 11 using NaOH. An automatic titrator was used to deliver dilute solutions of sodium hypochlorite (NaClO) as an oxidising agent and sodium dithionite (D.T) (Na₂S₂O₄) as a reducing agent to set and maintain the Eh at the test value. The pulp was conditioned for 10 minutes. A fresh sample of potassium ethyl xanthate (KEX) as a collector was then added and the pulp was conditioned for a further two minutes. Make-up water used in the tests was Brisbane tap water. The pulp was deoxygenised by bubbling the nitrogen through the pulp for the tests being performed at Eh -200 and 0 mV SHE.

In this stage, a 200 ml sample was syringed for the EDTA extraction test and then the impeller was turned off. The 200 ml of collected sample was weighed and leached by 5 % solution Na₃EDTA for 10 min using an electrical stirrer, same as for the above test. After filtering using Whatman number 40 filter paper and 0.45µm Millipore filter, the filtered EDTA solution was submitted to ICP-AES for measuring the solubilised metals assays.

The percentage of oxidised mineral present in a pulp from EDTA extraction data was calculated from the following equation, which was developed by Rumball and Richmond (1996):

\[
% \text{EDTA extractable } M = \frac{\text{Mass of } M \text{ in EDTA solution}}{\text{Mass of } M \text{ in solids}} \times 100
\]

*Equation 3-1*

where $M$ is the metal under study.

---

**Figure 3-10, Schematic of the EDTA extraction and water chemistry test procedure**
The water chemistry tests were conducted on the flotation feed samples. After the sample was collected for EDTA tests, the impeller was turned off; the slurry was filtered using a Whatman number 40 filter paper by pressure filter and was again filtered through a 0.45µm Millipore filter. The solution was then poured into six different bottles, which were each preserved differently for measuring dissolved metals, anions, cations, reactive phosphate, alkalinity, hardness, nitrate, nitrite, ammonia, reactive phosphorus, total sulphur, TIC, TOC, and TC (Figure 3-11).

The results were then modelled by PHREEQC version 3 (Parkhurst and Appelo, 1999), which is a computer program for simulating a wide variety of aqueous geochemical calculations. In this study, the MINTEQ database was used for modelling aqueous solutions to calculate the ion speciation and precipitation/dissolution of minerals by calculating the saturation indices (SI).

Figure 3-11, Different bottles for the water chemistry tests
3.2. Analysis method

The following section firstly presents the calculations used in this thesis for determining the recovery of mineral of interest and secondly the error analysis method.

3.2.1. Flotation analysis

Flotation analysis was used to understand the floatability behaviour of minerals of interest. These calculations were performed on an unsized, size-by-size, and size-by-liberation basis. These were calculated using the metallurgical information for the feed, tail, and concentrate products and the liberation data from mineralogical information, Figure 3-12.
3.2.1.1. Overall Recovery ($R_{ovr}$)

The recovery ($R_{ovr}$) of the Cu, As, Fe, and S and the minerals of interest was determined by the following equation:

$$R_{ovr} = \frac{Cc}{Ff} \times 100$$

Equation 3-2

where $F$ and $C$ are the mass of solids in the feed and concentrate respectively (g) and $f$ and $c$ are the grades of the feed and concentrate respectively (wt.%).

3.2.1.2. Size-by-size and size-by-liberation recovery

The size-by-size and size-by-liberation recovery ($R_{ij}$) were calculated from the equation 3-3 (Welsby, 2009):

$$R_{ij} = \frac{C_{ij}}{F_{ij}} \times 100$$

Equation 3-3

where: $C_{ij}$ and $F_{ij}$ are the mass of the particle class $i$ and liberation class $j$ in the concentrate and feed respectively.

3.2.1.3. Water Recovery ($R_w$)

Water recovery ($R_w$) was calculated (Vianna, 2004), as follows:

$$R_w = \frac{W_c}{W_f} \times 100$$

Equation 3-4

where $W_c$ and $W_f$ are the mass of the water in the concentrate and in the feed respectively (g), including top up water.
3.2.1.4. Degree of Entrainment (ENT_i)

The overall and size-by-size degree of entrainment of a fully liberated, fully dispersed, non-floatable mineral (tracer) occurring in the ore, in this case fully-liberated quartz, were calculated using Equation 3-5 (Savassi, 1998):

\[
ENT_i = \frac{\text{W}^\text{conc}_i}{\text{W}^\text{tail}_i}
\]

Equation 3-5

where \( ENT_i \) is the degree of entrainment of tracer calculated in size class \( i \), \( W^\text{conc}_i \) and \( W^\text{tail}_i \) are the mass of free gangue in size class \( i \) per unit mass water in the concentrate and tailings respectively.

It should be noted that the degree of entrainment is independent of the mineral composition. Hence the degree of entrainment is the same for all liberation classes for a given size interval (Vianna, 2004).

The recovery of minerals by entrainment (\( R^\text{ENT} \)) and true flotation (\( R^\text{True Flotation} \)) were calculated using the equation 3-6 and 3-7 as follow (Savassi et al., 1999):

\[
R^\text{ENT} = \frac{1 - R^\text{Ovr}}{1 - R^w} \times ENT_i \times R^w
\]

Equation 3-6

\[
R^\text{True Flotation} = R^\text{Ovr} - R^\text{ENT}
\]

Equation 3-7

3.2.1.5. Flotation rate constant (k)

The flotation rate constant (\( k \)) of minerals was calculated from the following flotation model (Garcia-Zuñiga, 1935):

\[
R^\text{Ovr} = 1 - \exp(-kt)
\]

Equation 3-8

where \( R^\text{Ovr} \) is the overall recovery at the cumulative flotation time \( t \).
3.2.2. Accuracy of MLA measurement

The calculated elemental assays from the MLA data have been compared to the size-by-size chemical assay data for quality control purposes. The plotted elemental assay for Cu, Fe, S and As from MLA and ICP-AES for both the HAS and the LAS samples on size-by-size basis are shown in Figure 3-13. The data shows excellent agreement for copper, iron, sulphur, and arsenic assays between the two techniques that confirmed the high quality of the MLA measurement on the samples. It was observed that the error in the measurements from the MLA data is increasing in the very low assay minerals.

![Figure 3-13, Comparison between grade of Cu, Fe, S, and As from ICP-AES and calculated grade from MLA](image)

The MLA mineral assays were also compared to those from the QXRD technique (Figure 3-4 and Table 3-3). It was found that the MLA data are more accurate than the data from QXRD. The reasons for this disagreement could be the lack of accuracy of the XRD measurement for the very low assay minerals.
3.2.3. Error associated with experimental data

The method of calculation of the error associated with the collected and analysed data in this thesis is presented in the following section.

3.2.3.1. Sizing data

The experimental error of the sizing measurement was determined by repetition on the feeds of the HAS and the LAS samples. The cumulative weight percent passing for these repeats are given in Table 3-4. The reported size distributions are the raw measurements, and as such have not been subjected to mass balancing. It can be seen that the relative standard deviations for the two repeats of each sample were quite close, giving confidence in the sizing technique.

<table>
<thead>
<tr>
<th>Mesh Size</th>
<th>HAS Average Cumulative Wt. Passing (%)</th>
<th>HAS Relative Standard Deviation (%)</th>
<th>LAS Average Cumulative Wt. Passing (%)</th>
<th>LAS Relative Standard Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>98.91</td>
<td>0.06</td>
<td>99.17</td>
<td>0.05</td>
</tr>
<tr>
<td>100</td>
<td>96.08</td>
<td>0.14</td>
<td>96.83</td>
<td>0.05</td>
</tr>
<tr>
<td>150</td>
<td>86.88</td>
<td>0.24</td>
<td>87.96</td>
<td>0.99</td>
</tr>
<tr>
<td>200</td>
<td>72.45</td>
<td>0.27</td>
<td>73.12</td>
<td>0.76</td>
</tr>
<tr>
<td>300</td>
<td>56.94</td>
<td>0.58</td>
<td>57.55</td>
<td>0.80</td>
</tr>
<tr>
<td>400</td>
<td>45.29</td>
<td>1.14</td>
<td>45.17</td>
<td>1.42</td>
</tr>
<tr>
<td>CS1</td>
<td>44.47</td>
<td>0.40</td>
<td>44.40</td>
<td>0.50</td>
</tr>
<tr>
<td>CS2</td>
<td>39.06</td>
<td>0.53</td>
<td>39.68</td>
<td>0.17</td>
</tr>
<tr>
<td>CS3</td>
<td>31.25</td>
<td>1.77</td>
<td>31.83</td>
<td>0.80</td>
</tr>
<tr>
<td>CS4</td>
<td>22.73</td>
<td>1.79</td>
<td>24.86</td>
<td>1.69</td>
</tr>
<tr>
<td>CS5</td>
<td>18.51</td>
<td>5.03</td>
<td>21.84</td>
<td>6.31</td>
</tr>
<tr>
<td>CS6</td>
<td>7.08</td>
<td>15.05</td>
<td>10.82</td>
<td>16.24</td>
</tr>
</tbody>
</table>

3.2.3.2. Errors from chemical assay

The error of the head feed assays is given in Table 3-5. Three samples of the HAS and the LAS feed sample were split and submitted for assay. The results are presented as measured so have not been subjected to mass balancing. It was estimated that the sampling error would be minor as rotary rifflers were used for splitting samples for analysis. The relative standard deviations are less than ten percent and have the greatest value for arsenic.
### Table 3-5, Unsized assays of the HAS and the LAS head samples and relative standard deviation

<table>
<thead>
<tr>
<th>Sample</th>
<th>HAS</th>
<th>LAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Average Assay</td>
<td>Relative Standard Deviation %</td>
</tr>
<tr>
<td>Cu (%)</td>
<td>0.64</td>
<td>7.58</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>2.91</td>
<td>3.72</td>
</tr>
<tr>
<td>S (%)</td>
<td>2.96</td>
<td>5.38</td>
</tr>
<tr>
<td>As (ppm)</td>
<td>233</td>
<td>5.43</td>
</tr>
</tbody>
</table>

#### 3.2.3.3. Flotation error

The unsized experimental variation of the calculated feed stream across the 32 batch flotation tests is given in Table 3-6; the reported values are those as measured prior to mass balancing. Assay error across all the tests was seen to be only slightly different from that for the head assays (Table 3-5), indicating that the overall composition of the feed stream was very stable.

### Table 3-6, Unsized assays of the feeds calculated from concentrate and tail of the flotation tests and relative standard deviation

<table>
<thead>
<tr>
<th>Sample</th>
<th>HAS</th>
<th>LAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Average Assay</td>
<td>Relative Standard Deviation %</td>
</tr>
<tr>
<td>Cu (%)</td>
<td>0.67</td>
<td>2.67</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>2.74</td>
<td>1.75</td>
</tr>
<tr>
<td>S (%)</td>
<td>2.85</td>
<td>2.97</td>
</tr>
<tr>
<td>As (ppm)</td>
<td>241</td>
<td>1.61</td>
</tr>
</tbody>
</table>

The average calculated size distribution for the feed from flotation tests is given in Table 3-7. These size distributions are as measured and have not been subjected to mass balancing. The relative standard deviation was calculated from the percentage retained in each size class. In all size classes, this variation was less than 5 %. The size distributions were all in the same region when compared with the repeat sizing in Table 3-4.

### Table 3-7, Size-by-size weight distribution of the feeds calculated from concentrate and tail of the flotation tests and relative standard deviation

<table>
<thead>
<tr>
<th>Sample</th>
<th>HAS</th>
<th>LAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>Average Retained Weight %</td>
<td>Relative Standard Deviation %</td>
</tr>
<tr>
<td>+106</td>
<td>12.82</td>
<td>1.47</td>
</tr>
<tr>
<td>-106 +53</td>
<td>28.45</td>
<td>0.49</td>
</tr>
<tr>
<td>-53+32</td>
<td>18.36</td>
<td>1.75</td>
</tr>
<tr>
<td>-32+11</td>
<td>20.94</td>
<td>1.01</td>
</tr>
<tr>
<td>-11</td>
<td>19.42</td>
<td>1.26</td>
</tr>
</tbody>
</table>
The variation of size-by-size assay of the feed stream determined from the flotation tests is presented in Table 3-8. Again, the errors were for the assays as measured, before mass balancing. The relative standard error follows a similar trend in both samples.

Table 3-8, Size-by-size assays distribution of the feeds calculated from concentrate and tail of the flotation tests and relative standard deviation

<table>
<thead>
<tr>
<th>Size</th>
<th>Average Assay</th>
<th>Relative Standard Deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Fe</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>HAS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+106</td>
<td>0.50</td>
<td>2.37</td>
</tr>
<tr>
<td>-106+53</td>
<td>0.66</td>
<td>3.25</td>
</tr>
<tr>
<td>-53+32</td>
<td>0.96</td>
<td>4.46</td>
</tr>
<tr>
<td>-32+11</td>
<td>0.61</td>
<td>2.10</td>
</tr>
<tr>
<td>-11</td>
<td>0.55</td>
<td>1.75</td>
</tr>
<tr>
<td>LAS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+106</td>
<td>0.58</td>
<td>1.94</td>
</tr>
<tr>
<td>-106+53</td>
<td>0.55</td>
<td>1.97</td>
</tr>
<tr>
<td>-53+32</td>
<td>0.79</td>
<td>2.65</td>
</tr>
<tr>
<td>-32+11</td>
<td>0.56</td>
<td>1.30</td>
</tr>
<tr>
<td>-11</td>
<td>0.38</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Therefore, the error in mass flow was assigned to be 10%, and the standard deviation of the assay data was assumed to follow the Whiten function in Equations 3.9 (Runge, 2007, Runge, 2010)

\[ SD = \text{assay}/10 + 0.1 \quad \text{if assay} \leq 9\% \]

\[ SD = 1 \quad \text{if assay} > 9\% \]

\[ \text{Equation 3-9} \]

3.2.3.4. Error in mineralogical liberation data

Ideally, each liberation analysis would be performed in replicate to determine the error associated with each liberation class recovery value. In practice, however, this type of repetition is not feasible because of the limited time and cost. Instead, the variance for liberation measurement, in cumulative form, was calculated using Equations 3.10 which was developed by Leigh et al. (1993):

\[ Var(Y_C) \approx 1.25Y_C^2(1 - Y_C)^2\left[\frac{1}{N_0} + \frac{1}{N_1}\right] \]

\[ \text{Equation 3-10} \]

Y\(_C\) cumulative liberation yield at composition C expressed as a proportion.
No: number of particles with the composition less than C.

N1: number of particles with the composition at least C.

The confidence limits on $Y_C$ are then (Napier-Munn, 2014)

$$Y_C \pm z_{a/2} \sqrt{Var(Y_C)}$$

**Equation 3-11**

In addition, confidence intervals for each individual composition class were estimated using a statistical method based on a Poisson distribution. It determines the relationship between the coefficient of variation of the particle class in terms of the mass proportion of the mineral and number of particles. The error model is shown in Equations 3.12 (Lamberg and Vianna, 2007)

$$CV\% = \frac{100}{\sqrt{N}}$$

**Equation 3-12**

where $CV$ is the coefficient of variation, and $N$ is the number of particles in the particular class.

### 3.2.4. Confidence limit

In this thesis, the error bars represent 95% confidence intervals. In the cases where repeat data was available, the error was calculated from the actual standard deviations according to equation:

$$confidence \ limits = 1.96 \times \mu \pm \sigma \sqrt{n}$$

**Equation 3-13**

where $\mu$ is the average, $\sigma$ is the standard deviation, and $n$ is the number of analysis (Napier-Munn, 2014).

In other cases, where repeat data was not available, the error was calculated from bootstrap resampling techniques. This method includes varying each experimental value used in the mass balance by a randomly created, normally distributed deviation. This involves repetitively (1000 times) creating a new “possible” set of experimental data based on the actual mean of the data and its standard deviation. This new data set is used to recalculate a new estimate of the recovery. The standard deviation is then calculated from the 1000 estimates of its value. The 95% confidence interval of the recoveries is then calculated using that standard deviation (Napier-Munn, 2014).
3.2.5. Mass balancing

The first stage of data analysis is to mass balance the experimental results so that firstly, the three flotation streams are consistent, thus preventing recoveries of greater than 100% being calculated; and secondly, that each stream is internally consistent through the three levels of analysis. This ensures that as a stream is split into components (be they mineral, size or liberation classes) that their flows add up to give the whole value for the stream. Internal consistency is achieved by balancing the data in a stepwise approach, beginning with the elements on an unsized basis, then moving to the elements in size classes and finally balancing the liberation classes within each size class for each element (Welsby, 2009).

Mass balancing of the data was carried out using the measured standard deviations in the case of the unsized data and using the equations presented in Section 3.2.1 for the size-by-size and size-by-liberation data. All levels of analysis were balanced using excel starting from unsized, size-by-size and then size-by-liberation. In each step, the previously balanced data was used to constrain the mass balance.

3.2.5.1. Unsized results

The unsized data for the HAS and the LAS samples was mass balanced independently based on the flow and assay data which was available for all individual tests Figure 3-15 and Figure 3-14. It can be seen that the flow and assay data are of excellent quality and no adjustments were required.

Figure 3-14, Unsized mass balance results for mass flow for the HAS (left) and the LAS (right) samples
3.2.5.2. Size-by-size results

All samples from each individual test were sized and assayed separately. Thereby, size-by-size mass balances could be carried out for all individual tests. To ensure that the size-by-size mass balance was consistent with the unsized balance, the unsized balances were used to constrain the size-by-size mass balance (Figure 3-16 and Figure 3-17). It can be seen that minimal adjustments were required for the sizing and assaying data, indicating that it is also of excellent quality.

The next step was to convert the elemental assays to mineral quantities, as the quality of chemical analysis is generally better than the modal composition based on MLA measurements. Mineral grades of each stream and size fraction from the balanced chemical compositions were calculated. Enargite, NECu, and pyrite were calculated directly from chemical assays, however, for the gangue minerals, MLA data was used.
3.2.5.3. Size-by-liberation

The distribution of a size class in liberation classes was balanced, with the mass balanced flows of minerals for each size fraction.

It should be noted that mineral liberation analysis was not conducted on all the tails samples and was just performed on the tail sample of Eh -200 mV SHE for both samples. For the tests carried out at Eh 0, +200, and +400 mV SHE, the recovery by liberation was calculated based on concentrate data and recalculated feed from -200 mV SHE.
3.3. Summary

This chapter has described the experiments conducted and the errors associated with the data generated. The key points of this chapter can be summarised as follows:

- The ore samples used in this study were supplied from two parts of the Tampakan copper-gold deposit to represent two levels of arsenic; high arsenic section (HAS) and low arsenic section (LAS).

- The grinding time was determined for the HAS and the LAS samples to achieve a P₈₀ of 90 µm. The HAS and the LAS ore samples were sized in eleven size fractions and analysed by ICP-AES and MLA for the chemical assays and detailed mineralogical analysis.

- The batch laboratory rougher flotation tests were conducted at four different Eh ranges -200, 0, +200, and +400 mV SHE with four repeats of each to generate the various types of mineral floatability information. The CSIRO standard procedure was used in selecting the types and amount of the reagents.

- Five concentrates at different time intervals were collected to calculate the flotation rate of the minerals of interest. The combined concentrates together with the tail of each flotation condition were sized by wet and dry sieving and cyclosizing to give five size fractions +106 µm, -106/+53 µm, -53+CS2 µm, -CS2+CS5 µm, and -CS5 µm. The chemical characterisation and mineralogical studies of each size fraction were undertaken using ICP-AES and MLA.

- The EDTA extraction tests were conducted on the grinding product and the conditioning stage of the flotation tests at different Eh conditions for both HAS and LAS samples.

- The water chemistry tests were performed on the conditioning stage of the flotation tests at different Eh conditions for both HAS and LAS samples.

- Repetitive testing and Bootstrap resampling techniques were used to estimate the error associated with this data.
Chapter 4

CHEMICAL AND MINERALOGICAL CHARACTERISTICS OF THE ORE SAMPLES

The main aim of this chapter is to present the results of chemical and mineralogical characterisation of the HAS and the LAS ore samples.

The chapter begins with the size-by-size assay and weight analysis of the HAS and the LAS flotation feed samples. It then presents the results of MLA analysis on the HAS and the LAS flotation feed samples in terms of modal mineralogy, mineral distribution, mineral liberation, mineral association, and locking characteristics of sulphide minerals and non-sulphide gangue.

This chapter addresses the first hypothesis namely “The two ore samples will be characterised by largely similar base metal sulphide components, with the mineralogical differences residing within the gangue mineral phase.”
4.1. Chemical analysis

The unsized head assays showed that the arsenic in the HAS sample is practically two times higher than that for the LAS, assaying about 230 ppm. While the copper assay is slightly greater in the HAS sample, the non-enargite copper assay (NECu) which indicates the amount of copper in other copper sulphide minerals except enargite, is similar in both samples, circa 0.55%.

Eleven size fractions including: +150 µm, -150+106 µm, -106+75 µm, -75+53 µm, -53+38 µm, -38+32 µm, -32+23 µm, -23+15 µm, -15+11 µm, -11+6 µm, and -6 µm of the HAS and the LAS samples were submitted for chemical analysis using ICP-AES for Cu, Fe, S, and As. The detailed results of the chemical analysis on the size-by-size basis of the flotation feed are presented in Appendix C. As mentioned in Chapter 3, these size fractions were combined to reduce the number of MLA measurements as follow: +106 µm, -106+53 µm, -53+32 µm, -32+11 µm, and -11 µm. The weight and assay distributions in the HAS and the LAS samples in the different size fractions are showed in Figure 4-1.

The weight distribution bar charts show that the mass distribution for the HAS and the LAS samples have similar trends; the major proportion of the samples (circa 30%) reports to the -106+53 µm size fraction. It also shows while about 18% of the HAS sample is less than 11 µm; the LAS sample has around 22% in this size fraction. This difference in the grinding patterns can be attributed to the differences in the gangue mineralogy of the HAS and the LAS ores. The size fraction +106 µm has the lowest proportion of weight and elements.

The assays distribution bar charts indicate that except for the size fraction +106 µm, arsenic has distributed evenly (circa 23%) in the HAS sample while it has the descending trend starting from 27% in size fraction -106+53 µm to 17% in -11 µm in the LAS sample. However, the proportion of arsenic in the very fine size fraction -11 µm, is relatively high in both samples; 21% in the HAS and 17% in the LAS sample, which is greater than the distribution of Cu, Fe, and S.

The distribution of copper is similar in both samples in all size fractions. Approximately 57% of copper is distributed in the medium size fractions (-106+53 µm and -53+32 µm). The proportions of Fe and S in the medium size range (-106+53 µm and -53+32 µm) are approximately 63% and 67% respectively.

Another important point is that by comparing the distributions of arsenic and copper in different size fractions, it can be seen that the amount of NECu is higher than the amount of arsenic in coarser size fractions (+106 µm, -106+53 µm, and -53+32 µm), while in the finer size fractions (-32+11 µm, and
-11 µm) arsenic distribution is greater than NECu. This trend is similar in both HAS and LAS samples.

![Figure 4-1, Distribution of NECu, Fe, S, As, and weight in different size fractions for the HAS (left) and the LAS (right) samples](image)

### 4.2. Mineralogy characterisation

The mineralogy of each of the HAS and the LAS samples was assessed using the MLA SEM based automated mineralogy system. The method of measurement was the MLA XBSE technique, which uses the back-scattered electron image to define each grain in the polished section and identify the mineral in each grain from its characteristic X-ray spectrum. The raw data files generated from the measurements of the feed samples were analysed using MLA-Dataview 3 (see Appendix D).

