



THE UNIVERSITY OF QUEENSLAND
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**The Effect of Regrinding Chemistry and Particle Breakage Mechanisms on
Subsequent Cleaner Flotation**

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Abstract

Regrinding rougher flotation concentrates is typically used to liberate valuable minerals from gangue prior to the cleaner separation stage in processing of low grade ores. Compared to the rougher flotation after primary grinding, it is usually more challenging to achieve a satisfactory performance in post-regrind cleaner flotation especially when fine particles are generated. One main factor which results in this reduction in flotation is the unsuitable particle surfaces produced after regrinding. However, this factor is not usually considered when designing and optimizing the regrinding process.

Extensive studies have demonstrated that grinding chemistry can influence mineral floatability. However, earlier studies focused on primary grinding and rougher flotation rather than regrinding and cleaner flotation. In addition, different types of regrind mills are used in industry, and these provide different particle breakage mechanisms which may also influence mineral floatability. Therefore, the overall objective of this thesis study is to investigate the effects of regrinding chemistry and particle breakage mechanisms on the cleaner flotation. The implementation of regrinding in the copper and pyrite flotation circuits at Telfer gold mine was taken as a case study and four research areas were addressed with the objective of developing fundamental understanding to provide practical guidance for the plant operation. The four areas investigated are:

1. Effect of regrinding chemistry on copper activation of pyrite and its flotation;
2. Separation of different copper sulphide minerals from pyrite after regrinding;
3. Importance of pulp chemistry during regrinding rougher concentrates;
4. Effect of particle breakage mechanisms on subsequent flotation.

In this study, it was found that copper activation of pyrite and its flotation in the cleaner stage were affected by regrinding. In general, a decrease in surface concentration of collectors due to the increased surface area after regrinding contributed to the low pyrite recovery in the cleaner. Surface analysis revealed that both the surfaces that were carried from the rougher flotation concentrate and those which were freshly created were modified by the strong electrochemical reactions occurring inside the regrind mill. Stainless steel media promoted pyrite oxidation, especially on the copper activated surfaces. Mild steel media produced a greater amount of iron oxidation species which could adsorb on the carried surfaces. It was also found that mild steel media generated a reducing condition which favoured the copper activation on the freshly created surfaces.

The research has also shown that the separability of chalcopyrite and chalcocite from pyrite was significantly different after regrinding, which was related to their electrochemical properties. Chalcocite was more active and therefore presented a stronger galvanic interaction with pyrite. Consequently chalcocite was more oxidised, which not only depressed its flotation but also produced sufficient copper ions to activate pyrite, making the separation of chalcocite from pyrite more difficult. In comparison, chalcopyrite was less active. Its oxidation generated hydrophobic surfaces which improved chalcopyrite floatability. At the same time pyrite flotation was depressed due to the insufficient copper ions for activation, leading to an effective separation of chalcopyrite from pyrite. However, these flotation differences were not significant at the rougher stage and this was thought to be due to weak galvanic interactions at the coarser particle sizes present in this stage of the process.

A pulp chemistry survey at Telfer indicated extremely low dissolved oxygen concentration and Eh after regrinding of pyrite concentrate resulting in poor subsequent copper and gold flotation. To develop a remedial strategy, the plant flotation conditions and performance were replicated in the laboratory and several methods were examined to increase the oxidising condition. It was found that oxidising conditions were beneficial to copper-gold flotation and pyrite depression. The surface analysis showed that the improved flotation was attributed to a combined effect of several factors, including pyrite surface oxidation which reduced its floatability, increased collector adsorption on copper-gold surfaces, and also the oxidation of chalcopyrite producing hydrophobic species.

Apart from the regrinding chemistry, another important factor considered in this study was the type of grinding mills which provide different particle breakage mechanisms. A significantly lower recovery was observed after regrinding in a stirred mill than in a rod mill. After examining all possible factors influencing the flotation, it was found that the predominating factor was the different distribution of collectors remaining from rougher flotation concentrates. In the tumbling mill, impact breakage dominated, causing the collector to remain on the surface of newly produced particles. In the stirred mill, attrition breakage removed collector from the surface, and decreased particle floatability. This was further confirmed by the analysis of collector intensity on mineral surfaces on a size-by-size basis by ToF-SIMS.

Overall, the results of this thesis study clearly show that both regrinding chemistry and particle breakage mechanisms play critical roles in changing pulp chemistry and the formation and

distribution of surface species and hence affect mineral flotation and separation in the subsequent cleaner flotation.

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 data analysis, survey design, 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

Peer-reviewed journal publications relevant to the thesis:

Chen, X., Peng, Y. and Bradshaw, D., 2013. Effect of regrinding conditions on pyrite flotation in the presence of copper ions. *International Journal of Mineral Processing* 125: 129-136.

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Contributor	Statement of contribution
Xumeng Chen (Candidate)	Conception and design (60%) Analysis and interpretation of data (70%) Wrote the paper (70%)
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Prof. Dee Bradshaw	Conception and design (10%) Analysis and interpretation of data (10%)

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Contributions by others to the thesis

Assoc. Prof. Yongjun Peng and Prof. Dee Bradshaw were responsible for setting up this thesis project, organising funding and establishing the initial project goals. They provided the initial idea of investigating the effect of regrinding chemistry and particle breakage mechanisms on subsequent cleaner flotation. They also made great contributions to the interpretation of experimental data.

Assoc. Prof. Yongjun Peng and Dr. Cathy Evans assisted in preparing the thesis and critically reviewed the draft of the thesis.

Dr. David Seaman, Mr. Fraser Burns and other plant metallurgists from Newcrest Mining Limited organized the chemistry survey in the pyrite flotation circuit at Telfer Gold Mine and provided assistance in collection of pyrite rougher concentrate samples used in Chapter 6.

Mr. John Tang conducted some flotation tests presented in Chapter 6 during his summer vacation work from December 2012 to February 2013.

Dr. Barry Wood performed the XPS analysis and provided assistance and training in peak fitting of the XPS spectra.

Dr. John Denman performed the ToF-SIMS analysis and processed the raw data and also drafted the analysis procedure used in Chapter 3.

Statement of parts of the thesis submitted to qualify for the award of another degree

None.

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Keywords

Regrinding chemistry, particle breakage mechanisms, cleaner flotation, pyrite, copper sulphide minerals

Australian and New Zealand Standard Research Classifications (ANZSRC)

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Fields of Research (FoR) Classification

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Statement of originality

I declare that the content of this research is composed of my original work, and contains no material previously published or written by another person, except when due reference is made in the text. The content in this thesis has not been submitted for the award of any other degree or diploma. The contributions to knowledge are outlined below:

1. Demonstration of the more significant influence to mineral floatability by chemical conditions during regrinding than during primary grinding due to the finer particle size and larger surface area.
2. Identification of the formation and distribution of various species on mineral surfaces during regrinding under different conditions and their influences on mineral floatability.
3. Identification of the mechanisms for the different separability of chalcopyrite and chalcocite from pyrite in the cleaner flotation after regrinding observed in the processing plant.
4. Development and evaluation of oxidization methods applied during regrinding pyrite rougher concentrates from Telfer plant to optimize the pulp chemistry to improve the subsequent copper/gold separation from pyrite.
5. Demonstration of an entirely different cleaner flotation behaviour after regrinding in a tumbling mill and a stirred mill due to the different particle breakage mechanisms which influence the particle properties and distribution of surface species.

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List of Abbreviations

EDTA	- Ethylenediaminetetraacetic Acid
DO	- Dissolved Oxygen
MLA	- Mineral Liberation Analyzer
PAX	- Potassium Amyl Xanthate
ToF-SIMS	- Time of Flight Secondary Ion Mass Spectrometry
XPS	- X-ray Photoelectron Spectroscopy
XRD	- X-ray Diffraction

Chapter 1 Introduction

1.1 Problem statement

Global demand for minerals and metals continues to rise. However, high grade ores that are most accessible and easily treated are being depleted worldwide. Therefore, more and more low grade and complex ores need to be processed (Giurco et al. 2010, Crowson 2012). Finer grinding is required for processing these low grade ores in order to achieve sufficient liberation of valuable minerals, which can significantly increase the energy consumption. In processing plants, instead of finely grinding the entire feed tonnage, a more energy efficient strategy is to coarsely grind the whole feed tonnage while rejecting the majority of liberated gangue minerals through flotation. In this approach, only the smaller tonnage of flotation concentrates which contain most of the valuable minerals is fed to the energy-intensive regrinding stage. For example, in Newcrest's Telfer gold mine, a significant amount of copper and gold minerals are associated with pyrite. In 2012 a regrinding section was commissioned to regrind pyrite flotation concentrates in order to increase overall copper and gold recovery (Burns et al. 2012). As shown in the circuit flowsheet in Figure 1.1, the pyrite concentrate is regrinded to liberate the locked copper and gold minerals which are recovered in the subsequent flotation, with the tailing passing to the carbon-in-leach (CIL) process.