MLA analysed a total of 935,172 grains within 420,158 particles for the HAS and 865,319 grains within 470,168 particles for the LAS sample. In MLA terminology, a “grain” is a distinct single mineral, whereas a “particle” is composed of just one or more mineral grains (Sylvester, 2012, Cropp and Goodall, 2013).

The data collected for each size fraction were combined according to their mass proportions to obtain the key mineralogical characteristics, such as modal mineralogy, grain size, and texture of the ore samples.
4.2.1. Modal mineralogy

The overall modal mineralogy of the HAS and the LAS samples is summarised in Table 4-1 and is consistent with both chemical analysis and QXRD analysis confirming the low quantity of sulphide minerals in both ore samples. The main copper minerals are bornite (Cu₅Fe₂S₄) and chalcopyrite (CuFeS₂) which represent about 75% of copper in each ore. The remaining copper is presented as enargite (Cu₃AsS₄), digenite (Cu₉S₅), covellite (CuS), and tetrahedrite ((Cu,Fe)₁₂Sb₄S₁₃). The dominance of chalcopyrite and bornite as the major copper minerals with the small proportions of the total copper present in other minerals simplifies the investigation of the ore since it is reasonable to assume that only chalcopyrite and bornite will best describe the copper mineral response in liberation and the flotation processes.

It can be seen that the major difference between the two samples is the distribution of the gangue minerals. The sulphide gangue consists of pyrite with 5.36% and 3.30% in the HAS and the LAS samples respectively. Quartz, muscovite, pyrophyllite, diaspore, and kaolinite are the major non-sulphide gangue minerals (NSG).

<table>
<thead>
<tr>
<th>Component</th>
<th>Major mineral</th>
<th>Nominal formula</th>
<th>HAS</th>
<th>LAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>0.39</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu₅Fe₂S₄</td>
<td>0.58</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>Digenite</td>
<td>Cu₉S₅</td>
<td>0.02</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>0.06</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Tetrahedrite</td>
<td>(Cu,Fe)₁₂Sb₄S₁₃</td>
<td>0.11</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-1, Overall modal mineralogy of the HAS and the LAS ore samples (% by weight)
The results show that the total amount of phyllosilicates which include muscovite, kaolinite, and pyrophyllite in the LAS sample is higher than that in the HAS sample, 36.17 vs. 22.96 wt% respectively. Muscovite content is about four times higher (28.71%) in the LAS sample than in the HAS sample, however the LAS sample contains less pyrophyllite, and no kaolinite compared to the HAS sample. The amount of diaspore in the HAS is greater than that in the LAS sample as well.

The size-by-size modal mineralogy of the HAS and the LAS samples are presented in Figure 4-2, and their mineral distributions on a size-by-size basis are shown in Figure 4-3 and Figure 4-4. It can be seen that the major proportion of the phyllosilicates reported to the -11 µm size fraction in both samples. About 45% of muscovite in both samples, as well as, 55% and 61% of pyrophyllite in the HAS and the LAS samples respectively report to the finest size fraction. Pyrite is mostly (about 70%) present in the medium size range (-106+53 µm and -53+32 µm) in both samples.

Observations on the modal mineralogy and the particle size distribution of the HAS and the LAS samples indicate that gangue mineralogy contributed a controlling role in the grinding of the ore samples. For example, diaspore is a much harder (Mohs hardness 8) mineral than phyllosilicates (Mohs hardness around 2) and need more grinding time or media.

According to Figure 4-3 and Figure 4-4, it is clear that the main copper minerals in all size fractions are chalcopyrite and bornite which are mostly distributed in medium size fractions (-106+53 µm and -53+32 µm) in both samples. Regarding the other copper minerals, the HAS sample has more covellite and the LAS sample has more digenite; both for which are less than 0.1 wt%. Tetrahedrite distributed similarly in both samples.

Figure 4-2, Size-by-size modal mineralogy of the HAS (left) and the LAS (right) samples
Figure 4-3, Size-by-size mineral distribution of the HAS (% by weight), (A: General, B: Copper Minerals)

Figure 4-4, Size-by-size mineral distribution of the LAS (% by weight), (A: General, B: Copper Minerals)
4.2.2. Particle size and mineral grain size distribution

The P$_{80}$ of the particles in the feed samples, after grinding, was 90 µm and the P$_{50}$ was 45 µm. The particle size distributions for all size fractions are similar for both the HAS and the LAS samples (Figure 4-5).

![Figure 4-5, Particle size distributions of the HAS (left) and the LAS (right) samples](image)

Grain size data, produced by MLA measurement, are one of the critical mineralogical factors that influence the processing of the ores and the efficiency of the process (Zhou et al.). The ore needs to be ground to such a degree that desirable minerals are liberated from other minerals to achieve an efficient separation of the minerals of interest. This information would assist in determining the suitable grind size to maximise the recovery and to avoid over-grinding (Kappes et al., 2007).

Mineral grain size data for non-enargite copper minerals, (chalcopyrite, bornite, digenite, covellite, and tetrahedrite), enargite, pyrite, phyllosilicates (kaolinite, pyrophyllite, and muscovite), and gangue minerals, (quartz, diaspore, and others) were obtained for the HAS and the LAS samples by MLA analysis (Figure 4-6).

The grain size distribution of the HAS and the LAS samples are similar. The P$_{80}$ grain size of NECu is 48 and 53 µm in the HAS and the LAS sample respectively. The P$_{80}$ grain size of non-sulphide gangue minerals for both samples is about 90 µm while the P$_{80}$ of the phyllosilicate group is 82 µm. Interestingly the grain size distribution of enargite is lower than other minerals. The P$_{80}$ grain size of enargite is 27 µm in the HAS sample, while it is 44 µm in the LAS sample.

Comparing the P$_{50}$ of minerals shows that while the P$_{50}$ of phyllosilicate group are 13 µm and 14 µm, the P$_{50}$ of enargite is 12 µm and 16 µm in the HAS and the LAS samples respectively.
Figure 4-7 compares the P80 size of all particles and P80 grain size of NECu, enargite, and pyrite. In all the size fractions, NECu, enargite, and pyrite are finer than the total particles. These results indicate that the sulphides tend to be ground more readily than the non-sulphides, a result, which is not unexpected because much of the gangue minerals group is quartz, which is difficult to grind.

While the 80 percent passing size by weight is 90 µm for both samples, the 80 percent passing size of enargite is 77 and 85 in the HAS and the LAS samples respectively. It can be seen that the amount of fine (-11 µm) particles is noticeably greater for enargite than for NECu. It shows that enargite tends to be ground more readily than the other copper sulphide minerals. The tendency for enargite to grind readily has been noted earlier (Senior et al., 2006).
4.2.3. Mineral locking and association characteristics

Liberation distributions were obtained using MLA measurements of the polished sections of the samples in 11 size fractions. The results were combined to the size fractions: +106 µm, -106+53 µm, -53+32 µm, -32+11 µm, and -11 µm. Figure 4-8 and Figure 4-9 show the overall distribution of the minerals in different locking classes for the HAS and the LAS samples respectively. In general the liberation distribution of minerals is the same in both HAS and LAS samples.

As mentioned in the literature review, a particle is considered liberated when it contains >95% by weight of a mineral of interest, binary when it contains a mineral of interest and one other mineral, and ternary if it contains a mineral of interest and more than one other mineral.

Looking at the gangue minerals, it can be seen that quartz is more than 90% liberated in both samples. Muscovite is more liberated in the LAS sample than in the HAS sample, while kaolinite and pyrophyllite have better liberation distributions in the HAS sample. However, it should be noted that the LAS sample has less than 1% kaolinite. Pyrite is more liberated in the HAS sample than in the LAS sample (67% vs. 55%), and where it is locked, it tends to be with muscovite and quartz.

It is clear that copper minerals are less liberated than gangue minerals in both samples. About 20% of copper minerals are ternary locked. Chalcopyrite is the most liberated copper mineral in both samples, circa 60%. Bornite has the least proportion liberated particles in both samples and is more liberated in the HAS sample (46% vs. 41%). The copper minerals in the HAS sample are binary locked with quartz and pyrite while in the LAS sample are more associated with quartz, pyrite, and muscovite.

Almost 50% of enargite is liberated in both HAS and LAS samples while 20% is ternary locked. Figure 4-10 and Figure 4-11 show the mineral association of enargite in the HAS and the LAS samples respectively. The results for the HAS sample indicate that enargite was associated mainly with quartz, pyrite, bornite, and other copper minerals (6% each). A small amount of enargite was found to be associated with phyllosilicates. In the LAS sample enargite was mostly associated with muscovite (13%) followed by quartz (10%), and to a lesser extent, with bornite and other copper minerals. 63% and 52% of the enargite, however, showed free surfaces, i.e., the proportion of the total surface of enargite that was exposed and ready for flotation.
Figure 4-8, Distribution of minerals in locking classes in the HAS sample

Figure 4-9, Distribution of minerals in locking classes in the LAS sample
Figure 4-10, Mineral association for enargite in the HAS sample

Figure 4-11, Mineral association for enargite in the LAS sample
The size-by-size distributions of the minerals in different locking classes for the HAS and the LAS samples are presented in Figure 4-12 and Figure 4-13 respectively. The results demonstrate an increasing degree of liberation toward smaller size fractions for both HAS and LAS samples.

The data presented in Figure 4-12 and Figure 4-13 shows that the majority of the minerals in size fraction -11 μm are more than 90% liberated in both the HAS and the LAS samples. However, quartz is well liberated in all size fractions in both samples.

Enargite in size fraction +106 μm is almost entirely locked with other minerals (especially pyrite and quartz). However its degree of liberation increases as the size decreases and is almost entirely liberated (>90% and >85%) in size fraction -11 μm in the HAS and the LAS samples respectively. Comparing the enargite liberation profile in the HAS and the LAS, shows that generally it has distributed similarly in both the samples with the exception in the size fraction -32+11 μm. While only 58% of enargite is liberated in size fraction -32+11 μm in the HAS sample, it is 71% liberated in the LAS sample.

The same trend can be observed for the copper minerals - poor liberation in the largest size fraction to almost entirely liberated in the finest size fraction. The results show that chalcopyrite is a better liberation than bornite in all size fractions for both samples. In addition, they have better liberation distributions than enargite.

It was seen from mineral distribution (Figure 4-1) that the majority of copper minerals were distributed in size fractions -106+53 and -53 +32 μm. However, bar graphs show that at those size fractions, there are not sufficient liberated copper minerals, and the majority of their particles are locked with pyrite, muscovite, and quartz, thus indicating that further grinding would be required to improve the degree of liberation of copper mineral particles.
Figure 4-12, Size-by-size distribution of minerals in locking classes in the HAS sample
Figure 4-13, Size-by-size distribution of minerals in locking classes in the LAS sample
4.2.4. Mineral liberation

The mineral liberation by particle composition diagrams for combined non-enargite copper minerals (NECu), enargite, and pyrite are presented in Figure 4-14, Figure 4-15, and Figure 4-16 respectively. The shape of the liberation curves also provides information about the distribution of the minerals across the composite particle classes. The shape of the different curves is related to the amount of the 100% liberation class. If the number of particles in 100% liberation class is low, the curve shows a sharp increase toward the 80-100% liberation class; however, curves with a higher starting point show a smoother rise.

In general, the liberation distribution of NECu in each of the particle size fractions follows a similar trend across both samples and increases as the particle size decreases.

The cumulative liberation distribution of enargite shows better results for the LAS samples. In general, in both samples, the liberation distribution increases as the particle size decreases. The cumulative liberation distribution of enargite shows that the confidence limits for the size fractions +106 µm and -106+53 µm are relatively wide due to the small numbers of particles containing enargite in these size fractions. The majority of enargite has reported to the finest size fraction -11 µm.

Pyrite has the same liberation distribution in both samples, and it's liberation distribution increases as the particle size decreases.

Figure 4-14, Mineral liberation by particle composition for NECu minerals in different size fractions in the HAS (left) and the LAS (right) samples
Figure 4-15, Mineral liberation by particle composition for enargite in different size fractions in the HAS (left) and the LAS (right) samples

Figure 4-16, Mineral liberation by particle composition for pyrite in different size fractions in the HAS (left) and the LAS (right) samples
4.2.5. Theoretical grade-recovery curves

The theoretical grade-recovery curve is defined by the maximum potential grade and recovery of a mineral that can be gained by in a perfect separator. This is related to the grain size and liberation characteristics of the valuable minerals (Goodall, 2009, Finch and Gomez, 1989).

The theoretical grade-recovery curves in Figure 4-17 show a better curve for NECu than for enargite, thus, it is expected to get better results for NECu than enargite in the flotation tests for the HAS and the LAS samples. Figure 4-18 present the grade-recovery curves for enargite in different size fractions. Despite the similarity between unsized grade-recovery curves of enargite in the HAS and the LAS sample, its size-by-size grade-recovery curves are a bit different. Except for size fraction -11 µm, slightly better size-by-size grade-recovery curves are observed in the LAS sample than those in the HAS sample. As would be expected, the grade-recovery curves for enargite follow the liberation trends observed in Figure 4-15.
Figure 4-19 and Figure 4-20 present a scenario where NECu theoretically floated out in the HAS and the LAS samples respectively. The left-hand graphs in these figures are the theoretical grade-recovery curves for NECu in different size fractions, and the right-hand graphs represent the corresponding arsenic grade of the concentrate through being locked with NECu particles, with the smelter limit of 2000 ppm indicated on the curve as well.

It can be seen that the arsenic grade is well below the allowed limit (2000 ppm) in the LAS sample, however, in the size fraction -32+11 µm for the HAS sample the arsenic which would be recovered to the concentrate by being locked by NECu minerals is higher than the allowed limit. It is due to the poor liberation of enargite in the HAS sample in this size fraction, as mentioned in section 4.3.4. These graphs show that the liberation of NECu minerals in both samples is good enough that if the selective flotation was successful, the separation between the NECu and enargite would be possible.
4.3. Key findings

Chemical and mineralogical properties (ICP-AES and MLA) of the HAS and the LAS feed samples were studied. The main findings of this chapter are as follow:

- The HAS and the LAS ore samples used in this work came from two parts of the same mine site. The modal mineralogy data obtained showed that the ore samples contain similar gangue minerals in different proportions. Gangue mineralogy mainly comprised of quartz, diaspore, and phylllosilicates including muscovite, pyrophyllite, and kaolinite. The amount of phylllosilicates (mostly muscovite) in the LAS sample was more than phylllosilicates proportion in the HAS sample (mostly pyrophyllite).

- Enargite was the only arsenic mineral present in both samples. The main copper minerals were bornite and chalcopyrite. However trace amounts of digenite, covellite, and tetrahedrite were observed.

- The size-by-size weight distribution of the HAS and the LAS samples showed similar trends in both samples. Most of the phyllosilicate minerals reported to the finest size fraction -11 µm.

- The chemical analysis on a size-by-size basis showed that NECu minerals (non-enargite copper minerals) were mostly distributed to the coarser size fractions (+106 µm, -106+53 µm, and -53+32 µm), while the proportion of enargite in the finer size fractions (-32+11 µm and -11 µm) was higher than NECu.

- The mineral grain size data showed that enargite had the finest grain size distribution compared to other copper minerals. The P80 grain size of enargite in the HAS sample (27 µm) was half of that in the LAS sample (43 µm).

- Enargite was mainly associated with copper minerals, pyrite and quartz in the HAS sample. It was widely associated with muscovite and quartz and in less extent pyrite and copper minerals in the LAS sample. In addition the percentage of the total free surface of enargite grains was higher in the HAS sample (63%) than in the LAS sample (52%).

- Mineral locking data indicated that both samples have similar liberation characteristics. In general, the liberation distribution of the minerals increases as the particle size decreased,
where in the finest size fraction -11 \( \mu \text{m} \) more than 90\% of the minerals grains were fully liberated.

- Liberation characteristics indicated that at \( P_{80} \) of 90 \( \mu \text{m} \), the overall liberation of the combined enargite was greater than 50\% in both samples. However, size-by-size liberation data showed that enargite was less liberated in the -38+11 \( \mu \text{m} \) size fraction in the HAS sample compared to the LAS sample: 58\% in HAS vs. 71\% in LAS.

- Liberation data also showed that more than 85\% of non-sulphide gangue minerals were fully liberated and pyrite was more than 55\% liberated in both samples.
Chapter 5

FLOTATION RESULTS

The main aim of this chapter is to describe the flotation performance of the HAS and the LAS ore samples under different Eh conditions.

The chapter begins with the results of the preliminary proof of concept tests on two other ore samples (A and B). It then presents the results obtained from the flotation tests without collector at the air set potential and with the collector at different Eh conditions on the HAS and the LAS samples. The results were analysed to establish the overall grade and recovery, the recovery by size, and then recovery in different liberation classes. The data are presented as a function of Eh to show how different minerals were floated at various Eh ranges and in which Eh region there is potential to separate enargite from other copper minerals.

As mentioned in Chapter 1 in the scope and limitations of this thesis, reagent optimisation tests were not performed in this study, and suitable types and dosage of the reagents and operating conditions were selected based on the actual confidential reports on the Tampakan ore samples.

In this chapter, the flotation data is presented for NECu, enargite, pyrite, and NSG (non-sulphide gangue). In order to have a clear understanding on the separability of enargite, the copper minerals, except enargite, are presented as one group named NECu (non-enargite copper minerals). It has been assumed that the flotation behaviour of NECu follows the flotation behaviour of chalcopyrite as the chalcopyrite and bornite have the similar floatability and also the proportion of other copper minerals is very low in the HAS and the LAS samples.

This chapter addresses the second hypothesis: “The high-arsenic ore sample (HAS) is expected to be characterised by higher enargite floatability than the low-arsenic ore sample (LAS), due to the greater proportion of the enargite mineral within its feed composition.”
5.1. Preliminary proof of concept experiments

The purpose of the proof of concept tests were to develop a batch flotation technique, reduce the experimental errors and conserve the limited amount of the main sample. In order to establish this, two sets of experiment were conducted as flotation test I and flotation test II.

5.1.1. Flotation tests I

The first series of proof of concept tests, which was the basis of this thesis, was done for a research project as part of the preliminary experimental investigations. It was tested on a confidential case study.

The mineralogy data showed that the copper-bearing minerals are mainly bornite and chalcopyrite. Main gangue minerals include pyrite, silicates, and clays. It also contains significant amounts of the detrimental metal arsenic carried by enargite (Cu₃AsS₄) and trace amounts of tetrahedrite [(Cu,Fe)₂Sb₄S₁₃]. The dominant alteration type was advanced argillic and this was the host to the majority of the valuable copper. The gangue mineralogy in this porphyry ore was dominated by quartz followed by muscovite, feldspar, pyrophyllite, and diaspare (Edraki et al., 2014).

Selected drill core samples from the high arsenic (HA) and low arsenic (LA) sections of the deposit were used for flotation tests. Samples for flotation were ground in a steel mill, 200 mm × 250 mm in size, using a charge of 15 rods, 22mm × 235mm mild steel rods with a weight of 11,161 grams at a pulp density of 60% solids using laboratory tap water. The grinding time to achieve the P₈₀ of 150 μm and 75 μm was determined (Edraki et al., 2014).

The flotation tests were conducted on the ore samples using a 5 L JKMRC Batch flotation cell, which gave a pulp density of 32 wt.% solids. Tap water was used for all flotation tests. 300 grams per tonne of PAX as a collector and 20 g/tonne of the frother MIBC were added in the conditioning stage. The pH was adjusted to 11 using lime before reagent addition. The total froth collecting time (600 s) was divided into periods of 60, 180, and 360 seconds. The froth was removed by scraping the whole surface of the cell, at a fixed depth, every 10 seconds. The feed, concentrates, and tailings samples were characterised by a Mineral Liberation Analyser (Edraki et al., 2014).

The results showed that the best grade-recovery curve was obtained by grinding the sample to P₈₀ of 75μm. The grinding and flotation experiments showed that the concentration of arsenic in tailings is reduced by decreasing of grind size. The decrease the grind size resulted in a higher degree in
liberation in tailings, and a reduction of pyrite in the tailings was also observed. The complete procedure and the results are presented in the Appendix E.

5.1.2. Flotation tests II

Recently, CSIRO was involved in a project to further demonstrate the technical feasibility of the early removal of arsenic minerals by selective flotation at bench scale. The major sulphide minerals in the ore sample were chalcopyrite and enargite. The flotation results indicated that a separation was possible over a narrow range of pulp potential (around 0 mV SHE), Figure 5-1.

The purpose of this proof of concept tests was to confirm the result obtained by CSIRO on an unidentified ore sample. In order to establish this, a number of tests were required to cover the pulp potential range of -50 mV to +450 mV.

The results were in good correlation with the findings of CSIRO, which proved that for this ore, the separation could happen at 0 mV SHE. The complete procedure are presented in the Appendix F.

![Figure 5-1, Cu and As recovery on the rougher feed versus pulp potential in the separation stage](image-url)
5.2. Flotation tests on Tampakan ore sample without collector

After the flotation equipment had been set up, a number of preliminary flotation tests were conducted to establish the flotation procedures and operating conditions and to reduce the experimental error. The details of each experiment can be found in the Appendix G.

Two flotation tests were performed in the absence of collector to determine the self-induced floatability of the mineral particles in the HAS and the LAS ore samples. The flotation tests were conducted at the air set potential and pH 11 without any redox reagents. The results of these tests versus time are given in Figure 5-2.

The recovery of NSG was lower than the recovery of water, which means that it was recovered by entrainment. In contrast, the recoveries of NECu and enargite particles were greater than the recovery of water suggesting that the principal mechanism for the flotation of these sulphide minerals would be by true flotation. As mentioned in Chapter 2, the mild oxidation of copper sulphide minerals can increase the floatability of these minerals by forming elemental sulphur or polysulphides on their surface.

![Figure 5-2](image)

**Figure 5-2, Recovery vs. time for flotation tests without collector at air set potential for the HAS (left) and the LAS (right) concentrates**
5.3. Flotation tests on Tampakan ore sample with collector

In this section, the results of the main flotation tests on the HAS and the LAS samples are presented. The details of each experiment can be found in the Appendix H.

The procedure for the calculation of overall recovery, recovery by size, degree of entrainment, water recovery, and recovery of composition particles has been given in Chapter 3. In this section, the results are presented.

A high level of repeatability was achieved using the control strategy at all Eh values except +400 mV SHE. The froth of the flotation tests at Eh +400 mV SHE was difficult to control for both HAS and LAS samples. The reason for is likely to be due to the high amount of sodium hypochlorite which was used (about 150-250 cc per tests) for controlling and maintaining the Eh at +400 mV SHE. Therefore, even without using any frother, and by reducing the gas flow rate to its lowest level, the froth was still uncontrollable. Investigating the cause of the frothing was outside of the scope of this work though the effect of gangue minerals is undeniable (see Chapter 7).
Figure 5-3 shows the photos of the flotation tests at various Eh conditions at time zero, just before the scraping has started. It was observed that the froth was grey/green and full of valuable particles in both samples at +200 mV SHE. In general, the flotation tests on the LAS sample was time-consuming especially during grinding and filtering as it consists mainly of phyllosilicate minerals and the very fine particles generated affected these processes adversely.