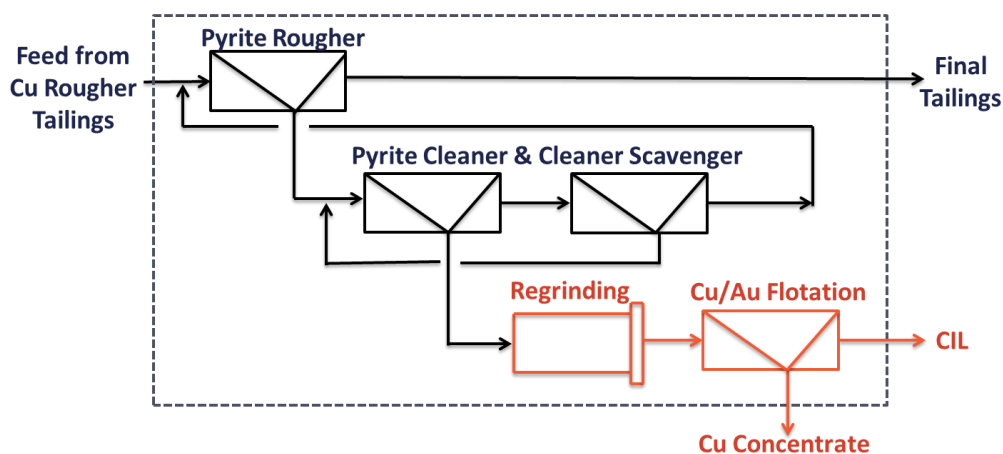


Figure 1.1 Pyrite flotation circuit including the new pyrite regrinding-flotation process prior to CIL at Telfer gold mine (Adapted from Burns et al. (2012)).

Although the valuable minerals are further liberated after regrinding, the separation of valuable minerals from gangue minerals in the subsequent cleaner flotation is not always straightforward. One reason is that regrinding usually reduces particle size to fine and ultra-fine fractions. It has been well known that fine particles have lower floatability due to the lower particle-bubble collision efficiency (Sutherland 1948, Trahar 1981). In addition, separation in cleaner floatation can also be affected by the modified surface properties of fine particles and the pulp chemistry after regrinding due to strong electrochemical reactions occurring inside the grinding mill. Intensive research has been carried out over last few decades to understand the effect of grinding conditions on the subsequent flotation, such as the use of different types of grinding media and pulp chemistry (e.g. pH, Eh and dissolved oxygen) (Adam et al. 1984, Yuan et al. 1996a, Yuan et al. 1996b, Peng et al. 2003a, Peng et al. 2003b, Greet et al. 2004, Bradshaw et al. 2006, Grano 2009, Kinal et al. 2009, Bruckard et al. 2011). However, most of the previous studies focused on primary grinding and rougher flotation, and the effect of various regrinding conditions on the subsequent cleaner flotation has not received much focus in the literature. This is particularly true in the aspect of fundamental understanding, such as the change of particle surface properties and the complex electrochemical reactions taking place during regrinding.

Grinding is the single largest energy consuming process in mineral processing plants. The stirred mills, recently introduced to mineral processing, have been proved to be more energy efficient than tumbling mills in fine grinding applications, and have been extensively used in many plants in the regrinding stage (Pease et al. 2006a, Pease et al. 2006a). In contrast to tumbling mills where motion is imparted to the charge via the rotating mill shell, stirred mills impart the motion to the charge by the movement of an internal stirrer, providing different particle breakage mechanisms. The different breakage mechanisms have been proved to influence the particle size distribution (Kelly and Spottiswood 1982), particle shape (Roufail and Klein 2010, Vizcarra et al. 2011) and liberation (Andreatidis 1995, Roufail and Klein 2010, Vizcarra 2010). These parameters may play a role in the subsequent flotation. Recent studies have also suggested that different grinding mills may affect the subsequent flotation through the change of surface properties (Ye et al. 2010a, Ye et al. 2010b). It is important to further investigate this aspect by well-defined experiments to isolate other factors which may have a similar effect on surface properties simultaneously during regrinding.

1.2 Scope of this thesis

A schematic diagram of the main topics addressed in the scope of this thesis, and equally importantly those which are outside its scope, is shown in Figure 1.2. The key factors which may influence regrinding and cleaner flotation performance are summarized in the diagram. Based on the problems stated in previous section, the main focus of this thesis is to study the effect of regrinding chemistry and particle breakage mechanisms on subsequent cleaner flotation. The factors considered in investigating regrinding chemistry will include the mineral composition of the regrind feed, the type of grinding media, and the pulp chemistry. Their effect on the mineral floatability will be studied by mainly considering the change of particle surface properties during regrinding, specifically, the surface oxidation, surface contamination, surface activation and the distribution of surface species on newly produced particles. Investigating the effect of particle breakage mechanisms on subsequent flotation is another focus of this thesis. Its influences on both the particle chemical properties and physical properties will be considered. Although mineral liberation is acknowledged to have a significant influence on the flotation performance, it is not part of this thesis and single minerals will be used when studying particle breakage mechanisms to rule out the potential influence of mineral liberation on flotation in the experimental programme. It is recognised that there are other operating factors that are important for the performance of regrinding and flotation, such as the operating conditions listed in Figure 1.2, however, they are not the focus of this thesis either and these conditions will be fixed in all of the experimental work.

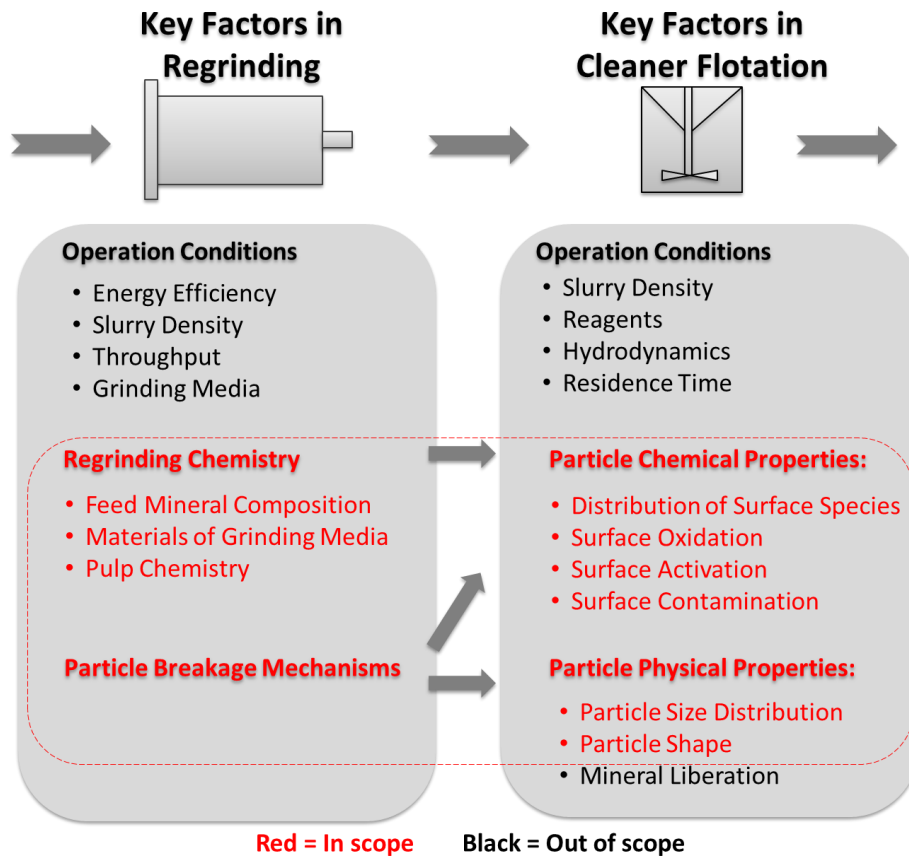


Figure 1.2 Schematic diagram of the main topics addressed in the scope of this thesis.

1.3 Research objectives and plan

This project is supported by Newcrest Mining Limited and the Australian Research Council with an objective of providing fundamental studies to guide the implementation and optimization of two regrinding circuits commissioned in Telfer plant in 2012. These new process sections regrind both copper concentrates and pyrite concentrates, followed by a cleaner flotation to separate copper/gold minerals from pyrite (Seaman et al. 2012). Although the valuable minerals can be well liberated after regrinding, efficient separation of valuable copper minerals from pyrite is still difficult, especially for the fine particles ($< 20 \mu\text{m}$). Several potential problems were identified, including the difficulty in depressing copper-activated pyrite after regrinding, the different flotation behaviours of primary and secondary copper minerals and their separation from pyrite in the cleaner flotation, and the undesirable pulp chemistry created after regrinding. These problems are all highly related to the changes of mineral surface properties and the electrochemical reactions taking place during regrinding. There has also been a debate whether the stirred mills implemented in the plant are

favourable for mineral flotation. As a result, this study will mainly focus on the following four aspects:

- 1) Investigating the effect of regrinding chemistry on pyrite flotation and pyrite activation by copper ions.
- 2) Investigating the separation of different copper sulphide minerals from pyrite in the cleaner flotation after regrinding and the relations with regrinding chemistry.
- 3) Optimizing the pulp chemistry during regrinding to improve the separation of copper/gold minerals from pyrite in the subsequent cleaner flotation.
- 4) Investigating the effect of particle breakage mechanisms during regrinding on subsequent cleaner flotation.

Although this study was designed to provide a guideline for Newcrest's Telfer Mine to optimise regrinding circuits, it has general implications in many copper-gold plants with ores that are similar to Telfer and any other plant with a regrinding circuit.

1.4 Thesis outline

This thesis is divided into eight chapters to systemically investigate the effect of regrinding chemistry and particle breakage mechanisms on subsequent cleaner flotation. Figure 1.3 shows the structure of this thesis and the summary of research outcomes obtained by addressing specific research problems.