The copper, arsenic, iron, and sulphur assays were determined at different time intervals (5 concentrates at 0.5, 1, 2, 4, and 10 minutes) for each of the flotation tests at different Eh values and were used to calculate grade and recovery of NECu, As, Fe, and S. The recovery versus time results for the flotation tests conducted at different Eh conditions are presented in Figure 5-4.
Figure 5-4, Recovery vs. time for flotation tests at different Eh conditions for the HAS (left) and the LAS (right) concentrates.
5.3.1. Unsized results

The overall recovery results of NECu, enargite, pyrite, non-sulphide gangue minerals at different Eh conditions (-200, 0, +200, +400 mV SHE) for the HAS and the LAS samples were calculated from the ICP-AES and MLA data and shown in Figure 5-5.

The NECu recovery displays a similar trend in both samples. There is a little floatability (about 45%) at Eh -200 mV SHE, followed by a gradual increase with increasing Eh, and finally reaching the maximum recovery circa 80% at an Eh range between 100 and 200 mV SHE. Subsequently the recovery decreases in the oxidative Eh range above +200 mV SHE. This trend is in agreement with the pure mineral studies of chalcopyrite by Heyes and Trahar (1977). However, it was expected that there would be little or no floatability of copper minerals in the Eh range below -100 mV SHE.

In contrast, there is a significant difference in the recovery of enargite from the flotation results of the HAS and the LAS. Although the enargite recovery trend is similar in both samples, its recovery is 10% to 25% lower in the HAS sample compared to the LAS sample. As for the NECu results, lower recovery is observed at Eh -200 mV SHE (47% for the HAS and 67% for the LAS), followed by a gradual increase with increasing Eh, where the maximum recovery is achieved at Eh +200 mV SHE (62% for the HAS and 82% for the LAS). The recovery then decreases as the Eh is increased toward more oxidative conditions (51% for the HAS and 60% for the LAS at Eh +400 mV SHE).

Pyrite recovery also showed a similar trend in both samples, starting from circa 74% at -200 mV SHE, reaching the maximum recovery circa 81% at 0 mV SHE and decreasing in the oxidative Eh range above +200 mV SHE. There was little selectivity against pyrite at reducing potentials. Although no specific depressants were added to depress the pyrite during flotation, it was partly depressed at Eh +400 mV SHE. It was observed by Senior et al. (2006) that 95% of enargite and 60% of pyrite were recovered from a composite sample after 10 minutes flotation at Eh 95 mV SHE. There are several possible reasons for the high recovery of pyrite. It can be due to the poor liberation of the pyrite particles and subsequent recovery of these composite particles. However, as mentioned in Chapter 4, more than 60% of the pyrite particles are fully liberated; hence, this assumption is not valid. Another reason for high recovery of pyrite could be the induced floatability that can happen from activation by Cu ion, galvanic interactions between minerals, and formation of a sulphur layer on the mineral surface. These will be discussed more in Chapter 7.

The NSG recovery gradually increases as the Eh is raised toward more oxidising conditions and reaching the maximum recovery at Eh +400 mV SHE. However, its recovery is less than 10% in all the Eh ranges in both samples, indicating that the recovery mechanism is principally entrainment.
There are some observations from the graphs presented in Figure 5-5:

Firstly, the recoveries of minerals at -200 mV SHE are higher than what was expected. According to the pure minerals studies by Guo and Yen (2005) and Senior et al. (2006), enargite should display little or no floatability at an Eh below -100 mV SHE. However, the results presented in Figure 5-5 clearly show circa 46% and 67% recoveries of enargite in the HAS and the LAS samples respectively. In addition, the recoveries of NECu (around 45% in both samples) in the reducing conditions are also higher than was expected from the pure mineral studies. These results are consistent with the findings of Smith and Bruckard (2007). They observed that the threshold potential of the tennantite and the non-tennantite minerals flotation was shifted about 100 mV SHE in a more reducing direction. They suggested that one of the reasons for this change in the pulp potential, and achieving higher recovery than expected, could be due to hysteresis effects. “In some systems, hysteresis in the threshold
potential occurs depending upon whether the potential is being shifted to more reducing conditions or more oxidising conditions” (Smith and Bruckard, 2007). In this project, the grinding was performed at the air set potential and then the flotation tests were conducted under nitrogen gas for the flotation tests at reducing conditions - this could be the cause for the hysteresis phenomena.

Secondly, based on the findings of Senior et al. (2006), enargite is more floatable than chalcopryite under slightly reducing conditions. Therefore it should be possible to float enargite selectively from chalcopryite. The comparison of NECu and enargite recoveries in the LAS sample shows that at -200 mV SHE enargite can potentially be separated from the other copper minerals since the recovery of enargite is 67%, but the recovery of NECu is about 46%. These results at -200 mV SHE are in agreement with the results obtained from Ore A by Smith et al. (2012). They found that there is a region between -200 and -130 mV SHE where tennantite can be floated from the other non-tennantite copper minerals (NTCu). The recovery of arsenic was 80-90% in this region while NTCu recovery was only 30%. They also observed that the selectivity between NTCu minerals and tennantite below and above this region was reduced; the floatability of tennantite decreased below -200 mV SHE and the floatability of the NTCu increased above -130 mV SHE (Smith et al., 2012). Hence, it was expected that a separation would be possible in the reducing region for the HAS sample. However, as the results show, the recoveries of NECu and enargite are similar at reducing potentials, and there is no separation between NECu and enargite.

Thirdly, by looking at the recoveries of enargite and NECu at Eh +400 mV SHE in the LAS sample, it can be seen that the recovery of NECu and enargite decreased in both samples. This is consistent with the study by Smith and Bruckard (2007). They observed the strong floatability of both tennantite and the non-tennantite copper minerals (NTCu) up to +400 mV SHE while their floatability decreased above +400 mV SHE. There was no significant difference in their recoveries where a separation should be possible at the oxidising conditions (Smith and Bruckard, 2007). The conclusion from the LAS data was that conditioning at +400 mV SHE brought about too strong a depressant effect. Therefore the selectivity of separation between enargite and NECu was largely lost.

Finally, it can be seen that enargite has not floated as expected in the HAS sample and there is a very low variation of recoveries as the Eh was increased. The difference between minimum and maximum recoveries in the LAS sample is about 22%; (60% at +400 mV SHE vs. 82% at +200 mV SHE), while this difference is only 15% in the HAS sample (47% at -200 mV SHE vs. 62% at +200 mV SHE). The reason for lower recovery of enargite can be due to either particle too large or small for flotation, poor liberation or locked with non-floating particles, or with a hydrophilic surface due to insufficient collector coverage or depressant coatings or surface oxidation (Runge, 2010). Further investigation
was done to address these responses of enargite in the HAS sample. Flotation tests were performed at Eh +100 mV SHE on the HAS sample to see if the recovery of enargite can be improved. The flotation time was increased to 16 minutes, and the collector dosage was doubled. No redox reagent was used, and the flotation gas was air. The maximum recovery of enargite was only 68% after 16 minutes flotation. At the same conditions, a flotation test was conducted on the LAS sample and a recovery of 93% was achieved for the enargite (Appendix I).

The actual grade-recovery curves of the NECu and enargite/arsenic from rougher flotation tests at different Eh conditions for the HAS and the LAS samples on unsized basis are presented in Figure 5-7 and Figure 5-8.

Comparing the grade of the NECu (Figure 5-7) for different Eh conditions shows that the flotation concentrates at Eh 0 mV SHE had the highest NECu grade in both samples. However, the best NECu recovery was achieved at Eh +200 mV SHE. It can be concluded that the best NECu grade-recovery curve happened between the Eh range 0 and +200 mV SHE for both samples.

In contrast, the flotation test at -200 mV SHE generally had the highest enargite grade when compared with the other Eh conditions (Figure 5-8). However, the level of arsenic in all rougher concentrates was less than 2000 ppm. It should be again noted that the enargite in the HAS sample had not floated as expected, otherwise the level of arsenic would be higher than 2000 ppm. On the other hand, the best recovery of enargite was achieved at Eh +200 mV SHE.

Comparing these rougher grade-recovery curves with the theoretical grade-recovery curves presented in section 4.2.5 of this thesis shows that the actual grades of NECu and enargite are much less than their theoretical grades. There are many factors which would cause the offset between theoretical and actual grade-recovery curves. It could be due to entrainment, the flotation of non-valuable minerals, and poor selectivity of the flotation reagents. The low grades of the NECu and enargite in the rougher concentrates emphasise the necessity of a cleaner stage flotation to improve the grade of the concentrate. Although by improving the grade of the concentrate, more enargite would be recovered to the concentrate, which would increase the level of the arsenic to higher than 2000 ppm. Cleaner studies were outside the scope of this thesis.
Figure 5-7, Actual grade-recovery curves for NECu at different Eh conditions for the HAS (left) and the LAS (right) concentrates

Figure 5-8, Actual grade-recovery curves for enargite/arsenic at different Eh conditions for the HAS (left) and the LAS (right) concentrates
5.3.2. Size-by-size results

As mentioned in Chapter 3, the combined concentrates of each flotation condition together with the tails were sieved and cyclosized into five size fractions (+106, -106+53, -53+32, -32+11, and +11 µm). Quantitative mineralogy was undertaken on concentrates and tails, using the Mineral Liberation Analyser (MLA) system. The size-by-size response was calculated to examine the relationship between Eh and particle size. The mass balanced data is presented in Figure 5-9.

The data for NECu, enargite, and pyrite show the typical mineral recovery by size trends for sulphide minerals; low floatability of coarse and fine particles, and high floatability of valuable minerals in medium size fractions. In addition, it is clear that the recovery of enargite in the HAS sample is lower than that for the LAS sample in all size fractions.

The maximum recovery of NECu and pyrite happened at size fraction -53+32 µm in all the Eh conditions for both samples. This is similar to recovery of enargite except at Eh -200 mV SHE, where the recovery reached a maximum value in the size fraction +32-11 µm in both samples.

A consequence of these different responses at Eh -200 mV SHE is that the optimum size for separation of the components occurs in the size fraction -32+11 µm. While maximum enargite recovery is 60%, recovery of NECu is only 42% in that size fraction in the HAS sample. This difference in recoveries of NECu and enargite is greater in the LAS samples; enargite 86% and NECu 53%. The selectivity ratio between enargite and non-enargite copper were 1.63 and 1.43 in the LAS and the HAS flotation test at size fraction -32+11 µm and at Eh -200 mV SHE. In the fine size fractions the selectivity decreases.

Although the overall recovery in Figure 5-5 showed there is no selectivity between enargite and NECu in -200 mV SHE in the HAS sample, the recovery by size indicates that there is a potential for separating these two minerals at the size fraction -32+11 µm in both samples.

It seems unlikely from the results at Eh +400 mV SHE that a good separation can be achieved between enargite and NECu at this pulp potential.

On the other hand, pyrite is depressed in all the size fractions at Eh +400 mV SHE in both samples; its maximum recovery is only 28% at size fraction -53+32 µm in the LAS sample.
Figure 5-9, Size-by-size recoveries of NECu, enargite, and pyrite at different Eh conditions for the HAS (left) and the LAS (right) concentrates
5.3.3. Particle composition

The results of the MLA analysis on the mineral composition of the particle surfaces were used to evaluate the flotation recoveries of particles with different liberation classes, which is called a size by liberation analysis. The modal mineralogy of the mineral components in the concentrates at different Eh conditions for the HAS and the LAS samples are presented in Figure 5-10. It is evident that as the Eh was increased toward the more oxidising condition, the proportion of NSG in the concentrate increased and pyrite decreased in both concentrates.

![Figure 5-10, Modal mineralogy of the concentrates at different Eh ranges for the HAS (left) and the LAS (right) concentrates](image)

The NECu, enargite, and pyrite particles in the surface composition class of 99-100% were used to represent the flotation behaviour of liberated particles.
5.3.3.1. Overall recovery of liberated NECu, enargite, and pyrite

The next stage in data analysis is determining the recoveries of liberated minerals at 10-minute flotation time. The overall recoveries of liberated NECu, enargite, and pyrite at different Eh conditions are presented in Figure 5-11. The maximum recoveries of liberated NECu, enargite, and pyrite was achieved at Eh range +100 to +200 mV SHE in both samples. It is clear that at Eh -200 mV SHE the recovery of liberated enargite is higher than liberated NECu in both samples and there is a potential to separate enargite from other copper minerals. However, it should be mentioned that even for liberated enargite, its recovery is still low in all Eh ranges in the HAS sample.

![Figure 5-11](image)

**Figure 5-11, Overall recovery of liberated NECu, enargite, and pyrite at different Eh conditions for the HAS (left) and the LAS (right) concentrates**

Comparison between recoveries of liberated minerals with the recoveries of pure minerals from literature (Figure 2-17), shows that the recovery of the liberated NECu, enargite, and pyrite are higher than was expected from pure minerals studies by previous researchers at Eh -200 mV SHE. There could be many reasons for this phenomenon. It may be due to the fluctuation of the pulp potential at the highly reducing conditions or due to the hysteresis effects that caused shifting of the flotation edge of these minerals toward a more reducing environment, thereby allowing a higher recovery than expected.
5.3.3.2. Size-by-size recovery of liberated NECu, enargite, and pyrite

The size-by-size recoveries of liberated NECu, enargite, and pyrite are presented in Figure 5-12. As can be seen, the recovery of the liberated NECu generally has the same trend in both the HAS and the LAS samples except at +400 mV SHE where the recovery is less in the LAS sample.

In contrast, the recovery of the liberated enargite is significantly different between two samples. Its recovery is lower in the HAS sample compared to the LAS sample over the entire Eh range. Although even the liberated enargite has not floated strongly at all Eh ranges and in all size fractions from the HAS sample, it has floated better than NECu at Eh -200 mV SHE. This means that there is a prospect for separating liberated enargite from liberated NECu at that pulp potential.

The recovery of liberated enargite at a given particle size does not vary significantly between Eh 0 and +200 mV SHE. The maximum recovery of enargite occurred at the Eh range 0 to +200 mV SHE with 88% and 99% recovery in the HAS and the LAS samples respectively in size fraction -53+32 µm. The recovery of liberated pyrite is very high in the Eh range below +400 mV SHE. It then decreases sharply at very high oxidation conditions.

The other important point is that the main losses of enargite were in the liberated form in the finest size fraction. As mentioned in Chapter 4, about 20% of enargite reported to the finest size fraction -11 µm in the HAS and the LAS ore samples and more than 90% was liberated, however, the recovery of enargite in that size fraction was the lowest compared to the other size fraction which is not unexpected.
Figure 5-12, Size-by-size recoveries of fully liberated NECu, enargite, and pyrite at different Eh conditions for the HAS (left) and the LAS (right) concentrates
5.3.3.3. Overall and size-by-size recovery of enargite-bearing particles

Figure 5-13 shows the enargite locking distribution in the liberated (particles that contain >95% by weight of enargite), the binary (particles that contain enargite and one other mineral); and the ternary (particles that contain enargite and more than one other mineral) classes in the HAS and the LAS concentrates at different Eh tests by weight%. The flotation behaviour of composite particles is important because recovery of these particles affect the separation efficiency of the flotation process.

The amount of enargite in the liberated class is higher at Eh -200 mV SHE compared to the other Eh ranges, in both samples, although the amount of mass recovered at that Eh (-200 mV SHE) is less than other Eh ranges, as shown before. It demonstrates that the tendency of enargite to recover to the concentrate is larger at Eh -200 mV SHE than in the other Eh ranges.

It can be seen that the amount of enargite recovered to the concentrate, which was composite with pyrite is generally greater in the HAS concentrates compared to that in the LAS concentrates. However, the recovery of enargite composite with NECu and with NSG is greater in the LAS concentrate than in the HAS concentrate.

Figure 5-13, Enargite liberation data at different Eh conditions for the HAS (left) and the LAS (right) concentrates
Figure 5-14 illustrates the recovery of enargite on a size-by-liberation basis (liberated, binary, and ternary classes) at different Eh conditions for the HAS and the LAS samples. The recovery-by-size for liberated enargite shows the classic inverted-U shape.

It can be seen that at each Eh condition, generally, the recovery of liberated enargite is higher than the recovery of enargite composite particles. This pattern is found for all of the size fractions except -11 µm at Eh +200, and +400 mV SHE in the HAS concentrate. In the HAS sample the fine particles tended to be recovered as liberated particles, as well as binary particles, while they are mostly recovered as liberated particles in the LAS sample. The finest size fraction -11 µm seems to behave differently at Eh +400 mV SHE in both samples; the recovery of 100% liberated enargite is less than the recovery of other liberation classes.

Another important point is that, similar to unsized and size-by-size results, increasing the Eh range from -200 mV SHE to +200 mV SHE, tends to increase the recovery of enargite composite particles in all size-by-liberation classes. However, it then decreases as the Eh increases to +400 mV SHE.

The coarsest size fraction +106 µm seems to be the most affected size fraction by changing the Eh. The recovery of liberation class in that size fraction increases more than other size fractions as the Eh increases to 0 and +200 mV SHE. In contrast, the finest size fraction -11 µm is hardly affected by Eh changes, however, the recovery of liberated particles decreases at Eh +400 mV SHE.

In an ideal world, the flotation experiment would be conducted and analysed three or four times to determine whether the behaviour of enargite in these size fractions and liberation classes are consistent with the results presented here. Unfortunately, the low mass of sample and limited time available prohibited the replication of tests (discussed previously in Chapter 3).
Figure 5-14, Recovery of enargite in different liberation classes at different Eh conditions for the HAS (left) and the LAS (right) concentrates
5.3.4. Entrainment results

It is well known that entrainment will result in dilution of the concentrate grade and can be highly detrimental to the selectivity of the flotation process hence the water recovery data was collected to enable estimation of the recovery by entrainment of the NSG (non-sulphide gangue) in the concentrate. Figure 5-15 shows the relationship between the cumulative recovery of NSG and cumulative water recovery at different Eh conditions for both samples. It is obvious that as water recovery increases non-sulphide gangue (NSG) recovery increases in an approximately linear relationship, which can be attributed to the entrainment. It should be mentioned that non-sulphide gangue group consists of quartz, diaspore, kaolinite, muscovite, and pyrophyllite. Pyrophyllite belongs to the phyllosilicate group of minerals, which shows natural hydrophobicity. That is why the relationship between NSG and water is not a perfect linear relationship. It will be discussed further in Chapter 8.

![Figure 5-15, Relationship between recovery of water and recovery of non-sulphide gangue at different Eh conditions for the HAS (left) and the LAS (right) concentrates](image)

Based on the detailed mineralogical characteristics of the ore samples, more than 90% of quartz particles were fully liberated. Therefore, the quartz particles were used as the tracer (i.e. fully liberated and non-floating minerals) to calculate the recovery by entrainment in all the flotation experiments.

The liberated quartz recovery, degree of entrainment, and the water recovery at different Eh conditions for the flotation tests on the HAS and the LAS samples are presented in Table 5-1. From the data it can be seen that in all test conditions being performed, the liberated quartz recovery is significantly lower than the water recovery, which indicates that the liberated quartz particles were mainly recovered by entrainment. In addition the liberated quartz recoveries change in a similar manner to water recovery; the overall recovery of liberated quartz increases with increasing water
recovery. The degree of entrainment (ENT) of mineral particles must be between 0 and 1 (Savassi, 1998) which follows a consistent trend in both HAS and LAS flotation tests, increasing as the Eh increases. Generally, the LAS sample shows a lower degree of entrainment at all Eh conditions compared to the HAS sample. The water recovery has a maximum value at Eh +400 mV SHE, as expected, and the minimum value at Eh -200 mV SHE for both samples.

The size-by-size degree of entrainment for the HAS and the LAS samples at different Eh conditions are presented in Figure 5-16. It can be seen that the degree of entrainment increases as the size decreases in an orderly fashion. And the finest fraction is most influenced by the entrainment mechanism, displaying the largest entrainment.

### Table 5-1, Overall entrainment performance

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eh (mV SHE)</th>
<th>ENT</th>
<th>Water Recovery (%)</th>
<th>Liberated Quartz Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAS</td>
<td>-200</td>
<td>0.128</td>
<td>16.241</td>
<td>2.415</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.135</td>
<td>18.530</td>
<td>2.982</td>
</tr>
<tr>
<td></td>
<td>+200</td>
<td>0.264</td>
<td>19.988</td>
<td>6.192</td>
</tr>
<tr>
<td></td>
<td>+400</td>
<td>0.351</td>
<td>20.237</td>
<td>8.184</td>
</tr>
<tr>
<td>LAS</td>
<td>-200</td>
<td>0.120</td>
<td>17.146</td>
<td>2.431</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.147</td>
<td>19.133</td>
<td>3.369</td>
</tr>
<tr>
<td></td>
<td>+200</td>
<td>0.153</td>
<td>20.407</td>
<td>3.782</td>
</tr>
<tr>
<td></td>
<td>+400</td>
<td>0.242</td>
<td>20.754</td>
<td>5.966</td>
</tr>
</tbody>
</table>

Figure 5-16, Size-by-size degree of entrainment (ENT) at different Eh conditions for the HAS (left) and the LAS (right) concentrates
The recovery by entrainment for enargite, NECu, and pyrite was calculated based on the degree of entrainment of liberated quartz particles in concentrates and feeds. The results as presented in Figure 5-17 clearly show that the recovery by entrainment has the maximum values at Eh +400 mV SHE.

When the recovery by entrainment of NECu is less than 2.5%, about 5% of pyrite has been recovered by entrainment at high oxidation conditions (+400 mV SHE). It is critical, as the recovery of pyrite was very high (more than 80%) at the Eh below +400 mV SHE and then decreased sharply as the Eh was increased to +400 mV SHE. In addition, pyrite was mostly liberated in both samples (about 65%). It is therefore most likely that pyrite was recovered by induced floatability at Eh ranges below +400 mV SHE. It will be discussed in detail in Chapter 7.

Enargite in the HAS sample shows a higher amount of recovery by entrainment than in the LAS sample in all Eh ranges. It can be due to the greater proportion of enargite in the finest size fraction. As observed in Chapter 4, the percentage of enargite in size fraction -11 μm was greater in the HAS sample than that in the LAS sample.

Figure 5-17, Recovery by entrainment of NECu, enargite, and pyrite at different Eh conditions for the HAS (left) and the LAS (right) concentrates
5.4. Key findings

Based on the pure mineral studies by previous researchers four Eh conditions were tested to select a condition for differential flotation of enargite from other copper sulphide minerals. The main findings from the flotation experiment on the HAS and the LAS samples are as follow:

- The flotation tests without collector showed induced floatability of enargite and NECu minerals that can be due to the mild oxidation of the sulphide minerals surface, which caused their flotation.

- For the LAS sample, unsized results confirmed that it is possible to separate enargite from non-enargite copper minerals (NECu). From the overall recoveries, it was observed that enargite (67.17%) was recovered preferentially at reducing potential (-200 mV SHE) at pH 11 while only 46.62% of NECu was recovered. In the oxidising pulp potential region, there was however no selectivity between enargite and the other copper minerals in the LAS sample.

- For the HAS sample no separation between enargite and NECu was observed at reducing potential. There appeared to be a window for separating enargite (54.38%) and NECu (73.75%) at oxidising potential (+400 mV SHE). Notably, enargite in the HAS sample showed very low recovery variations as the Eh was increased and, generally, it did not float very well as the Eh was changed. This window of separation at +400 mV SHE was therefore not considered as feasible for separating these two minerals.

- Extra flotation time and collector dosage were not able to increase the enargite recovery in the HAS sample.

- The overall recovery of NECu, enargite, and pyrite were higher than what was expected from pure minerals studies by other researchers at -200 mV SHE. This may be due to the fluctuation of the pulp potential at the highly reducing conditions or due to the hysteresis effects that caused shifting in the pulp potential of these minerals toward the more reducing direction resulting in higher recovery than expected.

- While pyrite showed high recovery at pH 11 and Eh values below +400 mV SHE, it was partly depressed at Eh +400 mV SHE without any depressant addition.

- The size-by-size studies showed that the best As/Cu selectivity results were produced in the size fraction -32+11 µm at Eh -200 mV SHE, where the As/Cu selectivity was 1.63 and 1.44
in the LAS and the HAS samples respectively. Therefore, by regrinding the rougher concentrate finer, it would be expected that a good separation could be achieved between enargite and NECu.

- The size-by-liberation data showed that the recovery of liberated enargite was higher than the recovery of liberated NECu at Eh -200 mV SHE for both samples.

- The size-by-size enargite recovery in different liberation classes showed higher recovery of liberated enargite compared to the binary and ternary classes in both samples.

- It was observed that using xanthate (in particular KEX: potassium ethyl xanthate) as the flotation collector enabled some Cu/As separation.

- There was very little entrainment of NECu, pyrite, and enargite into the concentrate at Eh below +400 mV SHE, however at Eh +400 mV SHE an increase in entrainment was observed. Enargite mass recovery by entrainment was higher in the finest size fraction -11 µm in the HAS sample compared to the LAS sample due to the greater amount of enargite mineral in the HAS sample.

- Flotation at a reducing pulp potential, in this test work, was the most promising condition to obtain an enargite separation from other copper minerals. This may not be the case for other ores.
Chapter 6

PREDICTION OF FLOTATION RECOVERY

The main aim of this chapter is to identify whether the flotation responses of the HAS and the LAS ores, in this case, the recovery of the NECu and enargite in flotation, could be estimated from the mineralogical characteristics of the HAS and the LAS feed samples.

It was observed in Chapter 4 that the HAS and the LAS feed samples have similar mineralogical characteristics as they both came from the same mine site. It is therefore expected that by using the flotation performance of one ore sample (in this case LAS sample), and the mineralogy data of the other ore sample (HAS sample), the flotation response of the HAS ore sample could be predicted. If this method can possibly predict the flotation results of the HAS sample, it would have the advantage of reducing the extent of laboratory testing required.

This chapter addresses the third hypothesis of this research which is “The flotation behaviour of the HAS ore can be estimated using a predictive Particle Kinetic Model, which uses the ore mineralogical composition of HAS ore and the flotation responses of LAS ore as inputs”.

6.1. Introduction

It is widely agreed that the ore mineralogy influences the flotation recovery of the stream being processed. Hence understanding the physical properties of the particles is important in design and operation of the flotation process (Wightman et al., 2010a). Despite this fact, very few processing models include mineralogical information as part of their input data and allow it to be directly related to the operating data.

As discussed in the literature review, Luitjens (2006) proposed a method termed Particle Kinetic Model to predict the flotation behaviour of minerals. This approach was used by Ford et al. (2009) in the prediction of the flotation response of nickel sulphide ores. Evans (2010) successfully used this approached to predict the batch flotation performance of samples of copper porphyry comprising mainly liberated chalcopyrite.

Two sets of data are required for this model:

- Size-by-size flotation rate constant for each mineral that must be obtained from a laboratory flotation experiment and from the recovery data for the 99-100% liberated surface composition class.

In this study, based on the modal mineralogy and the flotation results of the HAS and the LAS samples, the minerals were classified into five groups including NECu (non-enargite copper minerals), enargite, pyrite, FG (floatable gangue mineral including pyrophyllite) and NFG (non-floatable gangue minerals including other non-sulphide gangue minerals).

The laboratory rougher flotation results that were performed on the HAS and the LAS ore samples, as discussed in Chapter 5, were used together with the size-by-size MLA particle composition data of the HAS and the LAS feed samples (Chapter 4).

The flotation rate was calculated for fully liberated (99-100% surface composition class) NECu, enargite, pyrite, FG, and NFG mineral groups in five size fraction (+106, -106+53, -53+32, -32+11, and -11 µm) in four different flotation conditions (Eh -200, 0, +200, and +400 mV SHE). It was assumed that the flotation rates of the five mentioned mineral groups in the 99-100% surface composition class represent the most likely value of the flotation rate of those minerals.
Recovery of valuable minerals happens either by true flotation or due to entrainment. However the model does not include a specific parameters to consider the effect of entrainment on the flotation recovery. The flotation rate constant was therefore also calculated for NFG to represent the recovery by entrainment.

In an ideal world the five individual concentrate samples, which were collected at 30 seconds, 1, 2, 4, and 10 minutes flotation time should have been sized and analysed separately. However, the low amount of sample mass in each concentrate meant that they had to be combined to generate enough sample mass for size, assay and MLA analysis, as mentioned in Chapter 3. Hence, the flotation rate was calculated for the 10-minutes flotation time and was assumed that this calculated K is the overall rate of the flotation test.

It should be mentioned that the flotation response predicted by the model would be valid as long as the flotation conditions have not changed (Evans, 2010).

6.2. Establishing the Particle Kinetic Model with the LAS sample

The LAS sample was selected to calibrate the model. In order to apply the model the following information of the LAS sample was collected:

- The particle composition data obtained from MLA measurements on five size fractions; +106, -106+53, -53+32, -32+11, and -11 µm for the LAS flotation feed sample.

- The flotation recovery data (10-minutes flotation) for the NECu, enargite, pyrite, FG, and NFG in five size fractions and at different Eh conditions for the LAS sample.

The analyses performed to generate the data required to calibrate the Particle Kinetic Model are described in the following sections.

6.2.1. Input data

The results of the flotation tests on the LAS sample, which were presented in Chapter 5, were used to estimate the flotation rate of each group of minerals. The flotation rates of the NECu, enargite, pyrite, FG, and NFG in the 99-100% surface composition class in five size fractions were calculated based on the equation 2-31. These values were the best representative of the overall flotation rate of those mineral groups at 10-minutes flotation. The calculated flotation rates at 10-minutes flotation for
the NECu, enargite, pyrite, floatable gangue, and non-floatable gangue at different Eh conditions and size fractions are presented in Table 6-1.

Table 6-1, Estimated flotation rates for liberated NECu, enargite, pyrite, floatable gangue, and non-floatable gangue at 10-minutes flotation for the LAS sample

<table>
<thead>
<tr>
<th>Eh mV SHE</th>
<th>Size Fractions</th>
<th>NECu</th>
<th>Enargite</th>
<th>Pyrite</th>
<th>Floatable Gangue</th>
<th>Non Floatable Gangue</th>
</tr>
</thead>
<tbody>
<tr>
<td>-200</td>
<td>+106</td>
<td>0.09</td>
<td>0.20</td>
<td>0.23</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>-106+53</td>
<td>0.09</td>
<td>0.27</td>
<td>0.24</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>-53+32</td>
<td>0.12</td>
<td>0.32</td>
<td>0.33</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>-32+11</td>
<td>0.08</td>
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The flotation feed of the LAS sample with P_{80} of 90 μm was used to calibrate the Particle Kinetic Model. As mentioned in Chapter 4, the MLA analyses on the feed samples were conducted on five size fractions; +106, -106+53, -53+32, -32+1, and -11 μm. The particle composition data of each size fraction from the MLA analyses on the LAS sample were used as input.

The flotation rate constants of the NECu, enargite, pyrite, FG, and NFG from Table 6-1 were used together with the particle composition data from the MLA measurements on the LAS feed sample to calculate the size-by-size recovery of NECu and enargite at different Eh conditions at 10-minute flotation tests for the LAS sample using equations 2-28 and 2-30.
6.2.2. Output results

The calculated results by the model and the actual flotation results for the NECu and enargite on a size-by-size basis are presented in Figure 6-1 for comparison.

![Figure 6-1](attachment:image.png)

**Figure 6-1.** Actual and calculated flotation results for the NECu and enargite in the LAS sample at different Eh conditions (using flotation rate data of the LAS sample to calculate the recovery of NECu and enargite from the LAS feed sample)

By looking at the NECu results, the size-by-size recovery of the NECu calculated by the model shows close agreement with the actual flotation values at all Eh conditions. For enargite, it can be seen that the Particle Kinetic Model successfully calculated the recovery of enargite in all specific size fractions finer than 106 µm. This can be due to the high degree of liberation of these size fractions. In contrast, in size fraction +106 µm, although the calculated recovery values show good agreement with the actual recovery values, the model did not calculate the absolute values of recovery correctly due to the poor degree of liberation of this size fraction. At the 10-minute flotation time, the model calculated lower recovery than was observed.
Figure 6-2 shows the comparison graph between the experimental recovery values and the calculated values for the NECu and enargite from the Particle Kinetic Model on a size-by-size basis over all Eh ranges for the LAS sample.

The lines have essentially the same slopes. The slope of the trend line between the actual recovery values and the calculated recovery values, and the regression number, $R^2$, are the indicators of the quality of the calculated values by the Particle Kinetic Model.

The model calculated the NECu recoveries on a size-by-size basis with the coefficient ($R^2$) of 0.99, which shows how well the experimental data are calculated. The enargite data show more dispersion compared to the NECu results due to the +106 µm size fraction, and the coefficient ($R^2$) of the enargite is 0.88, but it is still within acceptable limits.

![Comparison of actual recoveries with those calculated by Particle Kinetic Model for the LAS sample](image)

Figure 6-2, Comparison of actual recoveries with those calculated by Particle Kinetic Model for the LAS sample (using flotation rate data of the LAS sample to calculate the recovery of NECu and enargite from the LAS feed)
6.3. Predicting the HAS recovery by Particle Kinetic Model

In order to test the validity of the model used in this research, the Particle Kinetic Model was applied to the HAS feed sample.

6.3.1. Input data

Two sets of information were required:

- The particle composition data obtained from MLA measurements on five size fractions; +106, -106+53, -53+32, -32+11, and -11 µm of the HAS flotation feed sample.

- The flotation kinetic data (10-minutes flotation) calculated from the 99-100% liberated minerals for the NECu, enargite, pyrite, FG, and NFG in five size fractions and at different Eh conditions for the LAS sample (Table 6-1).

The MLA particle composition data on five size fractions of the HAS flotation feed samples together with flotation kinetic data for the NECu, enargite, pyrite, FG, and NFG in each size fraction obtained from the LAS sample were used to predict the size-by-size NECu and enargite recoveries in the HAS samples using the Particle Kinetic Model.

6.3.2. Output results

The results of applying the Particle Kinetic Model to the HAS feed sample for the NECu and enargite on a size-by-size basis are shown in Figure 6-3. Comparison of the actual flotation recoveries with the predicted recovery values, shows that the Particle Kinetic Model could not correctly predict the recoveries of the NECu and enargite in theHAS sample. The difference between actual and predicted recoveries was lower for the NECu than for the enargite.

While the model correctly predicted the size-by-size recoveries of the NECu at Eh +200 mV SHE in the HAS sample, the recovery values predicted by the model were higher than the actual flotation recoveries at Eh -200 and 0 mV SHE. In addition, the model could not predict the absolute values of recovery at Eh +400 mV SHE correctly, and the predicted values were lower than the experimental flotation results in all size fractions. These consistently higher actual values for the recovery of NECu at Eh +400 mV SHE in the HAS sample could be due to the large amount of pyrophyllite in the HAS sample, which is a naturally floatable gangue mineral. It will be explained in detail in Chapter 8.
Comparing the observed enargite recovery value with the predicted ones shows that the predicted values for the enargite were higher than the actual values at all size fractions and Eh ranges.

Figure 6-3, Actual and predicted flotation results for the NECu and enargite in the HAS sample at different Eh conditions (using flotation rate data of the LAS sample to predict the recovery of NECu and enargite from the HAS feed sample)
Figure 6-4 shows the comparison graph between the experimental recovery values and the actual values for the NECu and enargite from the Particle Kinetic Model on a size-by-size basis and for all Eh ranges for the HAS sample.

The regression line indicates that the model imperfectly predicted the recovery of the NECu and enargite and there is a large degree of scatter in the results. It clearly shows that the enargite trendline is above the NECu trendline. The results obtained from using the Particle Kinetic Model for the HAS sample show good agreement with the actual flotation data with a coefficient of determination ($R^2$) of 0.87 for NECu. However the enargite data show more dispersion compared to the NECu results, and the $R^2$ Value for enargite is only 0.68.

The ANOVA test was performed to determine if the NECu and enargite trendlines were significantly different to each other. It indicates the differences between the NECu and enargite trendlines are 9.0% and that difference is significant with 99.5% confidence ($P = 0.0043$). It means that the enargite predictions are on average 10 units above the NECu predictions compared with actual values. The results are presented in Appendix J.

![Figure 6-4. Comparison of actual recoveries with those estimated by Particle Kinetic Model for the HAS sample (using flotation rate data of the LAS sample to predict the recovery of NECu and enargite from the HAS feed)](image-url)
6.4. Discussion

The predicted value of enargite recovery by the Particle Kinetic Model showed higher enargite recovery in the HAS sample when compared with the results of physical flotation tests on the HAS sample. There could be several reasons for the poor prediction of the model for the HAS sample.

One possible reason could be due to differences in ore mineralogy of the tested ore samples. However comparing the predicted recovery values from the LAS sample (Figure 6-1) with those from the HAS sample (Figure 6-3) shows a similarity in the prediction of the results suggesting similar mineralogical and liberation characteristics of the HAS and the LAS samples, as confirmed in Chapter 4. Therefore, this explanation cannot be correct.

The only other reason for these observations can be due to the change in the flotation conditions for the HAS sample. The wide scatter of predicted data for enargite in the HAS sample indicates that there are other factors affecting the recovery of enargite particles which are not considered in this model. The model does not include the parameters that can affect flotation performance such as surface oxidation or surface slime coatings. These factors were accounted in the flotation rate data of the LAS sample and were calibrated to that ore. However, for the HAS sample the flotation rates of the LAS sample were used which were not calibrated to the actual HAS flotation condition. There could be several reasons for the change in the flotation condition of the HAS sample and lower recovery achieved by flotation tests than the predicted recovery of enargite by model:

- One possible factor would be the higher levels of pyrite present in the HAS sample compared to the LAS sample. It was shown by many researchers that the galvanic interactions between sulphide minerals in flotation pulps can significantly affect the flotation behaviour of minerals of interest (Ekmekçi and Demirel, 1997). As observed in Chapter 4, the pyrite content of the LAS sample was 3.40%, while the HAS sample had 5.36%. It will be further discussed in Chapter 7.

- The other reason for these observations could be due to the geological alterations of the enargite surface in the HAS ore sample that can affect its flotation performance. Further detailed surface analysis such as ToF-SIMS would be required to confirm this effect.

- Another reason for the lower recovery observed from the flotation test on the HAS sample might be due to the different amount of gangue content in the HAS and the LAS sample. This will be further discussed in Chapter 8.
6.5. Key findings

A Particle Kinetic Model was used to predict the flotation response of each particle in a flotation feed. This model used the particle surface composition data from MLA analyses and the actual flotation kinetic data for each mineral group. The LAS sample was used to develop and calibrate the model and then the flotation response of the HAS sample was predicted by using the flotation rate constant of the LAS sample. The main findings are as follow:

- The use of the Particle Kinetic Model was shown to be successful in calculating the NECu (R²=0.99) and enargite (R²=0.88) recoveries in the LAS sample. The NECu size-by-size recovery values calculated by the Particle Kinetic Model showed close agreement with the actual recovery values at all Eh conditions. The model calculated the recovery of enargite with high accuracy for the size fractions finer than +106 µm at all Eh ranges. However, it could not correctly calculate the enargite recoveries in the size fraction +106 µm due to the poor degree of liberation of this size fraction.

- When the actual recovery of NECu for the HAS sample from the flotation tests was compared with the recovery values predicted by the Particle Kinetic Model, it was observed that although the model correctly ranks the size-by-size recoveries of NECu, it was unable to predict the absolute values of recovery correctly (R²=0.87). In contrast, when the actual recovery values of enargite were compared with the recovery values predicted by the Particle Kinetic Model, the predicted values were 5% to 30% higher than actual values.

- It is suggested that a change in the flotation conditions of the HAS sample caused its poor prediction by the model. There are some possible reasons for such a change in the flotation conditions of the HAS sample such as surface oxidation or slime coating which will be discussed in detail in the next two chapters.

- Since flotation is a consequence of the interaction between mineral surfaces and bubbles (Runge et al., 2003), the model may be more accurate if it included factors which can affect flotation performance, such as pulp chemistry.
Chapter 7

EDTA EXTRACTION AND WATER CHEMISTRY RESULTS

The chapter consists of two sections. The first section details the results of the EDTA extraction tests on the HAS and the LAS samples and the second section includes the water chemistry test results on the HAS and the LAS samples and the environmental considerations of the results obtained.

In the EDTA extraction section, the observed results in terms of the amount of extracted Cu, Fe, and As under different flotation conditions and mill discharge are presented and compared to other researchers’ work. In the discussion section, the obtained results are used to explain the enargite and pyrite flotation results obtained in Chapter 5.

In the water chemistry section, the chemical composition of the flotation pulp water is presented. The results are then analysed by using the PHREEQC software, and the equilibrium solution speciation and saturation indices calculated. At the end of this section the environmental implications of the water chemistry results are discussed.

This chapter addresses the fourth hypothesis of this thesis: “The degree of oxidation of the enargite mineral surfaces has a significant influence on enargite flotation behaviour.”
7.1. EDTA extraction tests

The surface oxidation of copper sulphide minerals plays an important role in their floatability and separation. It also affects the floatability of other minerals such as pyrite by copper activation. It was observed in Chapter 5 that the recovery of enargite in all size fractions and at all Eh conditions was lower in the HAS sample compared to the LAS sample. Thus, the surface chemistry tests were undertaken by an EDTA extraction technique to find out whether the poor floatability of enargite was due to its surface oxidation.

Ethylendiaminetetraacetic acid (EDTA) tri-sodium salt was used to solubilise metal sulphide oxidation products from the surface of particles to determine the type and amount of oxidation species from the minerals surface.

As mentioned in Chapter 3, two sets of experiment were conducted:

- The first set of analysis was conducted on the HAS and the LAS samples, which were ground to P80 of 90 µm (mill discharge).
- The second set of analysis was performed on the conditioning stage of the flotation tests (flotation feed).

In the following section, the results of EDTA extraction tests on mill discharge and flotation feed will be discussed.

7.1.1. Observed results

The filtrate of the EDTA dissolution tests showed a darker greenish colour for the HAS sample compared to the LAS sample in all sets of the experiment. The greenish colour can be due to the mixture of yellowish colour from iron hydroxide and bluish colour from copper hydroxide (Figure 7-1).
The results in Figure 7-2 represent the amount of Cu, Fe, and As extracted by EDTA from the ground pulp for the mill discharge and flotation feeds (conditioning stage) at different Eh values for both samples.

It should be noted that the water chemistry test data (before adding EDTA), as presented in Table 7-1, shows that the level of metal (Cu, Fe, and As) ions in solution is less than 1 mg/L. Therefore, the metal values determined from precipitated oxide products and EDTA extraction tests are from extracted surface products.
7.1.1.1. EDTA extractable Cu in the mill discharge and flotation feed

Copper is the predominantly extracted metal. There is a general upward trend in Cu extraction towards the higher pulp potential levels. He (2006) also observed that the surface copper oxidation species (extracted by EDTA) increased with increasing Eh values.

The EDTA extracted copper originating from the oxidation of copper minerals including chalcopyrite, bornite, and enargite. It can be seen that the amount of extracted copper is higher in the HAS sample in all the Eh ranges.

The copper oxidation species might not be critical in the flotation of copper minerals; however, they can activate some other minerals present in the ore samples such as pyrite or non-sulphide gangue minerals, which then affect the separation of different minerals. It will be discussed in the discussion section.

7.1.1.2. EDTA extractable iron in the mill discharge and flotation feed

The EDTA extractable iron after grinding is about 2%. It indicates that the pulp entering the flotation circuit contained elevated levels of EDTA extractable iron. Interestingly, the levels of EDTA extractable iron decreased through the conditioning stage.

The sharp increase in EDTA extractable iron in the grinding circuit may be due to the rapid oxidation of pyrite or other copper/iron sulphides in the grinding circuit rather than the stainless steel media. It has been suggested by Rumball and Richmond (1996) and Greet et al. (2006) that one possible reason for the decrease in the amount of EDTA extractable iron may be due to further oxidation of the iron species to higher level iron oxides that are more resistant to extraction and are insoluble in EDTA (Rumball and Richmond, 1996, Greet et al., 2006).

There is a downward trend in Fe extraction as the Eh is increased. These results seem to be similar to those observed by Rumball and Richmond (1996). They found that iron hydroxyl species, which was present on particle surfaces, formed in the first stages of flotation, and had a significant effect on galena floatability. They mentioned that ferric salts might be insoluble due to adsorption of EDTA rather than dissolution by EDTA. It means that as the Eh of a pulp increase and ferrous salts are oxidised to ferric salts, the amount of EDTA extractable iron decreases (Rumball and Richmond, 1996).

Another important point is that the percentage of EDTA extractable iron in the mill discharge tests is higher in the HAS sample than in the LAS sample. However, it sharply decreased in the conditioning
stage in the HAS sample and hence the level of extractable iron in the conditioning stage of the flotation tests is lower in the HAS sample than in the LAS sample.

**7.1.1.3. EDTA extractable arsenic in the mill discharge and flotation feed**

The EDTA extractable arsenic after grinding is negligible. However, the levels of EDTA extractable arsenic increase through the conditioning stage. It means that more enargite became oxidised during the conditioning stage which was then dissolved by EDTA.

Another important point is that the amount of arsenic extracted by EDTA is much higher (2 to 6%) in the HAS sample compared to that in the LAS sample. This can be seen as evidence for the role of oxidation in the recovery of enargite from the HAS sample. The only other explanation can be inferred is that the mineral is being dissolved by EDTA. However, that would apply to both ores, and there would be little difference between the EDTA extractable arsenic from the HAS and the LAS samples. Therefore, this explanation cannot be correct.

A plot of EDTA extractable arsenic in the flotation feed corresponding to enargite recovery (Figure 7-3) also shows that arsenic recovery is lower in the HAS sample which has the higher amount of EDTA extractable arsenic.

![Figure 7-3, Relationship between oxidised arsenic and flotation recovery values](image-url)
7.1.2. Discussion

It was observed in Chapter 5 (Figure 5-5), that the floatability of pyrite was higher than expected from the pure mineral studies by other researchers at Eh values lower than +400 mV SHE. The pyrite flotation recovery decreased sharply at high Eh values of +400 mV SHE. On the other hand, enargite recovery in the HAS sample was much lower than that in the LAS sample. In this section, the electrochemical reactions that caused these phenomena are discussed.