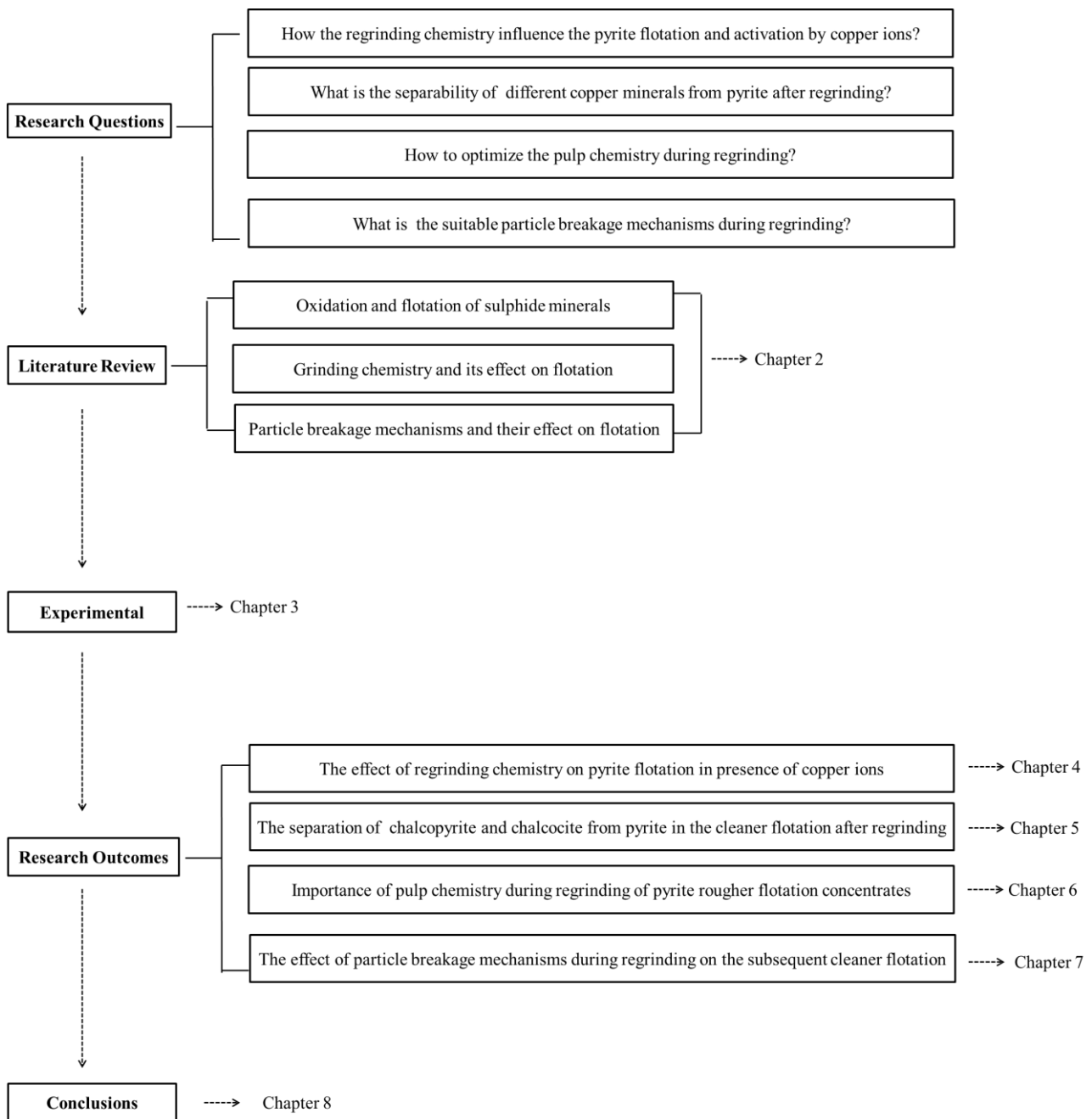


Figure 1.3 The overall structure of the thesis.

Chapter 2 is a critical literature review of the existing knowledge relevant to this thesis research. In line with the research objectives and research questions, this review is divided into three areas: (1) the oxidation of sulphide minerals; (2) grinding chemistry and its effect on subsequent flotation; (3) different particle breakage mechanisms during grinding and their potential effects on flotation. The literature review provides an overall picture of the current status of studies in this area and pinpoints the gaps in knowledge and hypotheses for future research which are presented at the end of this Chapter.

Chapter 3 presents the experimental details of this thesis study, including description of the minerals and reagents used, the grinding and flotation test procedures and the surface analysis techniques used in this study.

Chapter 4 describes an investigation into the effect of regrinding chemistry on pyrite cleaner flotation in the presence of copper ions. This research addressed a key issue in the plant, which is how to effectively depress copper activated pyrite after regrinding and how to prevent or reduce the undesirable copper activation during regrinding. The research outcome indicates that the regrinding chemistry manipulated by different grinding media has a significant influence on pyrite flotation and copper activation. In general, the decrease in overall surface concentration of adsorbed collectors due to the increased surface after regrinding contributed to the low pyrite flotation in the cleaner stage. Surface analysis revealed that both surfaces carried from previous rougher flotation and freshly created during regrinding were modified by the strong electrochemical reactions occurring inside the grinding mill, and regrinding chemistry played an important role in the formation of surface species. Stainless steel media promoted the pyrite surface oxidation, especially the copper activated surfaces, while mild steel media produced a greater amount of iron oxidation species which could be adsorbed on the carried surfaces further depressing the flotation. Moreover, the different media also affected the pyrite activation by copper ions during regrinding due to the generation of different pulp chemistry. Overall, this study demonstrated the critical role of regrinding chemistry in pyrite flotation and activation, and the fundamental understanding can assist the plant operation to optimize the regrinding chemistry to achieve a more efficient pyrite depression. The research described in this chapter was published in the *International Journal of Mineral Processing* in 2013 (Chen et al. 2013).

Chapter 5 details a study which investigates the separation of different copper sulphide minerals from pyrite in the cleaner flotation after regrinding. It addresses the important question of whether different copper sulphide minerals present different separability from pyrite after regrinding and, if this is the case, what is the role of regrinding chemistry? The results show that the separation of chalcopyrite and chalcocite from pyrite was significantly different after regrinding at the same condition. This behaviour was related to the electrochemical properties of copper minerals which not only influences the floatability of copper minerals but also governs pyrite oxidation and activation as a result of the galvanic interaction. Chalcocite was more electrochemically active than chalcopyrite and therefore, the galvanic interaction between chalcocite and pyrite was stronger than that between chalcopyrite and pyrite. Consequently more chalcocite was oxidised depressing

chalcocite flotation while providing a sufficient amount of copper ions to activate pyrite, resulting in a difficult separation of chalcocite from pyrite. In comparison, chalcopyrite was less active and its oxidation produced a hydrophobic sulphur rich surface and a smaller amount of copper ions to activate pyrite, leading to a high separability of chalcopyrite from pyrite. In addition, different regrinding chemistry provided by different grinding media can influence the separation of copper minerals from pyrite in the subsequent cleaner flotation. However, all these influences are not significant during primary grinding and rougher flotation at the coarser particle size. The mechanisms identified in this study have important implications for the processing plants treating different copper ores and can also provide guidelines for the plant optimization. The research described in this chapter includes work published in *Minerals Engineering* in 2014 (Chen et al. 2014b).

Chapter 6 examines the changes in pulp chemistry during regrinding and their effect on the subsequent cleaner flotation. It addresses an important question which is how to optimize the pulp chemistry during regrinding to improve the subsequent cleaner flotation. In this study, the pyrite regrinding-flotation process in Newcrest's Telfer gold mine was taken as a case study. Significantly low values of dissolved oxygen and Eh were observed in the regrinding product. This was due to the consumption of oxygen by the large amount of fresh reactive pyrite surfaces generated during regrinding, which prohibited the collector adsorption and promoted the pyrite activation by copper ions, resulting in a poor copper-gold separation from pyrite. After identifying the problems, optimization of the pulp chemistry was conducted. It was found that the application of proper oxidizing methods during regrinding was beneficial for both copper-gold flotation and pyrite depression, and the mechanisms underlying this were studied by surface analysis. The improved flotation was attributed to a combined effect of several factors, including pyrite depression caused by the surface oxidation, an increased collector adsorption rate on copper and gold surfaces due to the higher Eh and DO, and the surface oxidation of chalcopyrite producing hydrophobic species. The results have important implications for the plant operation when dealing with the high sulphide content feed, and the methods tested in this study may be also applicable in the plant to optimize the regrinding chemistry. The research described in this chapter includes work published in *Minerals Engineering* in 2014 (Chen et al. 2014c).

Chapter 7 describes the investigation of the effect of particle breakage mechanisms during regrinding on subsequent cleaner flotation. It addresses the important question of whether tumbling mills or stirred mills used to regrind rougher flotation concentrates provide suitable pulp and surface

chemistry for the subsequent cleaner flotation stages. In this study, different flotation behaviour was observed after regrinding in the tumbling mill and stirred mill. The factors contributing to the different recovery included particle size, the amount of created fresh surfaces, surface oxidation and the redistribution of collector carried from rougher flotation. After examining all these related factors, it was found that the predominating factor was the different distribution of collectors on mineral surface, which was associated with different particle breakage mechanisms in these two types of mills. In the tumbling mill, the impact breakage predominates, causing the collector to remain on the surface of newly produced particles. In the stirred mill, the attrition breakage removes collector from the surface, and decreases particle floatability. It was further proved by the analysis of collector intensity on mineral surfaces on a size-by-size basis by ToF-SIMS. This study demonstrated that the selection of regrind mills should not only consider their energy efficiency but also consider the potential influences of particle breakage mechanism on subsequent flotation. The research described in this chapter was published in *Minerals Engineering* in 2014 (Chen et al. 2014a).

Chapter 8 summarises the major findings from this thesis research based on the proposed hypotheses and provides recommendations for the implications in plant practice and future studies.

Chapter 2 Literature Review

2.1 Introduction

A comprehensive literature review was conducted based on the research objectives and research questions described in Chapter 1 and it was divided into three main parts, namely the oxidation and flotation of sulphide minerals, the effect of grinding chemistry on mineral flotation and particle breakage mechanisms during regrinding and their effects on flotation.

The property of mineral surfaces plays an important role in mineral flotation. In this study, before answering each research question, it is important to understand the surface change of minerals during regrinding and its effect on mineral flotation. One of the main surface changes during processing is the oxidation of the fractured and cleaved surfaces when exposed to air and solutions. Therefore, the oxidation and flotation behaviour of pyrite and copper sulphides will be reviewed firstly.

To answer the first three research questions listed in Figure 1.3 which are all relevant to regrinding chemistry, it is essential to understand the past studies on grinding chemistry and its effect on mineral flotation. This forms the second part of this literature review. In this part, the galvanic interactions between grinding media and sulphide mineral and between different sulphide minerals will be firstly discussed due to its importance in grinding chemistry. Then, the previous studies on the effect of grinding chemistry during primary grinding on mineral flotation will be outlined. The grinding chemistry factors considered will include the grinding media, pH and gas purging. Since the regrinding reduces most particles to fine and ultra-fine fractions, the effect of grinding chemistry on flotation of fine particles will be particularly discussed to provide the guidelines for this thesis study. In addition, past studies on the effect of grinding chemistry on pyrite activation by copper ions will also be discussed, which can assist the understanding and explanation of the copper activation under different regrinding chemistry and the flotation behaviour of copper activated pyrite after regrinding.

To answer the last research question about the suitability of the particle breakage mechanisms during regrinding for the subsequent cleaner flotation, it is important to outline the past studies on

particle breakage mechanisms in different grinding mills and their potential effects on flotation, and this will form the third part of this literature review.

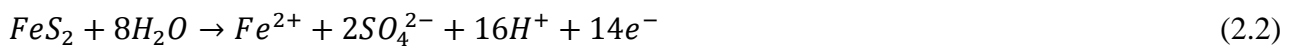
2.2 Oxidation and flotation of sulphide minerals

2.2.1 Pyrite oxidation and flotation

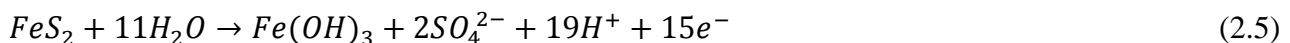
Pyrite (FeS_2) is the most commonly occurring sulphide mineral in nature (Craig and Vaughan 1978). It is a semiconductor with a band gap of nearly 0.9 eV and a cubic lattice. The band gap is an energy range in a solid where no electron states can exist. The lower the band gap, the more conductive the material. The oxidation of pyrite could produce various species on its surface, and then influence the mineral floatability. Thus the study of pyrite oxidation has been of significant interest over the last several decades.

Hamilton and Woods (1981) studied the oxidation of pyrite in the solutions of different pH by using linear potential sweep voltammograms. It was found that pyrite could be oxidized to both sulphur and sulphate. The formation of sulphur was restricted to the order of a monolayer at pH 9.2 and 13, but significant yield occurred at pH 4.6. The proportion of sulphate formed increased rapidly with an increase in pulp potential. The following steps of pyrite oxidation were proposed.

In acid solutions:



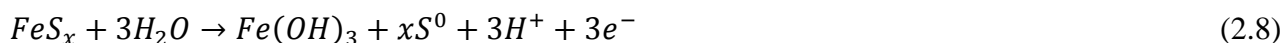
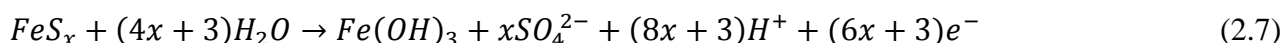
In alkaline solutions:



The kinetics of pyrite oxidation was further investigated by Chander and Briceno (1987) through cyclic voltammetry and AC impedance measurements. On oxidation, metastable phases of $Fe(OH)_2$ and $Fe(OH)_3$ were found on surfaces, and transformed to more stable phases on aging. The authors suggested that different sulphur oxidation intermediate species ($S_xO_y^{2-}$) were generated rather than just elemental sulphur and sulphate as proposed by Hamilton and Woods (1981).

X-ray Photoelectron Spectroscopy (XPS), as a surface sensitive technique, was used by Buckley and Woods (1987) to study the surface oxidation species of pyrite in air and in air-saturated aqueous solutions. It was found that, when exposed to air, pyrite was oxidized and iron sulphate was produced on the surfaces within the first several minutes. After prolonged exposure, iron oxide was formed together with the sulphur product which was suggested to be an iron-deficient sulphide rather than elemental sulphur. In acid solutions, oxidation of pyrite resulted in the formation of a surface sulphur layer. While, in the alkaline solutions, sulphate was the only sulphur oxidation product, with iron oxide remaining at the surface, which is in agreement with their earlier studies by using electrochemical techniques (Hamilton and Woods 1981).

Later studies by Mycroft et al. (1990) and Turcotte et al. (1993) suggested that not only elemental sulphur but also polysulphides (FeS_x) were formed on the pyrite surface in near-neutral aqueous or neutral solution. The formation of a surface polysulphide film was proposed by Zhu et al. (1994) based on cyclic voltammetry and kinetics of film growth. The proposed reactions are:



It was suggested that polysulphides (FeS_x) formed as intermediates during oxidation. The iron concentration in the surface layer decreased continuously from the inner to the outer surface while the sulphur concentration increased. Sulphur species varied from S^- (pyrite) on the inner surface to S^0 (elemental sulphur) on the outer surface. The sulphur formed increased with the applied potential up to a maximum value after which less sulphur was produced because of the rapid formation of sulphate ions. Sulphur and its intermediates were detected in both acidic and basic solutions (pH 2.6 to 10.5).

The surface oxidation species of pyrite and reaction kinetics have also been investigated by using in-situ Fourier transform infrared spectroscopy (FTIR). Kelsall et al. (1999) observed the surface intermediates of pyrite in 1 M HCl solution including $S_2O_3^{2-}$, $S_2O_4^{2-}$, $S_2O_5^{2-}$, HSO_3^- , SO_2^{4-} . In an aqueous solution at pH 9.2, Chernyshova (2003) suggested that the anodic oxidation of pyrite occurred in two stages. At the first stage, the S deficient clusters or FeS defects degraded by the reaction: $FeS=Fe^{2+}+S^{2-}$, forming the elemental sulphur and iron hydroxide by hydrolysis and (electro) chemical oxidation-precipitation. The second stage started with depopulation of the negatively charged iron acceptor surface states located at the valence band edge. After that, the bulk pyrite oxidation took place through the thiosulphate pathway.

Based on the extensive research focused on pyrite oxidation, a general reaction scheme was proposed by Rimstidt and Vaughan (2003). They suggested that the oxidation of pyrite could be described by an electrochemical-based model including three steps. In the first step, a cathodic reaction transfers electrons from the surface of the pyrite to oxidant species, usually O_2 or Fe^{3+} . The second step transports charge from the site of an anodic reaction to replace the electron lost from the cathodic site. In the third step, at an anodic site, the oxygen atom of a water molecule interacts with a sulphur atom to create a sulfoxy species. This releases an electron into the solid and one or two hydrogen ions to the solution. The oxidation of S by molecular oxygen to ultimately form a thiosulphate intermediate is similar to what was previously proposed by Kelsall et al. (1999). Based on previous studies and the suggestion by Chernyshova (2004), the cathodic site could include to some degree the more metallic like Fe–S defect.

Although pyrite oxidation has been extensively studied for several decades, the reaction pathways and oxidation species are still the subject of debate. This is mainly because the reactions are highly dependent on the source of pyrite, study methods and chemical conditions, such as pH, Eh, temperature and availability of different oxidants. Figure 2.1 shows the crystal structure of pyrite and a schematic representation of some possible pyrite oxidizing pathways and oxidation products. In general, the iron species are mainly Fe^{2+} or Fe^{3+} at acid conditions and iron hydroxide forms at alkaline conditions. However, the reactions on the sulphur site are complex, involving several different oxidizing pathways and oxidation intermediates.

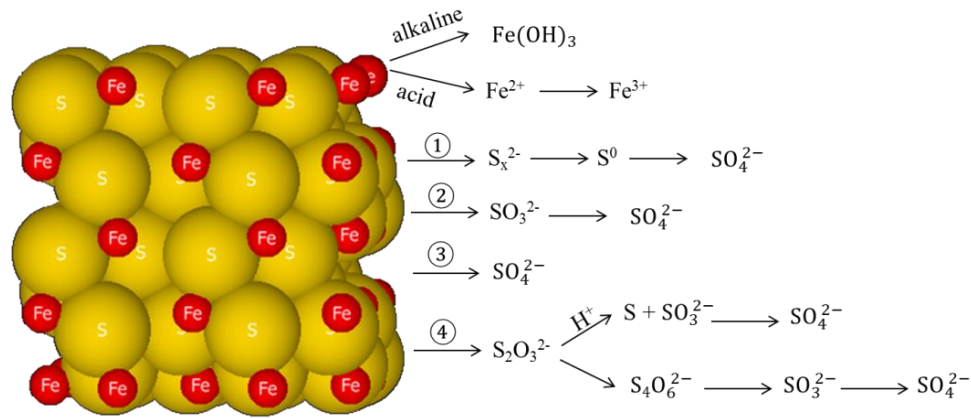


Figure 2.1 Crystal structure of pyrite and schematic representation of some possible pyrite oxidizing pathways and oxidation products (oxidizing pathways adapted from Druschel and Borda (2006)).