7.1.2.1. The effect of copper(II) ions on pyrite floatability

As mentioned in the literature review, the sulphide minerals easily oxidised in the presence of water and oxygen and the slight surface oxidation increases the flotation performance of sulphide minerals by forming elemental sulphur or polysulphides. The oxidation of chalcopyrite, for instance, causes the dissolution of Cu and Fe ions from its surface and produces a polysulphide layer on the mineral surface in alkaline conditions. The collectorless floatability of chalcopyrite is attributed to the presence of this polysulphide layer (Walker et al., 1989, Woods, 1976, Smart et al., 1998, Smart, 1991). However, further oxidation of the sulphide minerals causes the precipitation of the iron hydroxides layer on the polysulphide layer, which reduces the flotation recovery of sulphide minerals and their selectivity (Senior and Trahar, 1991, Clarke et al., 1995). On the other hand the presence of dissolved Cu ions from chalcopyrite surface may affect the floatability of other sulphide minerals such as pyrite; its recovery increases due to the adsorption of copper ions on the surface and formation of CuS (Chandra and Gerson, 2009, He, 2006, Huang and Grano, 2006, Peng and Grano, 2010, Trahar et al., 1994, Yoon et al., 1995).

Yoon et al. (1995) found that the activation of sulphides by Cu$^{2+}$ was strongly dependent on the redox potential of the pulp. In a study by Peng et al. (2012) the effect of electrochemical potential on pyrite flotation in the presence and absence of $1.5 \times 10^{-3}$ mol/dm$^3$ copper ions was investigated (Figure 7-4). They observed that in the absence of copper ion pyrite showed very poor floatability at different Eh ranges while in the presence of copper ions the floatability of pyrite increased significantly. They also observed that at reducing conditions the recovery of the activated pyrite was higher than that in the oxidising condition; the maximum recovery of activated pyrite was achieved at Eh -185 mV SHE. He (2006) also observed the same results and concluded that the maximum pyrite recovery obtained at this Eh value was due to the increased adsorption of copper and therefore pyrite activation, resulting in more collector adsorption. It was also observed by He (2006) that the pyrite recovery decreased at more oxidising conditions.
Chandra and Gerson (2009) stated that Cu$^{2+}$ and Cu(OH)$_2$ are the two main Cu species in solution for the activation of sulphide minerals and can cause loss of selectivity through reaction with xanthate. Ekmekci et al. (2006) discussed that the Cu(OH)$_2$ and Cu(OH)$^+$ are dominant compounds at pH 9. This is consistent with the copper species as a function of the pH diagram by Yang et al. (2016) (Figure 7-5). At higher pH values, Cu(OH)$_2$ as a dominant species would be precipitated on the mineral surfaces (valuable and silicate minerals) and causes the activation of that mineral.
Based on the Cu extracted results from the EDTA tests, it is most likely that the pyrite activation during conditioning stage was due to the precipitation of copper ion on its surface from the copper sulphide oxidation, which caused high recovery of pyrite at a pulp potential lower than +400 mV SHE.

On the other hand, it was observed that the Fe extracted by EDTA decreased as the Eh increased toward the more oxidising conditions. That most probably indicates that at the highly oxidising conditions the pyrite surface is strongly oxidised and covered with iron oxide/hydroxide/sulphate on its surface. These hydrophilic species prevent collector adsorption, and as a result, pyrite recovery has decreased at Eh +400 mV SHE. These observations of pyrite flotation in oxidising conditions are in good agreement with previous studies (Trahar et al., 1994, Yang et al., 2016).

7.1.2.2. The effect of iron hydroxide on enargite floatability

Iron in the samples of this study is present from the iron-bearing sulphide minerals in the ore. It also may originate from galvanic interactions occurring between sulphide minerals during milling. The oxidation of the ball mill before grinding is insignificant because the mill was cleaned by grinding a sample of quartz for 5 minutes prior to each test. Stainless steel media was also used to reduce the galvanic interactions between sulphide minerals and media during grinding. In addition the mineral samples were stored in a dry cupboard to prevent oxidation.

In a study by Fullston et al. (1999c) the zeta potential of the copper sulphide minerals (chalcocite, covellite, chalcopyrite, bornite, enargite, and tennantite) was investigated and the oxidation rates of them compared. It was stated that the oxidation rate of the copper sulphide minerals at pH 11 follows the order:

\[
\text{chalcocite} > \text{tennantite} > \text{enargite} > \text{bornite} > \text{covellite} > \text{chalcopyrite}
\]

It can be seen that enargite is more electrochemically active than other copper minerals in the HAS and LAS ore samples (bornite and chalcopyrite), it is anticipated therefore that enargite flotation is more susceptible to the grinding condition than other copper flotation.

Rao and Natarajan (1990) suggested that there is a special distribution of the iron species among the minerals present in a slurry depending on the relative electrochemical activity of the minerals. The iron distribution is more favoured on more noble minerals relative to the active minerals. Owusu et al. (2014) also observed that the Fe$^{2+}$ ions released into the solution would rapidly oxidise to Fe$^{3+}$ and formed Fe(OH)$_3$ precipitates on the mineral surface under strong alkaline environments (Owusu et
al., 2014). Bradshaw et al. (2006) mentioned that the galvanic interactions between sulphide minerals affects their flotation behaviour by the formation of iron hydroxy species on their surface. Jacques et al. (2016) stated that the galvanic interactions and redox reactions in a slurry are the main factors causing the precipitation of iron oxyhydroxy species at the sulphide minerals surfaces, which lead to poor floatability of sulphide minerals.

Based on the previous studies by other researchers (Cheng and Iwasaki, 1992, Rao et al., 1992, Pauporte and Schuhmann, 1996, Fullston et al., 1999a, Fullston et al., 1999b, Hu et al., 2009, Chen et al., 2014) it can be concluded that enargite has the lowest rest potential compared to other main sulphide minerals present in the HAS and the LAS ore samples. The rest potential of the main sulphide minerals present in the HAS and the LAS ore samples follows the order:

pyrite > chalcopyrite > bornite> enargite

Pyrite is the most cathodic sulphide mineral in the current study and would draw electrons from all of the other sulphide minerals in the ore. As enargite has the lowest rest potential of the other copper minerals in the HAS and LAS ore samples, a stronger galvanic interaction happens between enargite and pyrite than between other copper minerals and pyrite. Consequently, strong oxidation occurs on enargite, which produces a hydrophilic oxidation layer on the enargite surface that depresses its flotation and a significant amount of copper ions, which is sufficient to activate pyrite.

As discussed in Chapter 2, the surface oxidation of enargite was studied by Fullston et al. (1999a), (1999b) which showed the amount of copper dissolved from the enargite was much higher than that of arsenic. XPS studies showed that even with weak oxidants such as dissolved oxygen, two oxidation layers form on the surface of the enargite: a thin layer comprised of copper and arsenic oxide, or hydroxide, and a layer made of metal-deficient sulphide and/or polysulphide. In addition, a small amount of iron as an impurity was observed on the minerals surface which can cause the galvanic interactions in these samples (Fullston et al., 1999a, Fullston et al., 1999b). Fornasiero et al. (2001) examined the separation of enargite and tennantite from other copper sulphide minerals (chalcocite, covellite, and chalcopyrite) by flotation in mixed mineral systems. The XPS results confirmed that the surface of the arsenic minerals was more oxidised than the non-arsenic minerals (Fornasiero et al., 2001). Lattanzi et al. (2008) mentioned that at alkaline conditions, the oxidation of enargite is fast with the formation of a copper-depleted layer and Cu-O species on its surface. XPS study of enargite surface at alkaline pH also indicated the presence of cupric oxide and arsenic oxide on enargite surface (Lattanzi et al., 2008). In another detailed study of the electrochemical behaviour of enargite, a passivation layer was found to form over a broad potential range (-660 to +1070 mV SHE) and that
the main oxidation product found on the mineral surface was copper hydroxide (Cu(OH)$_2$) (Guo and Yen, 2014).

The modal mineralogy of the HAS and the LAS samples showed a greater proportion of pyrite in the HAS sample compared to that of the LAS sample. It is therefore anticipated that the flotation of the HAS sample would be affected by the higher amount of pyrite present in this ore sample. Further, from the flotation study on the HAS and the LAS sample, it was observed that enargite showed lower recovery in the HAS sample compared to that in the LAS sample. Its recovery was not changed as the Eh was increased. In addition, the EDTA experiment on the HAS and the LAS sample showed a higher amount of extracted Cu and As in the HAS than in the LAS sample. Based on the previous studies by other researchers, and the flotation and EDTA results obtain in this study, it can be concluded that during grinding of the HAS ore sample, galvanic interactions occurred between enargite and pyrite which caused the poor recovery of enargite in the HAS sample.

On the other hand, it is generally agreed that iron hydroxide species are hydrophilic and are detrimental to the flotation of sulphide minerals (Grano et al., 1997, Peng et al., 2003a, Peng et al., 2003b, Greet, 2009). However, these hydrophilic species did not depress the flotation of NECu minerals in the HAS sample. It has also been found by some researchers that in the presence of the hydrophilic iron hydroxides, the flotation recovery of very fine valuable minerals would be affected detrimentally a greater extent than the intermediate size fractions (Johnson, 2005a, Grano, 2009, Peng and Grano, 2010, Chen et al., 2014). From the mineralogical characteristics of the HAS (Chapter 4) it was observed that about 22% of enargite reported to the finest size fraction -11 µm. In addition, enargite had the lowest grain size distribution amount of all the copper sulphide minerals (P$_{80}$ of 27µm). It is therefore concluded that the very fine grain size of enargite in the HAS ore sample had a critical role on its floatability. Overall, the results demonstrate that the separation of enargite from other copper sulphide minerals is highly affected by the presence and amount of pyrite and is depended on the minerals’ electrochemical properties.
7.2. Water chemistry tests

Process water chemistry has a significant impact on flotation performance. The dissolved species can significantly affect the surface properties and floatability of the minerals. On the other hand, the important role of water chemistry in tailings management is known. A good understanding of the chemical composition of process water is therefore essential, especially in the case of arsenic.

The water chemistry tests were performed at the conditioning stage of the flotation tests (flotation feed) to determine the chemical composition of the flotation pulp water and its environmental implications.

7.2.1. Observed results

The flotation conditions and the amount of the reagents used for each test, and the chemical compositions of the sampled water are presented in Table 7-1.

The flotation reagents, which were used in conditioning stage, were mentioned in Chapter 3. The redox reagents were sodium hypochlorite (NaOCl) for oxidising conditions and Sodium dithionite (Na2S2O4) for reducing condition. Sodium hydroxide was used to set the pH to 11 and potassium ethyl xanthate (KEX) (CH3CH2OCS2K) was used as a collector. Consequently, the amount of ions in the solution will be affected by the addition of these reagents. Therefore, for the tests performed at Eh 0 mV SHE, the Eh was adjusted by using sodium hydroxide only, and no redox reagents were used. Hence this can be used as a reference test.

Sodium dithionite was added to set the Eh value to -200 mV SHE. Consequently, the amounts of Na and SO4\(^-\) are higher compared to those at 0 mV SHE. Likewise, sodium hypochlorite was used to increase the Eh value to +200 and +400 mV SHE, which caused an increase of Na and Cl in the water. Similarly for the flotation tests at Eh +400 mV SHE, it was observed again that controlling the Eh at +400 mV SHE was difficult and needed a lot of oxidants. The potassium (K) concentration of the process water is around 4 mg/L, which is due to the collector addition.

It can be seen that the amount of Cu, Fe, and As in the water is less than 1 mg/L.
# Table 7-1, Flotation conditions and geochemical data from water samples of the HAS and the LAS samples

<table>
<thead>
<tr>
<th>Test Name</th>
<th>Unit</th>
<th>LOR</th>
<th>HAS-200</th>
<th>HAS 0</th>
<th>HAS+200</th>
<th>HAS+400</th>
<th>LAS-200</th>
<th>LAS 0</th>
<th>LAS+200</th>
<th>LAS+400</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flotation Conditions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH, Sodium hydroxide</td>
<td>ml</td>
<td>1</td>
<td>40</td>
<td>35</td>
<td>30</td>
<td>40</td>
<td>35</td>
<td>30</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>NaOCl, Sodium hypochlorite</td>
<td>ml</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>50</td>
<td>200</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>Na₂S₂O₄, Sodium dithionite</td>
<td>ml</td>
<td>1</td>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CH₃CH₂OCS₂K,</td>
<td>ml</td>
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<td>15</td>
<td>15</td>
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</tr>
<tr>
<td>Condition gas</td>
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<td></td>
<td>N₂</td>
<td>N₂</td>
<td>Air</td>
<td>Air</td>
<td>N₂</td>
<td>N₂</td>
<td>Air</td>
<td>Air</td>
</tr>
<tr>
<td>Condition time</td>
<td>min</td>
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<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
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<td>12</td>
</tr>
<tr>
<td>Eh</td>
<td>mV/SHE</td>
<td>-200</td>
<td>0</td>
<td>200</td>
<td>400</td>
<td>-200</td>
<td>0</td>
<td>200</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td>11</td>
<td>11</td>
<td>11</td>
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</tr>
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<td>pH</td>
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<td>9.95</td>
<td>10.1</td>
<td>9.61</td>
<td>10.6</td>
<td>9.97</td>
<td>10.2</td>
<td>10.4</td>
<td>10.4</td>
</tr>
<tr>
<td>Electrical Conductivity @ 25°C</td>
<td>µS/cm</td>
<td>1</td>
<td>1050</td>
<td>957</td>
<td>1070</td>
<td>1460</td>
<td>891</td>
<td>858</td>
<td>1020</td>
<td>1140</td>
</tr>
<tr>
<td>Total Dissolved Solids (TDS)</td>
<td>mg/L</td>
<td>1</td>
<td>682</td>
<td>622</td>
<td>696</td>
<td>949</td>
<td>579</td>
<td>558</td>
<td>663</td>
<td>741</td>
</tr>
<tr>
<td>Total Alkalinity as CaCO₃</td>
<td>mg/L</td>
<td>1</td>
<td>143</td>
<td>118</td>
<td>126</td>
<td>236</td>
<td>117</td>
<td>157</td>
<td>180</td>
<td>187</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>mg/L</td>
<td>1</td>
<td>80</td>
<td>67</td>
<td>64</td>
<td>66</td>
<td>65</td>
<td>44</td>
<td>49</td>
<td>48</td>
</tr>
<tr>
<td>Sulfate (SO₄2-)</td>
<td>mg/L</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
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<tr>
<td>Sulfide as S₂</td>
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<td>64</td>
<td>114</td>
<td>171</td>
<td>62</td>
<td>63</td>
<td>84</td>
<td>131</td>
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<tr>
<td>Calcium (Ca)</td>
<td>mg/L</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>&lt;1</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>mg/L</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>mg/L</td>
<td>1</td>
<td>193</td>
<td>170</td>
<td>197</td>
<td>267</td>
<td>162</td>
<td>160</td>
<td>190</td>
<td>207</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>mg/L</td>
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<td>5</td>
<td>4</td>
<td>4</td>
<td>&lt;1</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1</td>
</tr>
<tr>
<td>Alumium (Al)</td>
<td>mg/L</td>
<td>0.01</td>
<td>1.04</td>
<td>1.18</td>
<td>1.6</td>
<td>1.66</td>
<td>1.46</td>
<td>1.36</td>
<td>1.85</td>
<td>1.58</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>µg/L</td>
<td>1</td>
<td>30</td>
<td>47</td>
<td>24</td>
<td>74</td>
<td>10</td>
<td>11</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>µg/L</td>
<td>1</td>
<td>44</td>
<td>10</td>
<td>47</td>
<td>22</td>
<td>40.7</td>
<td>32.7</td>
<td>43</td>
<td>49</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>µg/L</td>
<td>50</td>
<td>60</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>60</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>µg/L</td>
<td>10</td>
<td>100</td>
<td>40</td>
<td>90</td>
<td>170</td>
<td>20</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>µg/L</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>µg/L</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>µg/L</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>µg/L</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>µg/L</td>
<td>5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>µg/L</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Reactive Phosphorus (P)</td>
<td>µg/L</td>
<td>10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Fluoride (F)</td>
<td>mg/L</td>
<td>0.1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Ammonia</td>
<td>mg/L</td>
<td>0.01</td>
<td>0.34</td>
<td>0.61</td>
<td>0.28</td>
<td>0.2</td>
<td>0.18</td>
<td>0.27</td>
<td>0.26</td>
<td>0.18</td>
</tr>
<tr>
<td>Nitrite</td>
<td>mg/L</td>
<td>0.01</td>
<td>0.09</td>
<td>0.13</td>
<td>0.17</td>
<td>0.17</td>
<td>0.19</td>
<td>0.09</td>
<td>0.12</td>
<td>0.25</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg/L</td>
<td>0.01</td>
<td>0.21</td>
<td>0.25</td>
<td>0.23</td>
<td>0.16</td>
<td>0.02</td>
<td>0.17</td>
<td>0.12</td>
<td>0.07</td>
</tr>
<tr>
<td>Total Anions</td>
<td>meq/L</td>
<td>0.01</td>
<td>9.38</td>
<td>8.26</td>
<td>9.69</td>
<td>13.5</td>
<td>7.44</td>
<td>7.68</td>
<td>9</td>
<td>10.3</td>
</tr>
<tr>
<td>Total Cations</td>
<td>meq/L</td>
<td>0.01</td>
<td>8.67</td>
<td>7.65</td>
<td>8.87</td>
<td>11.7</td>
<td>7.17</td>
<td>7.06</td>
<td>8.34</td>
<td>9.13</td>
</tr>
<tr>
<td>Ionic Balance %</td>
<td></td>
<td>0.01</td>
<td>3.97</td>
<td>3.93</td>
<td>4.45</td>
<td>7.1</td>
<td>3.87</td>
<td>4.26</td>
<td>3.88</td>
<td>6.19</td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>mg/L</td>
<td>1</td>
<td>11</td>
<td>5</td>
<td>12</td>
<td>10</td>
<td>9</td>
<td>6</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>Total Inorganic Carbon (TIC)</td>
<td>mg/L</td>
<td>1</td>
<td>12</td>
<td>10</td>
<td>16</td>
<td>16</td>
<td>15</td>
<td>14</td>
<td>13</td>
<td>14</td>
</tr>
</tbody>
</table>
The equilibrium solution speciation was calculated using PHREEQC for each test with the input of Eh, pH, temperature, alkalinity, and concentrations of Cl, Ca, Mg, Na, K, Al, As, Cu, Fe, NH₄⁺, NO₃⁻, NO₂⁻, SO₄²⁻, CH₄, and CO₂. The results of the speciation calculation using MINTEQ database for the four different Eh values and both samples, HAS and LAS, showed that the main species in the solutions are OH⁻, Al(OH)₄⁻, CO₃²⁻, NaCO₃⁻, HCO₃⁻, Ca²⁺, Cl⁻, K⁺, Mg²⁺, Na⁺, NaSO₄⁻, NaCO₃⁻, SO₄²⁻, NaSO₄⁻.

The saturation index of minerals shows whether a mineral has the tendency to dissolve or precipitate in water under the thermodynamic conditions of the solution. It can be negative showing the mineral is being dissolved, positive when the mineral is precipitating, and zero when the mineral and water are at chemical equilibrium. Saturation Index is defined by SI=log(IAP/K), where IAP is the ion activity product, and K is the equilibrium constant for the considered reaction (Frau and Ardau, 2003).

The calculated saturation indices at different conditions are presented in Figure 7-6. The only saturated mineral is lepidocrocite (FeOOH), with a saturation index around three. It can be seen that the minerals controlling the chemistry of water at equilibrium are aragonite (CaCO₃), calcite (CaCO₃), Cu(OH)₂, ferrihydrite (Fe(OH)₃), and tenorite (CuO).

![Figure 7-6, Selected saturation indices calculated using PHREEQC for the HAS and the LAS sample](image)

From the geochemical modelling, the only important copper species which was detected in the tested water samples was Cu(OH)₂ in both samples which are consistent with Figure 7-5, observed by Yang et al. (2016).
7.2.2. Discussion

Arsenic (As) is one of the most abundant elements that typically occurs in four oxidation states; a) As\(^0\), i.e. metallic arsenic, (b) As\(^3\), e.g. arsine, AsH\(_3\), a by-product of electro-refining which is highly toxic, c) As\(^{3+}\) (arsenite), e.g. AsO\(_3^{3-}\), which is also highly toxic and often known as ‘white arsenic’, and d) As\(^{5+}\) (arsenate), e.g., AsO\(_4^{3-}\), which is more stable and less toxic than As\(^{3+}\), Figure 7-7 (Smith et al., 1998, McSweeney and Forbes, 2014).

![Figure 7-7, Common forms of arsenic: arsine, arsenite, arsenate, modified from (McSweeney and Forbes, 2014)]

The arsenic levels in natural waters range between 1-2 µg/L, although concentrations can be significantly higher (up to 12 mg/L) in areas containing natural sources. The world Health Organization (WHO) recommended 10 µg/L for the limit of arsenic in drinking water (WHO, 2011). According to Table 7-1, the amount of arsenic in water samples from the LAS sample in all the Eh ranges is less than 12 µg/L, which is similar to that recommended by WHO (2011). However, the As levels in the tested water from the HAS samples is between 24-74 µg/L.

Filippou et al. (2007) mentioned that enargite is generally characterised as a “refractory mineral,” as it cannot be easily digested in aqueous media. Even in alkaline solutions, enargite is not dissolved easily and is the last in the order by which copper sulphides dissolve in ammonia solutions: chalcocite > covellite > bornite > chalcopyrite > enargite (Filippou et al., 2007).

As discussed in Chapter 2, the metal ion concentration in solution depends on the oxidation characteristics of the mineral and is a function of pH. In the case of arsenic minerals, the species formed at various pH and Eh values can be represented on an Eh-pH diagram (Figure 7-8) (Couture and Van Cappellen, 2011).
Figure 7-8, Eh-pH equilibrium diagram for the system arsenic-water at 25°C and 1bar total pressure, modified from (Pourbaix, 1966, Smedley and Kinniburgh, 2002), hachure part: pH≈11, Eh -200 to +400 mV SHE

The equilibria for arsenic acid and arsenous acid in aqueous solutions are given in the equations below (Smith et al., 1998):

Arsenic acid:

\[
\begin{align*}
H_3\text{AsO}_4^+ + H_2O & \leftrightarrow H_2\text{AsO}_4^- + H_3O^+ \\
H_2\text{AsO}_4^- + H_2O & \leftrightarrow H\text{AsO}_4^{2-} + H_3O^+ \\
H\text{AsO}_4^{2-} + H_2O & \leftrightarrow \text{AsO}_4^{3-} + H_3O^+ \\
\end{align*}
\]

Equation 7-1

Arsenous acid:

\[
\begin{align*}
H_3\text{AsO}_3 + H_2O & \leftrightarrow H_2\text{AsO}_3^- + H_3O^+ \\
H_2\text{AsO}_3^- + H_2O & \leftrightarrow H\text{AsO}_3^{2-} + H_3O^+ \\
H\text{AsO}_3^{2-} + H_2O & \leftrightarrow \text{AsO}_3^{3-} + H_3O^+ \\
\end{align*}
\]

Equation 7-2
The most thermodynamically stable species under a very wide range of pH-Eh conditions are arsenate species $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$, and $\text{AsO}_4^{3-}$ (Smith et al., 1998, Frau and Ardau, 2003). The surface of arsenic minerals in the flotation process tends to be rich in oxidation products such as arsenic acid As(V) and arsenous acid As(III) (Frau and Ardau, 2003, McSweeney and Forbes, 2014).