In the real ores processed at mineral processing plants, pyrite is normally associated with other minerals, such as copper sulphides, which may affect the bulk conductivity and surface electronic structure of pyrite, and then the pyrite oxidation (Savage et al. 2008). Thus the pyrite oxidation during the mineral processing of these ores is more complicated. When investigating the surface oxidation of pyrite in the processing plant, a specific study for each ore with suitable conditions and methodologies is necessary.

Among the various oxidation species, the metal deficient sulphide, polysulphide and elemental sulphur are hydrophobic, while other species, including metal hydroxides and higher valence sulphur oxidation species, are hydrophilic. It is obvious that both hydrophobic and hydrophilic oxidation species can be formed during flotation and upstream processes depending on the pulp chemistry (e.g. pH, Eh and DO). As studied by Kocabag et al. (1990), un-oxidized pyrite was hydrophilic in a mineral/vapour/water system and the hydrophobicity of oxidized pyrite was Eh-pH dependent. In alkaline and neutral pH conditions, hydrophobicity decreased with oxidation due to the formation of iron hydroxides. In acidic solutions of $\text{pH} < 4$, the hydrophobicity firstly increased with oxidation due to the formation of elemental sulphur, then decreased as the iron hydroxide was also formed on the surface. Therefore, pyrite can be floated without collector under some conditions if enough hydrophobic oxidation species are formed on the surface. For example, Fuerstenau and Sabacky (1981) reported that pyrite single mineral was almost completely floatable without collector in water containing less than 5 ppb of oxygen at near neutral pH. Although some other laboratory studies could also manage to get a high pyrite recovery without any collector by

controlling the solution chemistry (Ekmekçi and Demirel 1997, Hu et al. 2009), this self-induced flotation of pyrite is weak under the normal plant conditions (Zheng and Manton 2010).

2.2.2 Oxidation and flotation of copper sulphide minerals

Copper sulphide minerals yield most of the copper production throughout the world, and are often associated with precious minerals, such as gold and silver. The chemical compositions of different copper-bearing minerals vary from one mineral to the next due to different formation conditions, and these different compositions result in different electrochemical properties. Fullston et al. (1999) studied the oxidation of some copper sulphide minerals using zeta potential measurements, and found that the oxidation rate of these copper minerals follows the order: chalcocite > tennantite > enargite > bornite > covellite > chalcopyrite. The study in this thesis focuses on chalcopyrite and chalcocite which are two of the most commonly floated copper sulphide minerals. Chalcopyrite is usually formed in the primary hydrothermal zone. Chalcocite can also be formed as part of primary mineralization (e.g. in iron oxide hosted copper-gold deposits), but more frequently occurs as a secondary enrichment mineral (Anthony et al. 1990). The electrochemical properties and surface oxidation of chalcopyrite and chalcocite have a significant influence on their floatability, which will be reviewed in the following section.

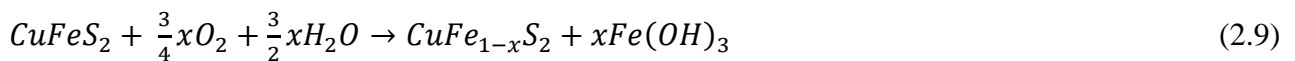
2.2.2.1 Chalcopyrite oxidation and flotation

Chalcopyrite (CuFeS_2) is a primarily n-type, less frequently p-type semiconductor with a band gap of 0.6 eV (Abramov and Forssberg 2005). It is one of the most common and abundant copper-bearing mineral of sulphide ore deposits (Crundwell 1988). Surface oxidation of chalcopyrite plays an important role in mineral processing. For example, the collectorless flotation of chalcopyrite can occur under mildly oxidizing conditions (Heyes and Trahar 1977).

The oxidation of chalcopyrite and the oxidation species formed on the surfaces have been widely studied for decades by using electrochemical and surface techniques. Gardner and Woods (1979) identified the electron transfer reactions taking place at a chalcopyrite electrode by employing linear potential sweep voltammetry. From the voltammograms, coupled with bulk thermodynamic data, it was indicated that the products of the oxidation reaction were CuS , $\text{Fe}(\text{OH})_3$ and elemental sulphur. High chalcopyrite recovery was achieved without collector after conditioning at high pulp potential. It is believed that the elemental sulphur produced in both acid and alkaline solutions render

chalcopyrite floatable in the absence of collectors. Kelebek and Smith (1989) also reported that multilayer quantities of sulphur could be extracted with ethanol from chalcopyrite after dry grinding. However, Buckley and Riley (1991) attributed this extracted sulphur to an experimental artefact introduced by the solvent.

XPS was used by Buckley and Woods (1984) to investigate the chalcopyrite oxidation. Unlike the previous electrochemical studies by Gardner and Woods (1979), it was concluded that a metal-deficient sulphide lattice rather than elemental sulphur was formed by the oxidation of chalcopyrite. Buckley and Woods (1984) proposed that the exposure of chalcopyrite to air resulted in iron atoms migrating to the surface to form an iron hydroxide, with the formation of a sulphur-rich copper sulphide with stoichiometry CuS_2 . Copper sulphate was also formed after extended exposure to air. Similar products were observed in the oxidation of chalcopyrite in air-saturated ammonia solution. In the oxidation in acid solutions, iron and some copper were dissolved, forming a surface layer with a composition near $Cu_{0.8}S_2$. The reactions for the oxidation of chalcopyrite in alkaline and acidic solutions have been proposed. The reaction in alkaline solution was proposed as:

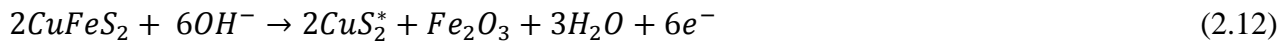
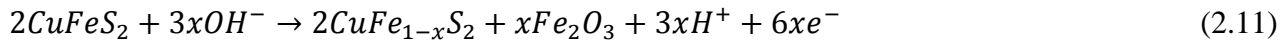


with $x \approx 1$ for the outermost layers and with the ferric hydroxide covering the sulphur-rich lattice. An analogous reaction in acidic solution was proposed as:



Zachwieja et al. (1989) confirmed that the oxidation of chalcopyrite resulted in the release of iron ions from chalcopyrite. They found that the oxidation rate increased with pH, because increasing pH resulted in an increase in the ease in which iron ions were removed from the chalcopyrite surface by the formation of iron-hydroxyl species. The metal-deficient sulphide formed on chalcopyrite electrodes in acid electrolyte solutions was confirmed by Biegler and Horne (1985) with a surface layer composed of CuS and S^0 . Zachwieja et al. (1989) also correlated the self-induced flotation response of air-exposed chalcopyrite in alkaline solutions with the surface composition and found that the floatability of the conditioned mineral was consistent with the hydrophobic sulphur-rich sulphide lattice.

It is well known that the oxidation rate and species are highly dependent on the rest potential. Vaughan et al. (1997) proposed the sequence of oxidation reactions with increasing Eh on chalcopyrite surfaces in a solution at pH 9.2 by using cyclic voltammogram together with XPS and XAS data:



At potentials just above the rest potential, a monolayer of Fe₂O₃/Fe(OH)₃ was formed, leaving Cu and S unoxidised as a metastable phase of CuS₂ stoichiometry. The first three steps (2.11-2.13) were similar to those proposed by Buckley and Woods (1984). The authors suggested that these phases could cause passivation, which was confirmed by Mikhlin et al. (2004). With increasing the potential, these reactions continued, removing iron from deeper within the chalcopyrite, and with solid state diffusion being the likely rate controlling mechanism. The CuS₂ phase decomposed above a critical potential by the further reactions as shown in the last two steps (2.14-2.15). Similar oxidation pathways were proposed by Yin et al. (2000), who investigated the surface oxidation of chalcopyrite in alkaline solutions of pH 9.2 and 12.7, showing that the oxidation process consisted essentially of three potential-dependent stages. At pH 9.2, when increasing the electrode potential from -0.6 to +0.02 V vs. SCE, the iron in the top layer of the chalcopyrite surface was oxidized, forming a monolayer of Fe(OH)₃ and Fe₂O₃. The copper and sulphur remained unoxidized as a phase designated as CuFe_{1-x}S₂ and CuS₂^{*}, which together with Fe(OH)₃ and Fe₂O₃ formed a film retarding the further oxidation. As the potential increased further, deeper layers were involved in the oxidation, but the passivating film was not destroyed. At this stage, the oxidation process was controlled by solid-state mass transport. When the applied potentials were higher than 0.4 V vs. SCE, CuS₂^{*} was no longer stable and was oxidized to CuO, S, and SO₄²⁻ ions. The passivating film then decomposes, accelerating the oxidation rate of the underlying CuFeS₂. At pH 12.7, the

oxidation mechanism is similar, however, because the equilibrium potentials are lower, the corresponding current peaks appear at less positive potentials.

Although the oxidation of chalcopyrite has been studied extensively under various conditions, there are still many aspects that are not well understood because of the complexity and variability of the interaction between chalcopyrite and the oxidizing environment. Figure 2.2 summarizes the possible oxidation species. It is generally agreed that the oxidation starts from the release of iron ions which may form iron oxidation species at alkaline conditions. As a result, a sulphur-rich surface is produced, although there remains an argument whether it is a metal-deficient sulphide lattice, a metal polysulphide or elemental sulphur.

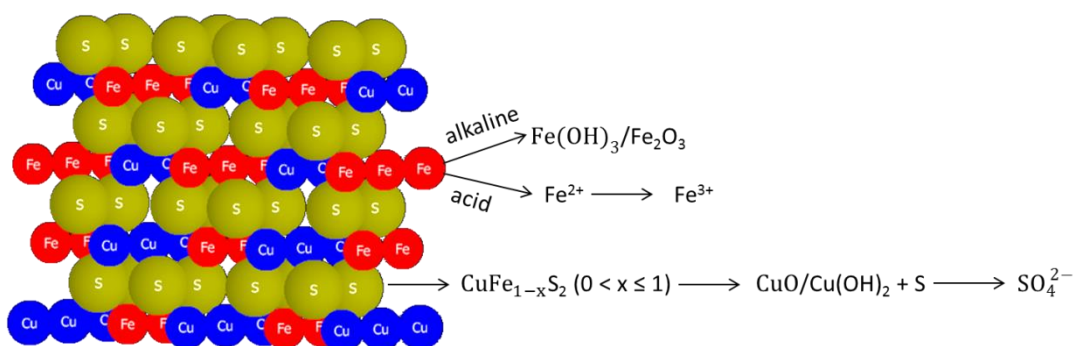


Figure 2.2 Crystal structure of chalcopyrite and schematic representation of some of the possible oxidation species for chalcopyrite oxidation.

It is well-known that chalcopyrite can be floated in the absence of collectors under oxidizing conditions, but cannot be floated under reducing environment (Heyes and Trahar 1977). Guy and Trahar (1985) attributed the strong collectorless floatability of chalcopyrite after grinding in an oxidizing environment to chalcopyrite surface oxidation, which produces hydrophobic sulphur-rich surfaces. However, an extensive oxidation may result in a production of high quantities of hydrophilic metal hydroxides or sulphates on the mineral surface, decreasing chalcopyrite flotation recovery (Senior and Trahar 1991, Gonçalves et al. 2003, Hirajima et al. 2014). Chander (1991) and Fairthorne et al. (1997) demonstrated that the hydrophobicity of the chalcopyrite surface and the self-induced chalcopyrite flotation were controlled by two oxidation processes, i.e. the metal dissolution that produced a hydrophobic surface and the metal hydroxide precipitation that produced a hydrophilic surface. Flotation results obtained by Guo and Yen (2003) further proved this process. As shown in Figure 2.3, the chalcopyrite presented a collectorless floatability only in

mild oxidizing environments. If the Eh is too high, the floatability will be decreased due to the destruction of metal-deficient sulphur layer.

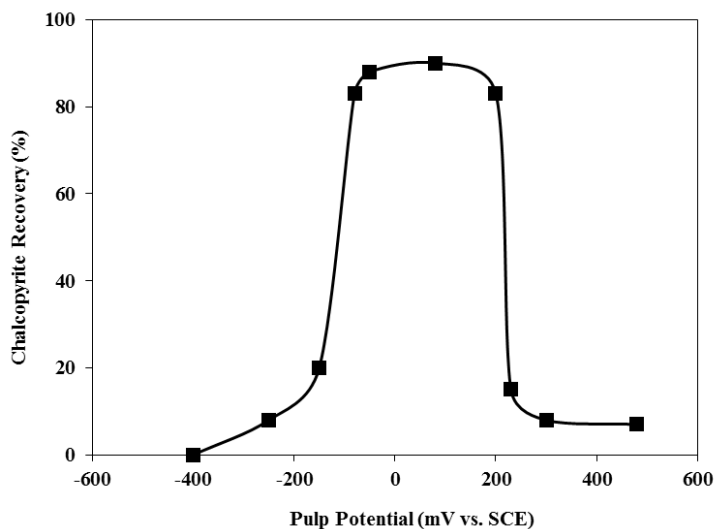


Figure 2.3 Floatability of natural chalcopyrite in pH 10 buffer solution without collector (Guo and Yen 2003).

2.2.2.2 Chalcocite oxidation and flotation

Chalcocite (Cu_2S) is a low-temperature p-type semiconductor with the band gap of 1.4 eV. Similar to pyrite and chalcopyrite discussed in the previous sections, the state of the oxidized chalcocite surface influences the surface hydrophobicity and the adsorption process of the flotation reagent and hence the mineral floatability.

Walker et al. (1984) investigated the electrochemical reactions of Cu_2S in a borate solution and analyzed the resulting changes in the solution composition using a combination of electrochemical and spectrophotometric techniques. It was found that Cu_2S underwent anodic dissolution at open circuit with the buildup of soluble copper species and oxidized sulphur species. The Cu^{2+} has a tendency to form insoluble hydroxides or oxides at an alkaline pH.

It has been proposed that the oxidation of Cu_2S processes either by:



or by consecutive reactions involving covellite as an intermediate:



It has also been found that the production of soluble copper is accelerated by controlling the potential to values anodic to the open circuit potential and the concentration of Cu^{2+} is directly proportional to the quantity of charge passed, while, the reverse of this reaction causes a decrease in the Cu^{2+} concentration followed by the identical relationship between charge and Cu^{2+} concentration. Moreover, a cathodic reaction is observed at -0.60 V which results in the buildup of HS^- in solution.

Walker et al. (1984) correlated the reactions of chalcocite in aqueous solution with its collectorless flotation response. A low collectorless flotation recovery was achieved at open circuit due to the hydrophilic hydroxides formed on the surface. However, the collectorless flotation slightly increased at moderate reducing potential conditions, which may be because the hydrophilic hydroxides can be reduced with the simultaneous reformation of Cu_2S . Maximum natural flotation occurs between -0.03 and 0.0 V, as a result of either elemental sulphur or excess sulphur in the lattice such that the coordination of surface copper with sulphur is maximised. One aspect of this electrochemical study is that the experiments were performed in borate solution. As pointed out by Hayes et al. (1987), borate ions can form complexes with frothers, and influence the floatability of minerals. Therefore, it is important to take proper precautions to ensure that it is not a contributor to the apparent hydrophobicity of the system.

The flotation of chalcocite in the absence of collector was also investigated by Heyes and Trahar (1979). It was found that chalcocite displayed a small degree of collectorless flotation over a range of Eh values at pH 11, especially for the fine particles (-10 μm), although the recovery is always much lower than that of chalcopyrite at the same flotation conditions. However, whether the collectorless flotation of chalcocite was induced by sulphur on the mineral surface or by adsorption of frother was not determined in that study.

Mielczarski and Suoninen (1988) studied the oxidation of chalcocite in aerated aqueous solution by using XPS. In acidic solution, an almost monolayer coverage of adsorbed oxygen, water and hydroxide groups was found. While, in neutral and basic solutions, the surface consisted mainly of copper(I) and copper(II) hydroxides and of some copper(II) carbonate, which is generally consistent

with previous studies by Walker et al. (1984). The amount of these products increased with the pH of the solution. However, no oxidized sulphur species were observed on the surface layer.

Abramov and Forssberg (2005) studied the oxidation state of chalcocite at different Eh and pH values theoretically by the plotting of Eh–pH diagrams of chalcocite in determined conditions. The oxidation products of chalcocite in the region with “more positive” Eh potential values were cupric hydroxycarbonate $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (pH<9), hydroxide $\text{Cu}(\text{OH})_2$ (pH>9), or cuprous oxide Cu_2O and at “more” negative Eh potential values-elemental copper, cuprous, or cupric sulphides. Although the diagram does not have fields of stable simultaneous existence of chalcocite and elemental sulphur, formation of elemental sulphur S^0 on the mineral surface is still possible in acidic and reducing medium. Furthermore, the rate and degree of chalcocite oxidation must increase with an increase in pH value (Abramov and Forssberg 2005). These theoretically calculated results are in a good correlation with experimental measurements of the phase composition of oxidation products at various Eh and pH values undertaken by electron microscope methods (Peabody et al. 1997). It is noted that the primary oxidation product of chalcocite at pH < 5.5 is copper sulphate hydrate $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$. At pH 5.5-9.5, it is copper hydroxycarbonate $\text{Cu}_2(\text{OH})_2\text{CO}_3$ which at pH > 9.5 goes over to the hydroxide of bivalent copper $\text{Cu}(\text{OH})_2$.

Overall, the oxidation products of chalcocite in a solution are mainly copper oxidation products, such as $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$, as summarized in Figure 2.4. Most of these species are hydrophilic, which is believed to be the main reason why chalcocite shows a significantly lower floatability than chalcopyrite in the absence of collectors. Sulphur rich surfaces may be formed at some conditions, which may increase the hydrophobicity, as reported by Walker et al. (1984), however, it has not been confirmed by surface analysis techniques.

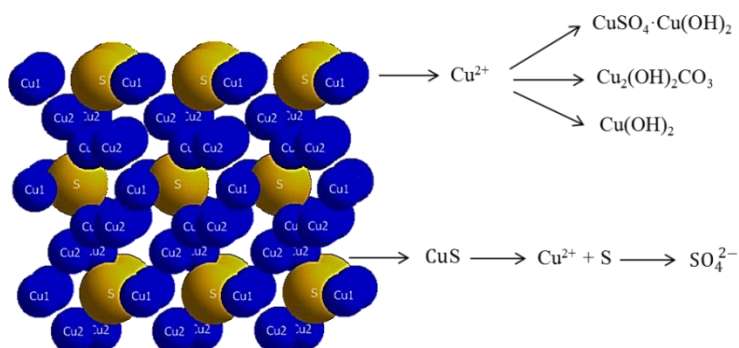


Figure 2.4 Crystal structure of chalcocite and schematic representation of some possible chalcocite oxidation species.