Arsenic species in the water samples, in this work, calculated by PHREEQC (Figure 7-9) showed that the predominant oxidation states of As were $\text{HAsO}_4^{2-}$ and $\text{AsO}_4^{3-}$ in both samples. Interestingly the amount of these species were much higher in the HAS sample in all the Eh ranges. These results are in good correlation with the results obtained by flotation and EDTA extraction.

**Figure 7-9, Arsenic species as a function of pulp potential (Eh) for the HAS and the LAS samples**
7.2.3. Environmental implications

If the concentrator and tailings storage facility are considered as an integrated system, the important environmental factors are pH as a master variable, which controls the solubility of heavy metals and metalloids, as well as the oxidation state, particularly in the case of arsenic.

The results showed the dominance of arsenate species which could be attributed to the oxidation during the sampling procedure. This is consistent with the immediate change of oxidation states and with very low iron concentrations in solution. The controls on arsenic recovery were explained which means the arsenic concentrations in tailings water can be predicted.

There is a chance of a release of salts particularly sulphate due to pyrite oxidation or direct addition of processing chemicals. The pyrite content in tailings and the mineralogy of gangue minerals particularly carbonates will dictate the acid/base balance of tailings. Therefore, understanding the controls on pyrite recovery helps to predict potential Acid Mine Drainage (AMD) formation in tailings seepage.

The process water chemistry is alkaline with the pH in the range of 9.60 to 10.60. Under the alkaline conditions, the chance of mobility of heavy metals is low. Nevertheless, the process water contained copper concentrations (10-49 µg/L) which is above the acceptable range, 1-2.5 µg/L, of ANZECC (2000) water quality guidelines for aquatic fauna in fresh-water environments. Copper was dominated by its hydroxide form [(Cu(OH)₂] which can be toxic to biota. The chemical form of copper in freshwater is important in controlling geochemical and biological processes.

The Cd, Cr, Pb, Zn, Hg concentrations were below detection limits. Electrical conductivities, as an indicator of salinity, were relatively high particularly for the HAS +400 mV SHE (1460 µS/cm) due to the addition of hypochlorite salt in the process. However, sulphate concentrations were moderate with maximum values of 228 mg/L for the HAS -200 mV SHE and chloride concentrations are low with a maximum value of 171 mg/L for the HAS +400 mV SHE. The very low levels of Ca and Mg mean low hardness process water, which may result in increased bioavailability hence more toxicity by heavy metals particularly copper.
7.3. Key findings

EDTA extraction tests were performed to determine the oxidation amount and proportion of surface species in the mill discharge and flotation feed as a function of Eh for both HAS and LAS samples. The main observations are as follows:

- The EDTA extracted Cu and As showed there was higher metal oxidation in the HAS sample compared to that in the LAS sample. Copper was the predominant extracted metal, and the amount of EDTA extracted Cu increased towards the higher pulp potential levels. The EDTA extractable arsenic after grinding was negligible in both samples however it increased through the conditioning stage in the HAS sample which showed that enargite became oxidised in the HAS sample. The EDTA extracted Fe was higher in the HAS sample compared to that in the LAS sample in the mill discharge tests. However, it decreased sharply in the HAS sample through the conditioning stage. There was a downward trend in Fe extraction as the Eh was increased in both samples.

- Enargite had the lowest rest potential compared to other main sulphide minerals present in the HAS and the LAS ore samples. The rest potential of the main sulphide minerals present in the HAS and the LAS ore samples follows the order:

  pyrite > chalcopyrite > bornite > enargite

- The EDTA extraction results shown that the galvanic interactions between sulphide minerals, and pulp potential conditions, determined the flotation performances of the HAS and the LAS ore samples.

- Based on enargite surface studies by other researchers and the results obtained from the current work, it is concluded that the strong galvanic interactions between enargite and pyrite in the HAS sample caused the oxidation of enargite and its poor floatability and consequently poor selectivity with respect to other copper minerals in the HAS sample.

- The galvanic interaction also produced copper ions in the flotation pulp, which activated the pyrite surface and affected its recovery.

- It should be noted that currently limited data is available on the arsenic extraction by EDTA and further work is required to fully understand the As-EDTA system and to adjust or confirm these conclusions.
Water chemistry tests were performed on the conditioning stage of the flotation tests as a function of Eh for both HAS and LAS samples. The main observations are as follow:

- As levels in the tested water from the HAS samples were higher than the standard limit recommended for drinking water.

- The predominant oxidation states of As were HAsO$_4^{2-}$ and AsO$_4^{3-}$ in both samples. The amount of these species were much higher in the HAS sample in all the Eh ranges.

- The process water chemistry was alkaline, and under the alkaline conditions the chance of mobility of heavy metals is low.

- The process water contained copper concentrations above the acceptable range which were dominated by hydroxide form [Cu(OH)$_2$] which can be toxic to biota.
Chapter 8

NON-SULPHIDE GANGUE

FLOATABILITY

The main aim of this chapter is to determine the floatability of different non-sulphide gangue minerals presented in the HAS and the LAS ore samples (i.e. quartz, muscovite, pyrophyllite, and kaolinite) and to identify whether the poor flotation responses of enargite in the HAS sample can be due to the different types of gangue minerals present in the ore samples.

It was observed in Chapter 5 that the size-by-size and size-by-liberation analysis could not provide a satisfactory explanation for the observed poor floatability of the enargite in the HAS sample. On the other hand, from Chapter 4, it is known that the main difference between the HAS and the LAS samples, is the proportion of gangue minerals; the LAS sample has more phyllosilicates, and most of that is muscovite, while the HAS sample has more pyrophyllite.

The chapter begins with a short review on the main non-sulphide gangue minerals presented in the HAS and the LAS ore samples their characteristics and their floatability behaviour. It then presents the overall and the size-by-size recovery results obtained from the flotation tests at different Eh conditions on both samples. The data are shown as a function of Eh to show how different minerals floated at various Eh ranges. The chapter finishes with the discussion on the results.
8.1. Non-sulphide gangue characteristics and floatability behaviour

The main non-sulphide gangue minerals in both samples are quartz, muscovite, pyrophyllite, and kaolinite. In this section a review of their main characteristics is presented.

Quartz (\(\text{SiO}_2\)) is a tectosilicate mineral with hardness 7 and specific gravity of 2.65 g/cm\(^3\). The ZPC of quartz is two, consequently, over the whole pH range the surface of the mineral is negatively charged. It does not show natural floatability and does not float with anionic collectors. However quartz recovers to the concentrate through being associated with valuable minerals or through entrainment (Smith and Scott, 1990).

Muscovite (\(\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2\)) is a non-swelling 2:1 phyllosilicate mica mineral comprising of T-O-T layers that are held together by interlayer potassium ions. It has a hardness of 2-3 and a specific gravity of 2.8-2.9 g/cm\(^3\). Muscovite displays perfect cleavage along the (001) plane. It is a direct consequence of the strong bonding within layers and the relatively weak bonding between layers. Muscovite occurs as small flakes that are tough, elastic, greasy, and resistant to grinding. In aqueous suspensions, the potassium ions enter into the solution, causing the development of a net negative charge on the crystal plane (Silvester et al., 2011) and the zero point of charge of muscovite is 0.95. Thus the face of the mineral is negatively charged over the whole pH range. Due to the cleavage planes being hydrophilic entirely and with permanent negative charges muscovite will not float with anionic collectors (Rao et al., 1995, Zhong et al., 2008, Silvester et al., 2011, Ndlovu et al., 2011).

Kaolinite (\(\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4\)) is a common 1:1 phyllosilicate clay mineral that has a hardness of 2-2.5 and a specific gravity of 2.6 g/cm\(^3\). Kaolinite has the very low swelling capacity and consists of plate-like particles that do not have an expanding lattice; therefore no water can enter between the layers (Brigatti et al., 2006). The basal face of kaolinite, displaying an inert siloxane structure, carries a permanent negative charge (Van Olphen, 1977) which makes kaolinite only moderately floatable (Zhong et al., 2008). However, kaolinite was found to have a strong adverse effect on the natural floatability of chalcopyrite (Forbes et al., 2014).

Pyrophyllite (\(\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2\)) is a 2:1 phyllosilicate clay mineral (talcaceous) composed of aluminium silicate hydroxide. Its hardness is 1-2 and specific gravity is 2.6-2.9 g/cm\(^3\). The ideal layer structure of pyrophyllite is electrically neutral, and hence no charge-balancing cation is present in the interlayer space (Brigatti et al., 2006). The edge of pyrophyllite is pH-dependent, while its faces are not (Burdukova et al., 2006). The face is hydrophobic and causes pyrophyllite to have natural floatability properties. Hence pyrophyllite shows perfect floatability in the pH range of 2-12 (Zhong...
et al., 2008). Pyrophyllite enhances froth stability and increases the entrainment of other non-sulphide gangue minerals (Lotter et al., 2008)

### 8.2. Overall recovery results

The recovery data for different non-sulphide gangue minerals present in the HAS and the LAS ore samples including quartz, muscovite, pyrophyllite, and kaolinite at various Eh conditions are presented in Figure 8-1. It can be seen that the recoveries of quartz, muscovite, and kaolinite are lower than the water recovery, suggesting that these particles are possibly recovered by entrainment. In contrast, the recovery of pyrophyllite is significantly greater than water recovery which means that this mineral was recovered by true flotation.

![Figure 8-1, Recovery of non-sulphide gangue minerals at different Eh conditions for the HAS (left) and the LAS (right) samples](image)

At Eh -200 mV SHE, the lowest recovery of NSG and water recovery is observed. The recoveries of all non-sulphide gangue minerals increase as the Eh increases toward more oxidation condition. At Eh +400 mV SHE the highest amount of recovery of NSG is observed except for muscovite. Muscovite recovery decreases from 6.8 to 6.3% in the HAS sample and 9.4% to 8.6% in the LAS sample as the Eh increased from +200 mV SHE to +400 mV SHE. The water recovery also increases as the Eh increases showing that the amount of NSG recovered is closely related to the amount of water recovered. Interestingly, the recovery of pyrophyllite in both samples is similar at Eh -200 and 0 mV SHE (circa 23% in the HAS and 24% in the LAS). However, it sharply increases at Eh +200 mV SHE in the HAS sample.
Based on the overall recovery results and their characteristics, the non-sulphide gangue minerals were classified into two main groups namely floatable gangue (FG) and non-floatable gangue (NFG). The floatable gangue group consists of only pyrophyllite, which is a naturally floatable phyllosilicate, and the non-floatable gangue group consists of the rest of the non-sulphide gangues (quartz, muscovite, kaolinite, etc.). The overall recovery data for FG and NFG at different Eh conditions are presented in Figure 8-2.

There is a general upward trend in NFG and FG recovery towards the higher pulp potential levels. The NFG recovery is less than 9% in all the Eh ranges in both samples. The minimum (3.6% for the HAS and 4.3% for the LAS) and maximum (8.4% for the HAS and 7.3% for the LAS) recoveries of NFG are at Eh -200 mV SHE and +400 mV SHE respectively.

Figure 8-2, Recovery of floatable gangue and non-floatable gangue minerals at different Eh conditions for the HAS (left) and the LAS (right) samples
8.3. Size-by-size recovery

In flotation non-sulphide gangue minerals are recovered into the concentrate stream by four principal mechanisms: a) recovery by entrainment, b) recovery by association (i.e. gangue minerals in composites with the hydrophobic valuable minerals), c) recovery by true flotation (i.e. hydrophobic NSG such as talc and pyrophyllite), and d) recovery by inadvertent ion activation (Cilek and Umucu, 2001, Lotter et al., 2008, Cropp et al., 2013).

The size-by-size recoveries of non-floatable gangue at different Eh conditions for both samples are shown in Figure 8-5. Non-floatable gangue, which mostly consists of quartz and muscovite, shows the typical trend for the recovery by entrainment, with an increase in recovery in the fine fractions. On the other hand, the recovery of coarse particles is due to the poor degree of liberation of this size fraction, being composite with the floatable valuable minerals. As mentioned by Cropp et al. (2013), rejecting this size fraction resulted in increasing the grade of the concentrate but losing the target grains of the valuable minerals thereby reducing overall recovery.

Comparing the HAS and the LAS floatability of NFG shows that the NFG recovery by size has a similar trend at reducing conditions (i.e. Eh -200 and 0 mV SHE). However, it has significantly different recovery by size at oxidising conditions (i.e. the Eh +200 and +400 mV SHE).

Cropp et al. (2013) mentioned that the main causes for the recovery of middle size gangue to the concentrate is recovery by activation. As the middle size fraction is typically considered to be fully liberated it is expected to show a high recovery of valuable minerals and low recovery of gangue minerals (Figure 8-4). They concluded that the high specific surface area of very fine-grained copper

![Figure 8-3, Size-by-size recovery of non-floatable gangue minerals at different Eh conditions for the HAS (left) and the LAS (right) samples](image-url)
minerals present in the ore sample might release Cu ions into solution during flotation, which change the flotation chemistry. As a result the surface of the gangue minerals will be activated, which cause the higher recovery of gangue minerals to the concentrate and lower concentrate grade and recovery of valuable minerals.

It was observed in Chapter 7 that the EDTA extractable copper was higher in the HAS sample compared to that in the LAS sample. On the other hand, the amount of copper minerals including enargite in the finest size fraction -11 µm was higher in the HAS sample compared to that in the LAS sample. It can be concluded that the higher recovery of NFG minerals in the middle size fraction at Eh +200 and +400 mV SHE in the HAS sample could be due to activation by copper ions.

![Figure 8-4](image)

*Figure 8-4, Common causes for the recovery of gangue minerals in the flotation concentrate based on the particle size, modified from (Cropp et al., 2013)*

Figure 8-5 show size-by-size recoveries of floatable gangue (pyrophyllite) at different Eh conditions for both samples. It can be seen that the size-by-size recoveries of the floatable gangue at different Eh conditions are significantly distinct from those of the non-floatable gangue. In contrast to the NFG recovery, which was increased as the particle size reduced, the FG recovery shows good floatability in middle size fractions.

Comparison of the size-by-size recoveries of the FG in the HAS and the LAS sample indicates that despite the similarity in the recovery trends, the HAS sample has more FG recovered to the concentrate than the LAS sample. It was observed from the mineralogy study on the HAS and the LAS feed samples (Chapter 4) that the HAS sample had 12.8% and the LAS sample had 6.9% pyrophyllite, with 86% of the mineral in the HAS sample and 83% of it in the LAS sample fully liberated.
Comparison of the liberation characteristics of FG (pyrophyllite) recovered in the concentrates of the HAS and the LAS at different Eh conditions (Figure 8-6) shows that the particles recovered to the concentrate are mostly liberated (circa 90% in the HAS concentrate and 80% in the LAS concentrate). Only circa 7% and 16% of the FG particles in the concentrates of the HAS and the LAS respectively are in binary with other NFG (quartz and muscovite in the HAS sample and muscovite in the LAS sample).
8.4. Discussion

It was mentioned in the literature review that the presence of the non-sulphide gangue minerals, in particular clay minerals, has various undesirable effects on the efficiency of the recovery of sulphide minerals by flotation, influenced by slime coating, changing the froth stability, increasing the pulp rheology, and thus the entrainment. Tabatabaei et al. (2014) investigated the reason for poor flotation recovery of sulphides from Carlin-type ore. They found that an increase in the amounts of NSG minerals, especially clays, had an opposing effect on concentrate grade; an increase in the proportion of the gangue minerals increased the entrainment and froth stability of the pulp, and as a consequence, the grade of the concentrate decreased.

Silvester et al. (2011) discussed that muscovite does not have any natural floatability. However, it decreases the grade of the concentrate by entrainment and reduces the recovery of the valuable minerals by increasing the pulp viscosity (Jorjani et al., 2011). In the current study, although the LAS feed sample has 27.2% muscovite, the grade and recovery of NECu are higher than those in the HAS sample with only 5.6% muscovite. It can be concluded that muscovite is not a major problem in the processing of these ore samples.

In the current study, the HAS and the LAS sample have circa 3% and <1% kaolinite respectively. Cruz et al. (2015) studied the flotation of a copper-gold ore and its mixtures with kaolinite at pH 10. They observed that the addition of 10 wt.% kaolinite to the ore at pH 11 increased the mass and water recovery compared to the baseline flotation condition and decreased the grade and recovery of copper and gold. It was also observed that with an increase in kaolinite content the froth was more viscous, which caused the reduction in copper recovery by true flotation. In addition, the entrainment of particles was increased with the increase in kaolinite concentration. In another study by Forbes et al. (2014) on the effect of kaolinite on the natural floatability of chalcopyrite it was observed that the overall flotation recovery of chalcopyrite significantly decreased by increasing the proportion of kaolinite to more than 30% in the flotation pulp. It also had a strong effect on flotation pulp rheology which became increasingly viscous. Based on previous research by other authors and the very low amount of kaolinite in the HAS and the LAS ore samples, it is concluded that the effect of kaolinite in the grade and recovery of NECu and enargite in this study is negligible.

Becker et al. (2009) mentioned that pyrophyllite is a naturally floatable gangue mineral which enters the concentrate by true flotation and carries other gangue minerals by association. It also increases the froth stability and water recovery, hence the mass recovery by entrainment would be increased. Comparing the final NECu grade of the different flotation tests on the HAS and the LAS showed
lower NECu grade in the HAS sample in all Eh ranges. Furthermore, the degree of entrainment was higher in the HAS sample compared to the LAS sample.

The obtained results did not show any direct effect of pyrophyllite on recovery of NECu and enargite, and there was no provision in this study in terms of surface study by ToF SIM or SEM, for determining the exact effect of pyrophyllite. However, one may relate the results to the natural floatability of pyrophyllite, and hence the decrease in the concentrate grade.

Either a guar gum or carboxymethyl cellulose (CMC) can be added to the flotation pulp to depress the magnesium-bearing gangue minerals (in this case pyrophyllite). These reagents are adsorbed on the hydrophobic surface of the floatable gangue silicate minerals and create a hydrophilic layer, which prevents particle-bubble attachment and hence depresses their flotation (Bradshaw et al., 2005, Lotter et al., 2008).
8.5. Key findings

Four different non-sulphide gangue minerals are present in the HAS and the LAS ore samples including quartz, muscovite, pyrophyllite, and kaolinite. Based on their floatability they were classified into two groups; FG (floatable gangue, i.e. pyrophyllite) and NFG (non-floatable gangue, i.e. quartz, muscovite, and kaolinite).

- The NFG recovery showed a similar trend at different Eh ranges in both samples. The lowest recovery of NFG was observed at Eh -200 mV SHE. Its recovery increased as the Eh was increased toward more oxidation conditions and finally reached the maximum values at Eh +400 mV SHE. The water recovery also increased as the Eh was increased. However, the recovery of NFG was lower than the water recovery at all Eh ranges, suggesting that these particles were mainly recovered by entrainment.

- There was a general upward trend in FG recovery towards the higher pulp potential levels in both samples. The recovery of FG was similar at Eh -200 and 0 mV SHE in both samples, however, it sharply increased at Eh +200 mV SHE in the HAS sample. FG recovery was higher than water recovery in all test conditions as pyrophyllite is a naturally floatable gangue mineral.

- Size-by-size recovery of NFG showed a common trend for the recovery by entrainment, with an increase in recovery at the fine fractions. However, the recovery of NFG at Eh +200 and +400 mV SHE showed a different recovery trend due to activation by copper ions.

- The size-by-size recovery of FG at various Eh conditions was significantly different from that of the NFG and shows good floatability in the middle size fractions. Moreover, the HAS sample had more FG recovered to the concentrate than the LAS sample.
Chapter 9

PROCESS IMPLICATIONS AND POSSIBLE FLOWSHEET

This chapter combines the results obtained in this work in order to propose some solutions as a flowsheet for separating enargite from other copper sulphides.

The emphasis of this study was more on increasing the understanding of the floatability of arsenic-copper minerals within complex ores than on developing a flowsheet to separate them. However, the observed results led to proposing a conceptual flowsheet, which would require further investigation to adjust or confirm.

In the first section of this chapter some of the main findings of the experimental work are presented and then in the second section the conceptual flowsheet is proposed.

This chapter addressed the last hypothesis of this research, which is “Appropriate control of flotation pulp potential enables an effective separation of enargite from other copper sulphide minerals within a complex ore system.”
9.1. Process implications

As discussed in the literature review there is currently no established methodology for separating enargite from other copper sulphide minerals by flotation. The most reliable method for this separation is through the controlling of the potential of the pulp due to the differences in the flotation behaviour of pure enargite from that of other copper sulphide minerals. Based on these differences, a conceptual flowsheet for the selective enargite separation was proposed by Senior et al. (2006). However, Smith and Bruckard (2007) observed different results on testing the new methodology on real ore systems. The importance of understanding the flotation response of enargite in the presence of other minerals in a complex ore system is undeniable. In this section, the most important findings of this work are discussed, and their impacts on the development of the enargite separation flowsheet are pointed out.

9.1.1. Key mineralogical attributes

The HAS and the LAS ore samples used in this work came from Tampakan deposit representing two levels of arsenic.

The modal mineralogy studies on these ore samples indicated that there are similarities in terms of mineral content, however there are some differences in the proportions of minerals present. Enargite was the only arsenic mineral present in both samples. The main copper minerals were bornite and chalcopyrite, however trace amounts of digenite, covellite, and tetrahedrite were observed. Gangue mineralogy mainly comprised of quartz, diaspore, and phyllosilicates including muscovite, pyrophyllite, and kaolinite. The amount of phyllosilicates (mostly muscovite) in the LAS sample was more than that in the HAS sample (mostly pyrophyllite).

The size-by-size weight distribution of the HAS and the LAS samples showed similar trends in both samples, where the phyllosilicate minerals largely reported to the finest size fraction -11 µm. It was also observed that the amounts of fine (-11 µm) particles were noticeably greater for enargite than for NECu (non-enargite copper minerals), which showed that enargite tended to be ground more readily than the other copper sulphide minerals.

The mineral grain size data showed that enargite had the finest grain size distribution compared to other copper minerals in both samples.
Mineral locking data indicated that both samples have similar liberation characteristics. In general the liberation of the minerals increased as the particle size decreased, and in the finest size fraction, -11 µm, more than 90% of the minerals grains were fully liberated.

Liberation characteristics indicated that at a P_{80} of 90 µm, the percentage of the total free surface of enargite grains was higher in the HAS sample than that in the LAS sample.

### 9.1.2. Key metallurgical attributes

For the LAS sample unsized results confirmed that it is possible to separate enargite from non-enargite copper minerals (NECu) at -200 mV SHE, while no separation between enargite and NECu was observed at reducing potential in the HAS sample. In the oxidising pulp potential region (+400 mV SHE), there was no selectivity between enargite and the other copper minerals in both samples. Although the results obtained varied for the HAS sample and the LAS sample, flotation at reducing pulp potential (-200 mV SHE), in this test work, was the most promising conditions to obtain an enargite separation from other copper minerals. The size-by-size studies showed that the best As/Cu selectivity results were for the size fraction -32+11 µm. In addition it was observed that pyrite was highly depressed at Eh +400 mV SHE.

The size-by-liberation data showed that the recovery of liberated enargite was higher than the recovery of liberated NECu at Eh -200 mV SHE for both samples. The size-by-size enargite recovery in different liberation classes showed higher recovery of liberated enargite compared to the binary and ternary classes in both samples.