2.3 The effect of grinding chemistry on mineral flotation

Regrinding rougher flotation concentrates not only further reduces particle size and liberates valuable minerals but also produces a large amount of fresh surfaces. Hu et al. (2009) commented that, “the leakage, dislocation and incoming of impurities may be produced in a mineral crystal during grinding resulting in the change of surface properties of the mineral such as electron energy level and electrode potential”. In addition, most sulphide minerals are semi-conductive, so various electrochemical reactions occur on mineral and grinding media surfaces during wet grinding. Finkelstein et al. (1975) observed that very small changes in the nature of the mineral surface resulted in pronounced effects on mineral floatability, and this influence will be more significant during regrinding because of the increased surface area as the particle size is reduced to fine and ultra-fine fractions. So it is important to study the effect of regrinding chemistry, including grinding media, pH, and purging gas, on the subsequent flotation. However, up to now, most previous research focused on the primary grinding, and the studies on regrinding environment are very limited. Thus in the following review, most of the conclusions are made by reviewing studies on primary grinding.

2.3.1 Galvanic interactions during grinding

2.3.1.1 Principles of galvanic interactions

The electrochemical activity of solids can be quantified by rest potential or electrode potential which is the “electromotive force of a cell in which the electrode on the left is a standard hydrogen electrode and the electrode on the right is the electrode in question” according to an definition by International Union of Pure and Applied Chemistry (IUPAC) (McNaught and Wilkinson 1997). Under the same chemical conditions, a lower rest potential indicates a higher electrochemical activity. Table 2.1 shows the rest potential of several sulphide minerals and mild steel grinding media. The mild steel has a significantly lower rest potential than all the three minerals, suggesting that the mild steel is more active than the sulphide minerals.

Table 2.1. Rest potentials of pyrite, chalcopyrite, galena and mild steel in distilled water at near neutral pH.

Minerals & Grinding Media	Rest Potential (mV, SHE)	References
Pyrite	445	(Pozzo and Iwasaki 1987)
Chalcopyrite	355	(Cheng et al. 1993)
Galena	172	(Learmont and Iwasaki 1984)
Mild steel	-335	(Adam et al., 1984)

When two or more semi-conductive or conductive solids with different rest potentials come into contact in an electrolyte solution, a galvanic couple is set up with a leakage of electrons from one to the other. The solid with a higher rest potential will act as a cathode on which reduction reactions occur, while the other solid with a lower potential will act as an anode on which oxidation reactions take place. This galvanic coupling has been intensively studied in the area of metal corrosion, which is usually called galvanic corrosion. It is generally accepted that, when both metals are in electrical contact and immersed in an electrolyte solution, the corrosion rate of one metal is accelerated while that of the other metal is retarded (Perez 2004). During grinding, the galvanic interaction can also occur between the species with different rest potential, such as between grinding media and sulphide minerals and influence the electrochemical reactions on both cathod and anode.

Every electrochemical reaction involves the transfer of charges or electrons. It is composed of two parts, an oxidation half-reaction:



and a reduction half-reaction:



According to the thermodynamic theory, the Gibbs free energy (ΔG) of the whole system is given by the relation:

$$\Delta G = -zF(E_{\text{cathode}} - E_{\text{anode}}) \quad (2.18)$$

The galvanic interaction occurs spontaneously when the equilibrium half-cell potential (E_{cathode}) is more positive than the equilibrium half-cell potential (E_{anode}). The potential difference between the cathode and anode is the driving force for this galvanic interaction.

During grinding, the galvanic interaction between sulphide minerals and grinding media involves more than one cathodic reaction and anodic reaction. According to mixed potential theory, in any Faraday galvanic interaction process, the equilibrium half-cell potential of the anode and cathode shifts to mixed potentials such that the sum of all electrons is zero (Huang 2005). Thus there is no net electron accumulation on both electrodes, as shown in the equation:

$$I_g = \sum I_{\text{oxid}} A_{\text{oxid}} = \sum I_{\text{red}} A_{\text{red}} \quad (2.19)$$

Where I_g is the galvanic current; I_{oxid} and I_{red} are oxidation and reduction current density, respectively; A_{oxid} and A_{red} are the surface area of oxidation and reduction, respectively.

2.3.1.2 Galvanic interaction between steel grinding media and sulphide minerals

Based on the mixed potential theory, several models about galvanic interactions during wet grinding of sulphide minerals have been developed and applied. Figure 2.5 (a) shows the model of galvanic interaction between steel grinding media and sulphide minerals. The iron grinding media has a lower rest potential than most of sulphide minerals. Therefore, when electrochemical interactions occur during grinding, grinding media acts as an anode, and the sulphide mineral acts as a cathode. The electrons flow from anodic grinding media to cathodic sulphide minerals (Adam et al. 1984). As a result, the corrosion of the grinding media is accelerated, and the reduction of oxygen on the cathode is enhanced, producing a large amount of hydroxyl ions. In the ‘real’ ore grinding system in mineral processing plants, the galvanic interaction is more complicated, due to the co-existence of various sulphide minerals with different rest potential. Pozzo et al. (1990) developed an electrochemical model for a mineral-mineral-grinding media system as shown in Figure 2.5 (b). The noblest mineral would always act as a cathode, whereas the grinding media with the lowest rest potential would always be the anode. The other mineral with the middle rest potential can act either as an anode as shown in Figure 2.5 (b) or a cathode as shown in Figure 2.5 (c), depending on its thermodynamic property, and the thermodynamic and kinetic properties of the other mineral and media.

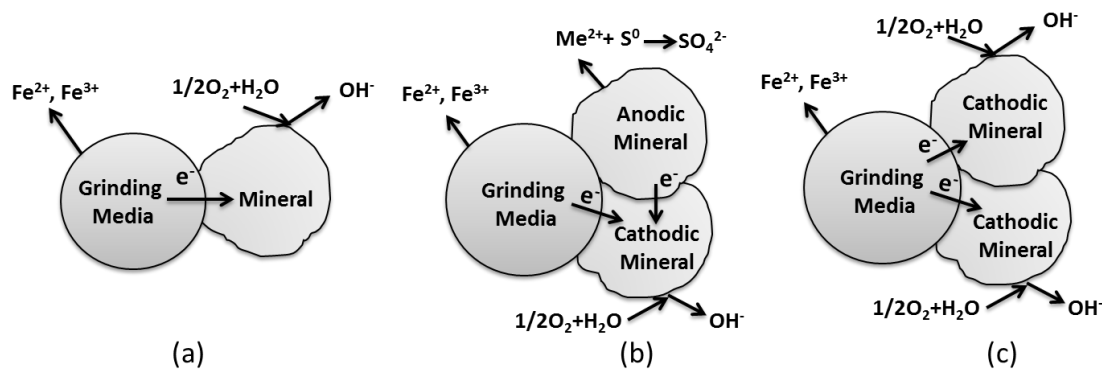


Figure 2.5 Schematic presentation of galvanic interactions occurring between a sulphide mineral and steel grinding medium (a), and between two different sulphide minerals and steel grinding medium(b, c) (Adapted from Pozzo et al. (1990) and Peng (2003)).

The electrochemical corrosion plays a dominant role in grinding media corrosion during wet grinding of sulphide minerals due to the galvanic interaction between steel grinding media and sulphide minerals (Natarajan and Iwasaki 1984, Pozzo and Iwasaki 1987, Natarajan 1996). The iron grinding media corrosion in alkaline solutions could produce a large amount of iron oxidation species, such as, iron hydroxide which can coat on mineral surfaces and depress mineral floatability (Adam et al. 1984, Peng et al. 2003a, Peng et al. 2003b).

Various grinding media are being used in mining industry, such as, mild steel, high chromium steel and ceramic media. Different grinding media have different rest potential, which can significantly influence the extent of galvanic interactions with minerals during grinding. Galvanic current measurements were conducted by Adam et al. (1984) to study the electrochemical interactions between pyrrhotite and several metal electrodes including mild steel, austenitic and martensitic stainless steels, zinc and magnesium. It was noticed that the galvanic current between pyrrhotite and metal decreased with increasing the rest potential of metals. Similar results were also observed by other researchers (Moore et al. 1988, Yelloji Rao and Natarajan 1988, Ahn and Gebhardt 1991, Huang 2005). Generally, the more electrochemically active the grinding media, the higher the galvanic current. Huang (2005) quantified the galvanic interactions between pyrite and different grinding media (mild steel, 15%, 21%, 30% chromium media) by using mathematical theoretical models and calculated the galvanic current from polarization curves of both grinding media and minerals. It was found that the galvanic current of mild steel media with pyrite was much higher than that with high chromium media. It was also observed that the oxidation rate of mild steel was proportional to the galvanic current on mild steel (Huang and Grano 2005). The higher the galvanic

current between mild steel and pyrite, the more mild steel is oxidized and the larger the amount of EDTA extractable iron products. Similar results were also found in the arsenopyrite and bornite grinding system (Huang 2005, Huang and Grano 2006).

The magnitude of galvanic interaction is not only dependent on the reacted materials (type of media and minerals) but also dependent on the given environment, such as, pH, Eh, dissolved oxygen and electrolyte conductivity. Ahn and Gebhardt (1991) observed that the galvanic current between high carbon steel and chalcopyrite was significantly influenced by pH and Eh. After pH was increased to 11, the extent of galvanic interaction became much lower, indicating that the high-carbon steel was passivated at higher pH. In addition, the galvanic current increased rapidly to above -0.57 V and -0.18 V in deaerated and aerated solutions, respectively. Galvanic coupling may also be influenced by the conductivity of the water used during milling, and grinding media show greater levels of oxidation with high ionic strength water (Grano 2009). The dissolved oxygen concentration in the slurry controls the magnitude of the galvanic current as well. Adam et al. (1984) observed that the currents of pyrrhotite-mild steel and pyrrhotite-magnesium couples were an order of magnitude higher when oxygen was bubbled in the solution, suggesting an increase in the rate of the corrosion reaction. During grinding, the DO concentration was highly dependent on the purging gas. The galvanic interaction of sulphide minerals with grinding media can be weakened by purging nitrogen during grinding to expel air, which was proved by measuring the galvanic current (Yelloji Rao and Natarajan 1988, Huang and Grano 2005, Huang et al. 2006) and also the amount of iron oxidation species (Peng et al. 2003a, Peng et al. 2003b).