EDTA extraction of Cu and As showed higher metal oxidation in the HAS sample compared to those in the LAS sample. It was observed that the oxidation of enargite in the HAS sample caused its poor floatability and consequently poor selectivity from other copper minerals in the HAS sample.

The study of the floatability of non-sulphide gangue minerals in the flotation of the HAS and the LAS sample showed that muscovite in the LAS sample increased the entrainment, but it did not have a negative effect on the recovery of the valuable minerals. In contrast, pyrophyllite as a natural gangue mineral has floated significantly in the HAS sample causing the lower recovery of valuable minerals compared to that in the LAS sample.
9.1.3. Consequences for the flowsheet

- The $P_{80}$ of 90 $\mu$m is sufficiently fine for the rougher flotation stage.

The mineral grain size data showed that enargite had the finest grain size distribution compared to other copper minerals. It can be an indication that fine grinding would be required to achieve sufficient levels of enargite liberation for flotation separation. On the other hand, it was also observed that the amounts of fine (-11 $\mu$m) particles were noticeably greater for enargite than for NECu, which showed that enargite tended to be ground more readily than the other copper sulphide minerals.

Considering these observations and the degree of liberation of enargite, it can be concluded that the $P_{80}$ of 90 $\mu$m is sufficient for this stage of flotation. Further grinding firstly increases the proportion of non-sulphide gangue minerals in -11 $\mu$m, causing more problems in flotation, and more importantly decreases the amount of valuable minerals in medium size fractions that are the most floatable size fractions.

- A fine treatment stage would be required before rougher flotation stage to separate the finest size fraction -11 $\mu$m.

As observed in Chapter 8, the presence of phyllosilicates had an adverse effect on the grade and recovery of the sulphide flotation. In addition, more than half of phyllosilicates reported to the finest size fraction. Therefore, a de-sliming stage can be an option to remove the fines prior to the flotation stage. On the other hand, as mentioned above, a noticeable amount of enargite reported to the finest size fraction -11 $\mu$m. Hence removing this size fraction also means losing copper through the enargite and increasing the arsenic content of the tailing which represents an unacceptable environmental risk. It would therefore be more beneficial to include a fine treatment stage to remove the NSG minerals and enargite fines, which can be further treated to separate enargite from NSG fines.

- A regrinding stage would be required to liberate the valuable grains, which are locked with other non-sulphide gangue minerals.

The size-by-size studies showed that the best As/Cu selectivity results were produced at size fraction -32+11 $\mu$m at Eh -200 mV SHE. In addition, the size-by-liberation data showed that the recovery of liberated enargite was higher than the recovery of liberated NECu at Eh -200 mV SHE for both samples. Hence it is necessary to further grind the coarse size fraction to 32+11 $\mu$m.
- A separation flotation stage at reducing pulp potential (-200 mV SHE) would be a promising option to separate enargite and NECu and produce two concentrates: High-As Low-Cu, and Low-As High Cu.

The overall flotation results confirmed that it is possible to separate enargite from NECu in the LAS sample at -200 mV SHE. In the highly oxidising pulp potential region (+400 mV SHE) there was no selectivity between enargite and the other copper minerals. Although the results obtained for the HAS sample was different to those for the LAS sample, flotation at reducing pulp potential (-200 mV SHE), in this test work, was the most promising conditions to obtain enargite separation from the other copper minerals.

- Adjustment of flotation chemistry would be required.

The EDTA extracted Cu and As showed higher metal oxidation in the HAS sample compared to those in the LAS sample. It was observed that the oxidation of enargite in the HAS sample strongly influenced its floatability and consequently poor selectivity from other copper minerals. In addition, the presence of Cu ions on the pyrite surface caused its activation and hence high recovery of pyrite in both samples. It is suggested that by adjusting the flotation chemistry via changing collector type, the galvanic interactions between minerals will be mitigated.
9.2. Proposed flowsheet

A flowsheet for improving the enargite separation from other copper sulphide minerals was devised based on the mineralogical and metallurgical results obtained and it is presented in Figure 9-1. It comprises de-sliming, a fines treatment, separation, and regrinding stages.

The first stage of the flowsheet is a de-sliming stage prior to the rougher flotation to remove -11 µm fine materials. The -11 µm product goes to a fine treatment stage to separate the enargite and any remaining NECu minerals from gangue minerals.

The +11 µm product goes to the first stage of flotation in which the sulphides are floated at air set potential and pH 11 to achieve a high-arsenic high-copper concentrate. Prior to this stage suitable reagents would be required to treat the surface of minerals.

The rougher concentrates then goes to a cyclone, which is in closed circuit with a regrind mill. The -20 µm overflow goes directly to the cleaner stage.

The second stage of flotation is a cleaner flotation stage, where the concentrate is re-floated at air set potential and pH 11 to depress the gangue minerals and pyrite.

The third stage of the flotation process is a separation stage, which has two stages. The first step is arsenic flotation at -200 mV SHE, under nitrogen gas, to selectively depress the non-enargite copper minerals and float the enargite. It produces a high-arsenic low-copper concentrate that would be further treated using other techniques like hydrometallurgy or pyrometallurgy. The second phase is copper flotation at air set potential and pH 11 to float the copper minerals and produce a low-arsenic high-copper concentrate. The low-arsenic high-copper concentrate can go directly to the smelter without paying any penalty.

It should be understood that this proposed flowsheet is an informed suggestion which would require further investigation to adjust or confirm, preferably on Tampakan ore.
Figure 9-1, Proposed flowsheet for separating enargite from other copper minerals.
9.3. Key findings

This chapter discussed the experimental results obtained in this work and proposed a conceptual flowsheet for separating enargite from other copper sulphide minerals. The key points of this chapter can be summarised as follows:

- The P<sub>80</sub> of 90 µm is sufficiently fine for the rougher flotation stage. Further grinding firstly increases the proportion of non-sulphide gangue minerals in the -11 µm size fraction that causes more problems in flotation, and more importantly decreases the amount of valuable mineral in medium size fractions that are the most floatable size fractions.

- A de-sliming stage and a fine treatment stage would be required prior to the rougher flotation stage to remove the NSG minerals and enargite fines, which can be further treated to separate enargite from NSG fines.

- A regrinding stage would be required to liberate the valuable grains, which are locked with other non-sulphide gangue minerals.

- A flotation separation stage at reducing pulp potential (-200 mV SHE) would be a promising option to separate enargite and NECu and produce two concentrates: High-As Low-Cu, and Low-As High Cu.

- Adjustment of the flotation pulp chemistry would be required via changing the collector type to mitigate the galvanic interactions between minerals and increase the floatability of enargite in the HAS sample.
Chapter 10

CONCLUSIONS AND
RECOMMENDATIONS

The main aim of this thesis was “to develop an understanding of the effect of ore mineralogy on the floatability of enargite in a complex ore system under controlled pulp potential conditions.” The impetus came from the observation that there is currently no established commercially methodology for separating enargite from other copper sulphide minerals by flotation.

This aim led to the overall hypothesis of the thesis, which was that: “The flotation behaviour of arsenic-bearing minerals within complex ores differs significantly from that of pure mineral systems due to the effects of mineralogical composition, the degree of liberation, and the surface oxidation. The understanding and manipulation of these effects can lead to improvements in the selective flotation recovery of arsenic-bearing species from complex ore systems.”

A full set of experiments was conducted to assess the above hypothesis. In this chapter, the major findings drawn from these investigations are summarised and concluded.
10.1. Objectives versus major findings

The major findings of this work are summarised in the following sections. They are presented as explanations of the objectives, which are presented in Chapter 1.

10.1.1. To identify the mineralogical characteristics of two ore samples

Comprehensive chemical and mineralogical analyses were performed on the HAS (high arsenic sample) and the LAS (low arsenic sample) samples from Tampakan deposit.

The modal mineralogy studies on these ore samples indicated that there are similarities in terms of minerals content, however there are some differences in the proportions of minerals present. Enargite was the only arsenic mineral present in both samples. The other non-enargite copper minerals (NECu) were bornite and chalcopyrite, however trace amounts of digenite, covellite, and tetrahedrite were observed. Gangue mineralogy mainly comprised of quartz, diaspor, and phyllosilicates including muscovite, pyrophyllite, and kaolinite. The amount of phyllosilicates in the LAS sample (mostly muscovite) was more than the phyllosilicates proportion in the HAS sample (mostly pyrophyllite).

The size-by-size weight distribution of the HAS and the LAS samples showed similar trends in both samples, where the phyllosilicate minerals largely reported to the finest size fraction -11 µm. It was also observed that the amounts of fine (-11 µm) particles were noticeably greater for enargite than for NECu (non-enargite copper minerals), which showed that enargite tends to be ground more readily than the other copper sulphide minerals. The mineral grain size data showed that enargite had a finer grain size distribution compared to the other copper minerals in both samples.

Mineral locking data indicated that both samples have similar locking characteristics and the liberation of the minerals increased as the particle size decreased, and in the finest size fraction -11 µm, more than 90% of the minerals grains were fully liberated. Enargite was mainly associated with copper minerals, pyrite and quartz in the HAS sample. It was widely associated with muscovite and quartz and to a less extent pyrite and copper minerals in the LAS sample.

Liberation characteristics indicated that at a P80 of 90 µm, the percentage of the total free surface of enargite grains was higher in the HAS sample than that in the LAS sample. In addition it showed that more than 85% of non-sulphide gangue minerals were fully liberated and pyrite was more than 55% liberated in both samples.
10.1.2. To understand the effects of applied potential on the floatability of enargite within these two ores

Based on pure mineral studies by previous researchers four Eh conditions were tested seeking a differential separation of enargite from other copper sulphide minerals. For the LAS sample, unsized results confirmed that it is possible to separate enargite from non-enargite copper minerals (NECu). From the overall recoveries, it was observed that enargite (67.17%) was recovered preferentially at a reducing potential (-200 mV SHE) and pH 11 while 46.62% of the NECu was recovered. In the oxidising pulp potential region, there was however no selectivity between enargite and the other copper minerals in the LAS sample.

For the HAS sample no separation between enargite and NECu was observed at reducing potentials. There was, however, a window for separating enargite (54.38%) and NECu (73.75%) at the oxidising potential, +400 mV SHE. Notably, enargite in the HAS sample showed very low recovery variations as the Eh was increased and it did not float very well as the Eh was changed. This window of separation at +400 mV SHE was therefore not considered as optimal for separating these two minerals. In addition, it was observed that pyrite was highly depressed at Eh +400 mV SHE in both samples without the addition of any chemical depressant.

The overall recovery of NECu, enargite, and pyrite were higher than was expected from pure minerals studies by other researchers at -200 mV SHE. This may be due to the fluctuation of the flotation edge at the highly reducing conditions or due to the hysteresis effects that caused shifting in the pulp potential of these minerals toward more reducing conditions, thus achieving higher recovery than expected.

The size-by-size studies showed that the best As/Cu selectivity results were produced for the size fraction -32+11 µm at Eh -200 mV SHE. Hence, by regrinding the concentrate, it would be expected to achieve a similar separation between enargite and NECu as for this size distribution.

The size-by-liberation data showed that the recovery of liberated enargite was higher than the recovery of liberated NECu at Eh -200 mV SHE for both samples.

There was very little entrainment of NECu, pyrite, and enargite into the concentrate at Eh values below +400 mV SHE. However at an Eh +400 mV SHE an increase in entrainment was observed. Enargite recovery by entrainment was higher in the finest size fraction -11 µm in the HAS sample compared to the LAS sample due to the greater amount of enargite mineral in the HAS sample.
10.1.3. To use the Particle Kinetic Model to predict the recovery of ore samples

A Particle Kinetic Model was used to predict the flotation response of each particle in a flotation feed. This model used the particle surface composition data from MLA analyses and the actual flotation kinetic data for each mineral group.

The LAS sample was used to calibrate the model. The use of the Particle Kinetic Model was shown to be successful in calculating the NECu and enargite recoveries in the LAS sample. The NECu size-by-size recovery values calculated by the Particle Kinetic Model showed close agreement with the actual recovery values over all Eh conditions.

The flotation response of the HAS sample was predicted by using the flotation rate constant of the LAS sample. It was observed that although the model correctly ranked the size-by-size recoveries of NECu and enargite, it was unable to predict the absolute values of recovery correctly. The predicted value of enargite recovery by the Particle Kinetic Model showed higher enargite recovery (5% to 30% higher) when compared with the results of physical flotation tests on the HAS sample.

The possible reasons for the poor prediction of the model for the HAS sample were, changes in the ore mineralogy or the flotation pulp conditions of the HAS sample. The possible factors for the change in the flotation response of the HAS sample could be the higher levels of pyrite present in the HAS sample compared to the LAS sample or the different amount of the gangue content in the HAS and the LAS sample.

The model did not include the parameters that can affect flotation performance such as surface oxidation or surface slime coatings. These factors were accounted for the flotation rate data of the LAS sample, and were calibrated to that ore. However, for the HAS sample the flotation rates of the LAS sample that were used, were not calibrated with respect to the HAS flotation conditions. The model may be more accurate if it includes these factors.

10.1.4. To identify the causes for the differences in flotation behaviour of the two ores

EDTA extraction tests were performed to determine the amount of oxidation and the proportion of surface species in the mill discharge and flotation feed as a function of Eh for both HAS and LAS samples. The EDTA extracted Cu and As showed higher metal oxidation in the HAS sample
compared to that in the LAS sample. Copper was the predominantly extracted metal, and the amount of EDTA extracted Cu increased towards the higher pulp potential levels.

Enargite had the lowest rest potential compared to the other main sulphide minerals present in the HAS and the LAS ore samples. The rest potential of the main sulphide minerals present in the HAS and the LAS ore samples follows the order: pyrite > chalcopyrite > bornite> enargite. The galvanic interaction between enargite and pyrite was stronger than that between other copper minerals and pyrite. Consequently, strong oxidation occurs on enargite, which produces a hydrophilic oxidation layer on the enargite surface and depressed its flotation in the HAS sample. The galvanic interaction also produced copper ions in the flotation pulp, which activated the pyrite and affected its recovery.

Four different non-sulphide gangue minerals presented in the HAS and the LAS ore samples including quartz, muscovite, pyrophyllite, and kaolinite. Based on their floatability they were classified into two groups; FG (floatable gangue, i.e. pyrophyllite) and NFG (non-floatable gangue, i.e. quartz, muscovite, and kaolinite). The water recovery increased as the Eh was increased. However, the recovery of NFG was lower than the water recovery at all Eh ranges, indicating that these particles were mainly recovered by entrainment. FG recovery was higher than water recovery in all test conditions as pyrophyllite is a naturally floatable gangue mineral.

The NFG recovery showed a similar trend at different Eh ranges in both samples. The lowest recovery of NFG was observed at Eh -200 mV SHE. Its recovery increased as the Eh was increased toward more oxidation conditions and finally reached the maximum values at Eh +400 mV SHE. Size-by-size recovery of NFG showed a common trend for recovery by entrainment, with an increase in recovery at the fine fractions. However, the recovery of NFG at Eh +200 and +400 mV SHE showed a different trend due to activation by copper ions.

There was a general upward trend in FG recovery towards the higher pulp potential levels in both samples. The recovery of FG was similar at Eh -200 and 0 mV SHE in both samples, however, it sharply increased at Eh +200 mV SHE in the HAS sample. The size-by-size recovery of FG at various Eh conditions was significantly different from that of the NFG and shows good floatability in the middle size fractions. Moreover, the HAS sample had more FG recovered to the concentrate than the LAS sample.

Analyses of the results indicated that there was not sufficient evidence to allow for statistically valid conclusions to be drawn on the effect of gangue minerals. Further work is required in terms of surface study by SEM, XPS, etc.
10.1.5. To evaluate the equilibrium water chemistry of the flotation tests and to predict the potential environmental hazards

Water chemistry tests were performed on the liquor from the conditioning stage of the flotation tests as a function of Eh for both the HAS and LAS samples.

It was observed that arsenic levels in the tested water from the HAS samples was higher than the standard limit recommended for drinking water. Arsenic species in the water samples calculated by PHREEQC showed that the predominant oxidation states of As were $\text{HAsO}_4^{2-}$ and $\text{AsO}_4^{3-}$ in both samples. The amount of these species were much higher in the HAS sample in all the Eh ranges.

The process water chemistry was alkaline, and under the alkaline conditions the chance of mobility of heavy metals is low. The Cd, Cr, Pb, Zn, Hg concentrations were below detection limits. The very low levels of Ca and Mg showed low hardness of the process water.

The process water contained copper concentrations above the acceptable range (1-2.5 µg/L) of ANZECC (2000) water quality guidelines and copper was dominated by its hydroxide form ($\text{Cu(OH)}_2$) which can be toxic to biota.

10.1.6. To propose a conceptual flowsheet to improve the separation of enargite from other copper sulphide minerals

The proposed conceptual flowsheet for separating enargite from other copper sulphide minerals was comprised of:

- A de-sliming stage and a fine treatment stage prior to the rougher flotation stage to remove the NSG minerals and enargite fines.
- A regrinding stage to liberate the valuable grains, which are locked with other non-sulphide gangue minerals.
- A flotation separation stage at reducing pulp potential (-200 mV SHE) to separate enargite and NECu and produce two concentrates: High-As Low-Cu, and Low-As High Cu.
- Adjustment of the flotation pulp chemistry via changing the collector type to mitigate the galvanic interactions between minerals and increase the floatability of enargite in the HAS sample.
10.2. Conclusions and implications

From all the data presented in this thesis the following conclusions and original contributions to knowledge can be drawn:

- In this study it was found that enargite tended to be ground more readily than the other copper sulphide minerals present in the HAS and the LAS samples tested, and it mostly reported to the fine size fractions.

- While the majority of the published papers address the removal of arsenic-bearing minerals from single mineral systems, this research studied a real orebody that contained the arsenic-copper mineral (enargite).

- Regardless of the reasons for the differences observed, the research showed that it is possible to make a separation between enargite and the other copper minerals in the real ore system using pulp potential control.

- This study provided a better understanding of the mechanism of the floatability of enargite in size-by-size and size-by-liberation basis under different Eh conditions.

- It was indicated that enargite had the lowest rest potential compared to the other main sulphide minerals present in the HAS and the LAS ore samples. The rest potential of the main sulphide minerals present in the HAS and the LAS ore samples followed the order:

  pyrite > chalcopyrite > bornite > enargite

- It was found that the oxidation of enargite in the HAS sample, due to a strong galvanic interaction with pyrite, caused its poor floatability and consequently poor selectivity from the other copper minerals present in the HAS sample.

- The galvanic interaction also produced copper ions in the flotation pulp, which activated the pyrite surface and affected its recovery.

- A novel processing strategy which considered the mineralogical characteristics of the ore and used controlled potential of the pulp, was proposed by a conceptual flowsheet to produce two concentrates: a high As-low Cu concentrate and a low As-high Cu concentrate.
10.3. Recommendations for future work

Based on the test work completed and the results obtained in this project a number of areas for further evaluation have been identified and the following is a brief outline of suggested areas for further study:

- There is a constant relationship between the potentials of the platinum electrode and the mineral electrode. However, when the mineral oxidises, it becomes less conducting and the relationship between the mineral electrodes and the platinum electrode changes. Therefore, it is recommended that flotation tests be performed at different Eh conditions using enargite and chalcopyrite mineral electrodes. Under these conditions it should be possible to distinguish different oxidation stages between the two minerals.

- It is highly recommended that flotation tests being performed at reducing conditions (Eh -200 mV SHE) to discover the reasons for high recovery of enargite and NECu at this potential.

- It is also recommended that scale up flotation tests be performed to evaluate the results obtained.

- Results from flotation tests and surface chemistry studies by EDTA extraction in this project indicate that enargite oxidation in the HAS sample strongly influenced the floatability and the degree of separation of this mineral. Thus a further investigation into the effect of collector type in Cu/As separation and the nature of the adsorption mechanism is necessary. Studying alternative collectors with a high selectivity and resistance to oxidation is highly recommended to facilitate an efficient separation of enargite from other copper sulphides.

- It is recommended that surface chemistry of the minerals in a real ore system be studied using surface chemical analytical techniques such as XPS (X-ray Photoelectron Spectroscopy) or Tof-SIM (Time of Flight Secondary Ion Mass Spectroscopy). By using these techniques the adsorption of the collector, alteration type, degree of oxidation, and oxidation species on the enargite surface in the presence of other minerals can be investigated.

- Another fruitful area of research is de-sliming before the flotation by using hydraulic classification or wash water to remove the ultrafine gangue (especially phyllosilicates) minerals and to determine the subsequent separation efficiency.
• The effect of fine grinding of the rougher concentrate on the selectivity of enargite against other copper minerals should be investigated. Fine grinding can be done before the cleaning stage of and after one stage cycloning for removing ultra-fine gangue minerals.

• If this separation technology be considered for full scale operation, it would be essential to confirm that the separations that have been made, are not influenced by the grinding media. Therefore, some additional tests using the stainless steel, mild steel, and ceramic grinding media could be carried out to evaluate the effect, if any, for grinding mill and media type.

• Another area of the future work is using the Magotteaux Mill® for changing the pulp potential at the grinding stage rather than in the flotation cell. It monitors and measures the pulp chemical conditions during grinding and aids understanding the impact on flotation performance.

• It is highly recommended that Particle Kinetic Model be modified to account for the surface oxidation or surface slime coatings.


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Appendix A: Sample preparation

Figure A-1, Sample preparation photos, from crushing to splitting
Appendix B: Sieving and cyclosizing procedure

Approximately 200gr of each HAS or LAS sample was split from the original sample for sizing using a bench top riffler, weighed and then wet sieved at 38µm sieve. The sieve products were dried in the oven and weighed. For preventing caking or re-agglomeration of the particles due to excess heat, all drying during the sizing was carried out at 65°C in the oven. After drying, the +38µm was sieved. The nest of sieves was shaken for 15 minutes on a RoTap sieve shaker machine. The individual sieves were brushed clean, and their content weighed and split to four fractions for a further experiment on chemical assays and mineral liberation analysis. The -38µm dry material was weighed and mixed with that obtained from wet sieving. The combined -38µm was wetted with 100 ml water to form a slurry, and two drops of cataflot P40, a polyacrylic acid, as a dispersant were added. The slurry was then ultra-sonicated for 15 minutes to break up any agglomerates.

The combined -38µm material was cyclosized using the standard procedure. At the end of the operation, the recovered cyclosized fractions were CS1, CS2, CS3, CS4, and CS5 which were collected in separate beakers. In addition, the cyclosizer discharge was fed directly to a 3-litre solid bowl centrifuge rotating at 3000 rpm. The cyclosizer bowl was carefully washed into a bucket, which is sample CS6. The overflow of the centrifuge was collected into other buckets, settled overnight with H₂SO₄ as a flocculent, and the solids were collected after each bucket has been carefully decanted. The combined products were dried and named as –CS6 or CS7. The cyclosizer cut sizes for the samples have been determined using the measured solids S.G. of the samples, cycle time, water temperature, and a rotameter reading, as per standard operating procedure.

Figure B-1, Schematic representation of a cyclosizer, modified from (Warman, 1997)
# Appendix C: Size-by-size weight distribution and chemical analysis

Table C-1, Size-by-size weight distribution and chemical analysis of the HAS sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>HAS 10 min grinding</th>
<th>Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>Weight Retained</td>
<td>Cumulative Wt. Passing</td>
</tr>
<tr>
<td></td>
<td>(gr)</td>
<td>(%)</td>
</tr>
<tr>
<td>mesh</td>
<td>micron</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>150</td>
<td>7.21</td>
</tr>
<tr>
<td>150</td>
<td>106</td>
<td>16.90</td>
</tr>
<tr>
<td>200</td>
<td>75</td>
<td>26.50</td>
</tr>
<tr>
<td>300</td>
<td>53</td>
<td>28.50</td>
</tr>
<tr>
<td>400</td>
<td>38</td>
<td>21.40</td>
</tr>
<tr>
<td>CS1</td>
<td>42</td>
<td>1.49</td>
</tr>
<tr>
<td>CS2</td>
<td>32</td>
<td>9.94</td>
</tr>
<tr>
<td>CS3</td>
<td>23</td>
<td>14.35</td>
</tr>
<tr>
<td>CS4</td>
<td>15</td>
<td>15.66</td>
</tr>
<tr>
<td>CS5</td>
<td>11</td>
<td>7.75</td>
</tr>
<tr>
<td>CS6</td>
<td>6</td>
<td>21.00</td>
</tr>
<tr>
<td>CS7</td>
<td>-6</td>
<td>13.00</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. P80 (µm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table C-2, Size-by-size weight distribution and chemical analysis of the LAS sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>LAS 13.5 min grinding</th>
<th>Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>Weight Retained</td>
<td>Cumulative Wt. Passing</td>
</tr>
<tr>
<td></td>
<td>(gr)</td>
<td>(%)</td>
</tr>
<tr>
<td>mesh</td>
<td>micron</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>150</td>
<td>5.90</td>
</tr>
<tr>
<td>150</td>
<td>106</td>
<td>16.51</td>
</tr>
<tr>
<td>200</td>
<td>75</td>
<td>27.63</td>
</tr>
<tr>
<td>300</td>
<td>53</td>
<td>29.00</td>
</tr>
<tr>
<td>400</td>
<td>38</td>
<td>23.05</td>
</tr>
<tr>
<td>CS1</td>
<td>42</td>
<td>1.43</td>
</tr>
<tr>
<td>CS2</td>
<td>32</td>
<td>8.79</td>
</tr>
<tr>
<td>CS3</td>
<td>23</td>
<td>14.61</td>
</tr>
<tr>
<td>CS4</td>
<td>15</td>
<td>12.98</td>
</tr>
<tr>
<td>CS5</td>
<td>11</td>
<td>5.61</td>
</tr>
<tr>
<td>CS6</td>
<td>6</td>
<td>20.52</td>
</tr>
<tr>
<td>CS7</td>
<td>-6</td>
<td>20.15</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. P80 (µm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix D: Mineralogy characterisation of the HAS and the LAS ore samples

Appendix D is an excel file.
Appendix E: Proof of concept experiments I

This section related to the preliminary experiment for a research project which was performed on a confidential ore I. These flotation experiments were the basis of this thesis. The aims of the flotation experiments were determining the effect of As deportment (High and Low), grinding size (P80 of 75 and 150µm) and pH (natural and alkaline) on the rougher flotation recovery.

Selected drill core samples from the high arsenic (HA) and low arsenic (LA) sections of the deposit were used for flotation tests. The samples were stage crushed to -4 mm, blended and riffled into individual charges of 2000 grams. The mineralogy data showed that the copper-bearing minerals were mainly bornite and chalcopyrite. Enargite was the main arsenic copper mineral. The non-sulphide gangue minerals were pyrite, silicates, and clays. The gangue mineralogy in porphyry ore was dominated by quartz followed by muscovite, feldspar, pyrophyllite, and diaspore. The samples used in this test work were:

<table>
<thead>
<tr>
<th>Test</th>
<th>As Level</th>
<th>P80 Grinding Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>HA150</td>
<td>High Arsenic P80=150 µm</td>
</tr>
<tr>
<td>Test 2</td>
<td>HA75</td>
<td>High Arsenic P80=75 µm</td>
</tr>
<tr>
<td>Test 3</td>
<td>LA75</td>
<td>Low Arsenic P80=75 µm</td>
</tr>
</tbody>
</table>

Samples for flotation were ground in the laboratory mild steel mill, 200 mm × 250 mm in size, using a charge of 15 rods, 22mm × 235mm mild steel rods with a weight of 11,161 grams. Samples were ground at a pulp density of 60% solids using Brisbane tap water. Three individual samples were ground for 20, 30 and 37 minutes and sized. Using this data the times required to give various grind sizes was calculated.

<table>
<thead>
<tr>
<th>Table E-1, Flotation parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage</td>
</tr>
<tr>
<td>Primary Grind</td>
</tr>
<tr>
<td>Conditioning</td>
</tr>
<tr>
<td>Cu Rougher Flotation 1</td>
</tr>
<tr>
<td>Cu Rougher Flotation 2</td>
</tr>
<tr>
<td>Conditioning</td>
</tr>
<tr>
<td>Cu Rougher Flotation 3</td>
</tr>
</tbody>
</table>
The flotation tests were conducted on the samples using a 5 l JKMRC Batch flotation cell, which gave a pulp density of 32 wt.% solids. Tap water was used for all tests; pH was adjusted to 10 using 1.2 gr lime before grinding. 300 grams per tonne of PAX as a collector and 20 g/tonne of the frother MIBC were used in the flotation tests with a rotation rate of 1000 rpm. The pH was adjusted to 11 using lime before reagent addition. The total froth collecting time (600 s) was divided into periods of 60, 180, and 360. The froth was removed by scraping the whole surface of the cell, at a fixed depth, every 10 seconds. The flotation tests were performed at air set potential.

The summary results of the flotation tests are presented below.

Table E-2, Flotation tests results

<table>
<thead>
<tr>
<th>Test Summary</th>
<th>HA150</th>
<th>HA75</th>
<th>LA75</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>As</td>
<td>Total S</td>
</tr>
<tr>
<td>Final Concentrate Grade (%)</td>
<td>6.61</td>
<td>0.30</td>
<td>15.72</td>
</tr>
<tr>
<td>Final Concentrate Recovery (%)</td>
<td>96.12</td>
<td>97.26</td>
<td>96.74</td>
</tr>
<tr>
<td>Final Tail Recovery (%)</td>
<td>3.88</td>
<td>2.74</td>
<td>3.26</td>
</tr>
<tr>
<td>Final Tail Grade (%)</td>
<td>0.04</td>
<td>0.00</td>
<td>0.07</td>
</tr>
</tbody>
</table>

It can be seen that the recovery of arsenic to the concentrate is around 98% and 88% for the HA and LA samples, respectively. And the grade of arsenic in the tails was less than 1% in all these tests. In addition high recovery of Cu was achieved in all experiments. The higher recovery and grade was achieved from the HA sample compared to the LA sample.

Comparing the HA150 and HA75 shows that increasing the grinding time of the HA sample to P80 75 µm, slightly increased the recovery and grade of arsenic and copper in the concentrate.
Appendix F: Proof of concept experiments II

The purpose of this proof of concept tests was to confirm the result obtained by CSIRO on a confidential ore sample. About 5 kg crushed ore (-1.7 mm) was received, and were split to 500 gr samples. The mineralogy data confirmed that the copper-bearing minerals were mainly bornite and chalcopyrite and tennantite was the main arsenic copper mineral.

For measuring the grinding time, sub-samples 500 gr were ground in a cast iron ball mill at a solid-liquid ratio of 2:1 i.e. 67% solids by weight for 12 and 20 minutes using 55 stainless steel 316 balls i.e. 30×1” and 25×1 1/8”, the total weight 4.435kg. The mill was cleaned by grinding a sample of quartz for 10 minutes prior to the each test series.

Ground products were then filtered, oven dried, rolled and carefully blended. Ground products were then wet and dry screened down to 38 µm for selecting the grind time. The wet and dry sizing results for the grind tests are provided in the table below. A grind time of 8’15” was selected for the primary grinding to achieve 80% passing 150 µm.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>1.29</td>
<td>126.01</td>
<td>98.99</td>
<td>0.00</td>
<td>130.40</td>
<td>100.00</td>
</tr>
<tr>
<td>100</td>
<td>5.59</td>
<td>120.42</td>
<td>94.60</td>
<td>0.30</td>
<td>130.10</td>
<td>99.77</td>
</tr>
<tr>
<td>150</td>
<td>16.47</td>
<td>103.95</td>
<td>81.66</td>
<td>3.29</td>
<td>126.81</td>
<td>97.25</td>
</tr>
<tr>
<td>200</td>
<td>20.28</td>
<td>83.67</td>
<td>65.73</td>
<td>11.68</td>
<td>115.13</td>
<td>88.29</td>
</tr>
<tr>
<td>300</td>
<td>16.41</td>
<td>67.26</td>
<td>52.84</td>
<td>19.36</td>
<td>95.77</td>
<td>73.44</td>
</tr>
<tr>
<td>400</td>
<td>12.17</td>
<td>55.09</td>
<td>43.28</td>
<td>17.27</td>
<td>78.50</td>
<td>60.20</td>
</tr>
<tr>
<td>-38</td>
<td>55.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>127.30</td>
<td></td>
<td></td>
<td></td>
<td>130.40</td>
<td></td>
</tr>
</tbody>
</table>

The ground pulp was floated in modified Denver style cells in which the impellers are driven from below to allow the whole surface of the froth to be scraped with a paddle at a constant depth and at constant time intervals. The pH and pulp potential (Eh) were either continuously monitored or manually recorded during testing. Pulp pH was measured with a Radiometer PHM82 laboratory pH meter and pHC2401 combined pH electrode (saturated KCl solution). The pH measurement system was calibrated using commercial pH 7 and pH 10 buffer solutions. Pulp potential (Eh) was measured using a Radiometer PHM82 standard pH/mV meter and a platinum flag /Ag-AgCl reference electrode.
pair. Measured potentials were converted to the standard hydrogen electrode (SHE) scale by the addition of 0.2 V.

Fresh samples of collectors were made up daily, usually as 0.25% solutions in distilled water. The frother used was also prepared as a 0.25% solution using distilled water as required. Makeup water used in the flotation testing was Brisbane tap water. The flotation gases used were either air or nitrogen from a bulk supply. For reducing the pulp potential sodium dithionite (Na₂S₂O₄) was used. For increasing the pulp potential the oxidants used was sodium hypochlorite (NaOCl). Other reagents used such as lime was added as required.

A list of the flotation tests identification numbers (ID) and a brief description of each test on this ore sample is shown in the table below.

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTK001</td>
<td>Preliminary Rougher Float, pH 10, Air-set Potential</td>
</tr>
<tr>
<td>MTK002</td>
<td>Preliminary Rougher Float, pH 10, Oxidising Potentials</td>
</tr>
<tr>
<td>MTK003</td>
<td>Rougher, Regrind, Cleaner, Separation at Air-set Potential</td>
</tr>
<tr>
<td>MTK004</td>
<td>Rougher, Regrind, Cleaner, Separation at Oxidising Potentials (+430 mV SHE)</td>
</tr>
<tr>
<td>MTK005</td>
<td>Rougher, Regrind, Cleaner, Separation at Reducing Potentials (-50 mV SHE)</td>
</tr>
<tr>
<td>MTK006</td>
<td>Rougher, Regrind, Cleaner, Separation at Reducing Potentials (0 mV SHE)</td>
</tr>
</tbody>
</table>

The results were in close agreement with the findings of CSIRO, which proved that for this ore, the separation could happen at 0 mV SHE.
Appendix G: Preliminary flotation tests on the HAS and the LAS ore samples

The details of the flotation tests without collector are presented in the following tables.

Table G-1, Flotation tests without collector for the HAS sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time min</th>
<th>Product</th>
<th>Wt %</th>
<th>Cu %</th>
<th>Fe %</th>
<th>S %</th>
<th>As %</th>
<th>NECu ppm</th>
<th>Cu %</th>
<th>Fe %</th>
<th>S %</th>
<th>As %</th>
<th>NECu %</th>
<th>NSG %</th>
<th>Water %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC1</td>
<td>0.50</td>
<td>1.04</td>
<td>3.31</td>
<td>3.85</td>
<td>4.95</td>
<td>871</td>
<td>3.09</td>
<td>5.08</td>
<td>1.42</td>
<td>1.80</td>
<td>3.60</td>
<td>5.23</td>
<td>0.98</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td>RC2</td>
<td>1.00</td>
<td>0.41</td>
<td>2.77</td>
<td>3.40</td>
<td>4.17</td>
<td>758</td>
<td>2.58</td>
<td>6.75</td>
<td>1.92</td>
<td>2.39</td>
<td>4.84</td>
<td>6.95</td>
<td>1.37</td>
<td>3.74</td>
<td></td>
</tr>
<tr>
<td>RC3</td>
<td>2.00</td>
<td>0.72</td>
<td>2.37</td>
<td>3.07</td>
<td>3.66</td>
<td>696</td>
<td>2.19</td>
<td>9.27</td>
<td>2.70</td>
<td>3.31</td>
<td>6.83</td>
<td>9.52</td>
<td>2.07</td>
<td>5.89</td>
<td></td>
</tr>
<tr>
<td>RC4</td>
<td>4.00</td>
<td>1.12</td>
<td>2.33</td>
<td>2.89</td>
<td>3.59</td>
<td>742</td>
<td>2.14</td>
<td>13.12</td>
<td>3.85</td>
<td>4.71</td>
<td>10.13</td>
<td>13.43</td>
<td>3.16</td>
<td>8.72</td>
<td></td>
</tr>
<tr>
<td>RC5</td>
<td>10.00</td>
<td>2.36</td>
<td>2.23</td>
<td>2.96</td>
<td>3.65</td>
<td>726</td>
<td>2.05</td>
<td>20.88</td>
<td>6.33</td>
<td>7.72</td>
<td>16.94</td>
<td>21.29</td>
<td>5.46</td>
<td>14.18</td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td></td>
<td>94.34</td>
<td>0.57</td>
<td>2.80</td>
<td>2.81</td>
<td>222</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Conc</td>
<td>5.66</td>
<td>2.51</td>
<td>3.16</td>
<td>3.92</td>
<td>754.36</td>
<td>2.314</td>
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<tr>
<td>Total Feed</td>
<td>100.00</td>
<td>0.679</td>
<td>2.82</td>
<td>2.87</td>
<td>252.07</td>
<td>0.615</td>
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</tr>
</tbody>
</table>

Table G-2, Flotation tests without collector for the LAS sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time min</th>
<th>Product</th>
<th>Wt %</th>
<th>Cu %</th>
<th>Fe %</th>
<th>S %</th>
<th>As %</th>
<th>NECu ppm</th>
<th>Cu %</th>
<th>Fe %</th>
<th>S %</th>
<th>As %</th>
<th>NECu %</th>
<th>NSG %</th>
<th>Water %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC1</td>
<td>0.50</td>
<td>0.64</td>
<td>3.81</td>
<td>4.30</td>
<td>5.42</td>
<td>716</td>
<td>3.63</td>
<td>4.02</td>
<td>1.64</td>
<td>1.82</td>
<td>3.99</td>
<td>4.02</td>
<td>0.58</td>
<td>2.54</td>
<td></td>
</tr>
<tr>
<td>RC2</td>
<td>1.00</td>
<td>0.47</td>
<td>3.51</td>
<td>3.95</td>
<td>5.09</td>
<td>709</td>
<td>3.33</td>
<td>6.74</td>
<td>2.75</td>
<td>3.07</td>
<td>6.88</td>
<td>6.73</td>
<td>1.01</td>
<td>4.28</td>
<td></td>
</tr>
<tr>
<td>RC3</td>
<td>2.00</td>
<td>0.96</td>
<td>2.52</td>
<td>2.74</td>
<td>3.39</td>
<td>505</td>
<td>2.39</td>
<td>10.72</td>
<td>4.32</td>
<td>4.77</td>
<td>11.10</td>
<td>10.71</td>
<td>1.93</td>
<td>6.68</td>
<td></td>
</tr>
<tr>
<td>RC4</td>
<td>4.00</td>
<td>1.37</td>
<td>2.08</td>
<td>2.27</td>
<td>2.75</td>
<td>492</td>
<td>1.95</td>
<td>15.39</td>
<td>6.16</td>
<td>6.73</td>
<td>16.92</td>
<td>15.31</td>
<td>3.26</td>
<td>9.84</td>
<td></td>
</tr>
<tr>
<td>RC5</td>
<td>10.00</td>
<td>2.19</td>
<td>1.85</td>
<td>1.56</td>
<td>1.80</td>
<td>442</td>
<td>1.74</td>
<td>22.03</td>
<td>8.19</td>
<td>8.79</td>
<td>25.30</td>
<td>21.87</td>
<td>5.42</td>
<td>16.04</td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td></td>
<td>94.36</td>
<td>0.50</td>
<td>1.64</td>
<td>1.85</td>
<td>91</td>
<td>0.48</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Conc</td>
<td>5.64</td>
<td>2.38</td>
<td>2.45</td>
<td>2.99</td>
<td>518.53</td>
<td>2.251</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Total Feed</td>
<td>100.00</td>
<td>0.610</td>
<td>1.69</td>
<td>1.92</td>
<td>115.54</td>
<td>0.580</td>
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<td></td>
</tr>
</tbody>
</table>
Appendix H: Rougher flotation tests on the HAS and the LAS ore samples

Appendix H is an excel file.
Appendix I: Rougher flotation tests on the HAS and the LAS ore samples for 16 min

The details of the flotation tests with the collector for 16 min are presented in the following tables.

### Table I-1, Flotation tests for 16 min for the HAS sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Assay</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Product</td>
<td>Wt Cu Fe S As NECu Cu Fe S As NECu NSG Water</td>
</tr>
<tr>
<td>min</td>
<td>% % % % ppm % % % % % % %</td>
<td></td>
</tr>
<tr>
<td>HAS</td>
<td>16.00</td>
<td>RC 16.96 3.65 12.71 15.57 1011 3.39 91.08 76.45 91.91 68.05 93.48 12.32 25.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RT 83.04 0.07 0.80 0.28 97 0.05</td>
</tr>
<tr>
<td></td>
<td>Total Feed 100.00 0.679 2.82 2.87 252.07 0.615</td>
<td></td>
</tr>
</tbody>
</table>

### Table I-2, Flotation tests for 16 min for the LAS sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Assay</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Product</td>
<td>Wt Cu Fe S As NECu Cu Fe S As NECu NSG Water</td>
</tr>
<tr>
<td>min</td>
<td>% % % % ppm % % % % % % %</td>
<td></td>
</tr>
<tr>
<td>LAS</td>
<td>16.00</td>
<td>RC 17.67 3.04 8.29 10.11 631 2.88 88.11 86.41 92.34 93.77 87.81 14.49 30.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RT 82.33 0.09 0.28 0.18 9 0.09</td>
</tr>
<tr>
<td></td>
<td>Total Feed 100.00 0.609 1.70 1.93 118.84 0.579</td>
<td></td>
</tr>
</tbody>
</table>
Appendix J: The ANOVA test

The ANOVA test were performed to determine if the predicted values of enargite and NECu by Particle Kinetic Model are significantly different to one another.

Table J-1, ANOVA results for enargite

<table>
<thead>
<tr>
<th>Regression Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiple R</td>
</tr>
<tr>
<td>R Square</td>
</tr>
<tr>
<td>Adjusted R Square</td>
</tr>
<tr>
<td>Standard Error</td>
</tr>
<tr>
<td>Observations</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ANOVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>df</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>Regression 1</td>
</tr>
<tr>
<td>Residual 21</td>
</tr>
<tr>
<td>Total 22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>13.218</td>
<td>9.182</td>
<td>1.440</td>
<td>0.165</td>
<td>-5.876</td>
</tr>
<tr>
<td>Enargite Actual</td>
<td>1.003</td>
<td>0.161</td>
<td>6.234</td>
<td>0.000</td>
<td>0.668</td>
</tr>
</tbody>
</table>

Table K-2, ANOVA results for NECu

<table>
<thead>
<tr>
<th>Regression Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiple R</td>
</tr>
<tr>
<td>R Square</td>
</tr>
<tr>
<td>Adjusted R Square</td>
</tr>
<tr>
<td>Standard Error</td>
</tr>
<tr>
<td>Observations</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ANOVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>df</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>Regression 1</td>
</tr>
<tr>
<td>Residual 21</td>
</tr>
<tr>
<td>Total 22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>14.708</td>
<td>4.894</td>
<td>3.005</td>
<td>0.007</td>
<td>4.529</td>
</tr>
<tr>
<td>NECu Actual</td>
<td>0.819</td>
<td>0.071</td>
<td>11.483</td>
<td>0.000</td>
<td>0.671</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>t-test for gradient</th>
<th>P(t) =</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.019</td>
</tr>
</tbody>
</table>
Table K-3, Comparing the predicted results of enargite and NECu

<table>
<thead>
<tr>
<th></th>
<th>Enargite</th>
<th>NECu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean x</td>
<td>53.989</td>
<td>63.673</td>
</tr>
<tr>
<td>Mean y</td>
<td>67.060</td>
<td>66.873</td>
</tr>
<tr>
<td>R</td>
<td>0.825</td>
<td>0.933</td>
</tr>
<tr>
<td>R(R)</td>
<td>7.06E-07</td>
<td>2.93E-11</td>
</tr>
</tbody>
</table>

Trendline correlation coefficients

Significance of correlation coefficients

<table>
<thead>
<tr>
<th></th>
<th>11.334</th>
<th>14.807</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>1.032</td>
<td>0.818</td>
</tr>
</tbody>
</table>

Analysis of Variance - Enargite

<table>
<thead>
<tr>
<th>Source</th>
<th>D.F.</th>
<th>SS</th>
<th>MS</th>
<th>F (p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regre</td>
<td>1</td>
<td>6275.679</td>
<td>6275.679</td>
<td>46.883</td>
</tr>
<tr>
<td>Residual</td>
<td>22</td>
<td>2944.860</td>
<td>133.857</td>
<td>0.000</td>
</tr>
<tr>
<td>Total</td>
<td>23</td>
<td>9220.539</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Analysis of Variance - NECu

<table>
<thead>
<tr>
<th>Source</th>
<th>D.F.</th>
<th>SS</th>
<th>MS</th>
<th>F (p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regre</td>
<td>1</td>
<td>8159.389</td>
<td>8159.389</td>
<td>148.619</td>
</tr>
<tr>
<td>Residual</td>
<td>22</td>
<td>1207.830</td>
<td>54.901</td>
<td>0.000</td>
</tr>
<tr>
<td>Total</td>
<td>23</td>
<td>9367.219</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Test for residual MSs

F = 2.438 D.F. = 22 22
p(F) = 0.0210 Significance of difference in data scatter

Test for slopes

F = 1.936 D.F. = 1, 44
p(F) = 0.1711 Significance of difference in gradients

Test for intercepts

F = 9.044 D.F. = 1, 45
p(F) = 0.0043 Significance of difference in intercepts

Test for separation of lines (y axis)

Separation (d) = 8.782 V(d) = 8.354 d = separation of lines (y axis)

Significance of diff. in separations

t = 3.038 df = 44
p(t) = 0.002 (one-sided)

Confidence level for conf. intervals % : 95 conf. level

Conf. interval ± 5.825 (2-sided) CI on separation
Lower conf. limit 3.926 (1-sided) Lower conf.limit on separation