2.3.1.3 *Galvanic interaction between different sulphide minerals*

As discussed in section 2.3.1.1, a galvanic couple can be set up as long as there is a rest potential difference between the two materials. Therefore, the galvanic interaction can not only occur between grinding media and sulphide minerals as discussed in the previous section but can also occur between different sulphide minerals with different rest potential, leading to the change of the electrochemical reactions on both anodic and cathodic mineral surfaces. The extent of galvanic interaction depends on the mineral properties and their relative rest potential.

More than half a century ago, Majima and Peters (1968) noted that the galvanic effect was one of the most important electrochemical factors which governed the dissolution rate of sulphide minerals in hydrometallurgical systems. Mehta and Murr (1983) examined the galvanic couples including

chalcopyrite and sphalerite in electrical contact with pyrite. Pyrite, with its more positive rest potential, acted as a cathode while chalcopyrite and sphalerite with more negative rest potential acted as anodes. It was observed that as the amount of pyrite in contact with another mineral increased, the rate of leaching of this mineral increased. Holmes and Crundwell (1995) developed a quantitative description of galvanic interactions between sulphide minerals (copper-pyrite and galena-pyrite) based on thermodynamic and kinetic parameters, and also included the solution voltage loss and mineral-mineral contact voltage loss into the quantitative description. The galvanic currents predicted by the mathematical model observed were in good agreement with the experimentally measured galvanic currents.

Since the galvanic interaction among sulphide minerals can affect the redox reactions occurring on mineral surfaces, it may influence the mineral surface hydrophobicity. Therefore, it is critical for the flotation process. As studied by Ekmekçi and Demirel (1997), the galvanic interaction between chalcopyrite and pyrite significantly influenced the collectorless flotation behaviour of both minerals. A galvanic cell formed between anodic chalcopyrite and cathodic pyrite. The anodic reactions at the chalcopyrite surfaces were enhanced in the presence of pyrite, producing more hydrophilic iron oxides and sulphur-oxygen compounds which depressed the chalcopyrite floatability. The pyrite collectorless floatability was improved due to the generated hydrophobic sulphur-rich surface or copper activation. Al-Harashseh et al. (2006) also found that, when chalcopyrite was in intimate contact with pyrite, it experienced an enhanced oxidation compared to when there was no contact with pyrite. Acres et al. (2010) studied the oxidation and leaching of heterogeneous chalcopyrite with bornite by using Synchrotron X-ray Photoelectron Spectroscopy (SXPS). It was found that the presence of bornite in intimate contact with chalcopyrite resulted in fewer hydrophobic polysulfide species and more hydrophilic sulphate species at the chalcopyrite surface after oxidation in flotation related conditions. Overall, the galvanic interactions between different sulphide minerals have a great effect on reactions on both anodic and cathodic mineral surfaces, which may lead to a significant change of the mineral floatability.

Furthermore, the pulp chemistry also plays an important role in the galvanic interactions among minerals. Qing You et al. (2007) used a three-electrode system to investigate the current density and mixed potential of a galvanic cell comprising a pyrite cathode and a chalcopyrite anode in a flowing system. It was found that the galvanic interaction was highly depended on the ion concentration, pH and also the flow rate of solutions. Same conclusions were also made in a pyrite-galena system by Liu et al. (2009). A recent study by Moslemi et al. (2011) further confirmed that pH and ions

(chloride and sulphate ions) significantly influenced the galvanic interaction between pyrite and pyrrhotite, and then affected the floatability of both minerals. Therefore, the galvanic interaction should be considered when investigating the effect of pulp chemistry during grinding on the subsequent flotation.

Overall, galvanic interaction occurs during grinding between grinding media and minerals or between minerals with different rest potential. It plays a critical role in the media corrosion and mineral surface oxidation and hence influences the mineral floatability.

2.3.2 Effect of grinding media on mineral flotation

There are various types of grinding media being used in mineral processing plants. Among them, forged and cast low alloy steel are the most widely used media due to their low manufacturing cost. However, over the last several decades, research has revealed that the type of grinding media has a significant effect on the subsequent flotation through the modification of pulp chemistry and mineral surface properties, which should also be considered when selecting grinding media.

Rey and Formanek (1960) firstly reported the effect of grinding media on flotation. They found that the steel media decreased the activity of sphalerite, benefiting the selective flotation separation of galena from sphalerite. The effect of different types of grinding media, including mild steel, high carbon steel, stainless steel, high chromium steel and ceramic media, on the floatability of sulphide minerals has been intensively investigated in both laboratory and plant operation.

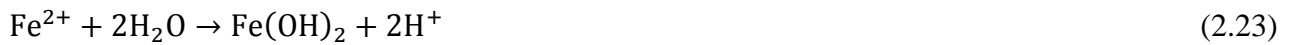
As stated by Kocabag and Smith (1985), the effect of grinding media on mineral flotation was mainly through the various electrochemical reactions occurring inside the grinding mill. Different types of media produce different amounts of iron oxidation species, provide different pulp chemistry, and determine the extent of galvanic interactions between grinding media and minerals, which play important roles in subsequent mineral flotation and the separation of different minerals and will be reviewed in the following sections.

2.3.2.1 Iron oxidation species

During wet grinding with steel grinding media, the electrochemical corrosion plays an important role in grinding media wear, producing iron oxidation species. Iron steel media can be oxidised through the reactions 2.21 and 2.22:



The iron ions hydrolyse through reactions 2.23 and 2.24:



The oxidation products of the grinding media, mainly iron hydroxide species at alkaline conditions, invariably precipitate onto the surface of the sulphide minerals thereby affecting their floatability. Generally, the active grinding media, such as mild steel, produces much more iron oxidation species than inert steel media, such as stainless steel. These hydrophilic iron oxidation species can depress the flotation of most sulphide minerals (Natarajan and Iwasaki 1984, Grano et al. 1997a, Grano et al. 1997b, Peng et al. 2003a, Peng et al. 2003b, Greet and Bartle 2008). As shown in Figure 2.6, a linear relationship was observed between the amount of iron oxidation species and flotation recovery of galena and chalcopyrite (Peng and Grano 2010b).

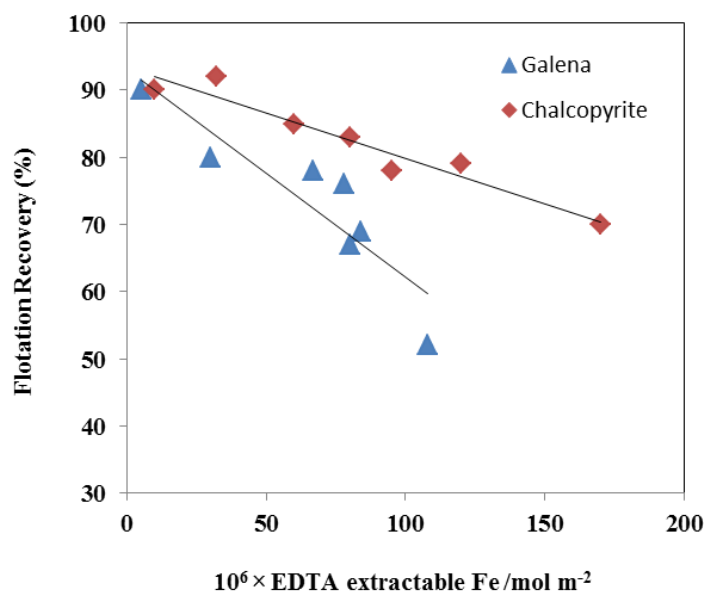


Figure 2.6 Galena and chalcopyrite flotation recovery as a function of the amount of iron oxidation species on the surface at grinding and flotation pH 9 (Peng and Grano 2010b).

Several mechanisms have been proposed to explain the detrimental effect of iron hydroxide on mineral flotation. The “consumption” of xanthate collector by grinding media oxidation products was suggested by Rey and Formanek (1960) as a possible mechanism to account for decreased sulphide mineral recovery with reactive steel grinding media. However, later studies showed that it was not possible for the common thiol collectors to react with iron oxidation products. A more likely explanation was related to the continuing presence of the iron hydroxide layer and the reduced area on the particle surfaces which can be rendered hydrophobic through collector adsorption. Grano et al. (1997a) and Grano et al. (1997b) observed that reduction in the adsorption of thiol collectors onto chalcopyrite was the principal mechanism responsible for the reduced chalcopyrite flotation in the presence of a small concentration of ferric hydroxides over the pH range of 6–8, and high affinity sites for thiol adsorption on chalcopyrite were obscured by the presence of ferric hydroxides. Hence, the effective contact angle on the chalcopyrite surfaces was reduced by the continuing presence of hydrophilic iron hydroxide over layers which do not interact with thiol collectors at neutral to alkaline pH values.

De F. Gontijo et al. (2007) observed that only a relatively small surface coverage of hydrophilic iron hydroxide, of the order of 20%, was enough to reduce the contact angle of the chalcopyrite to less than the critical contact angle required for the attachment of fine particles to bubbles. Moreover, experimental evidence has shown that the flotation recovery of intermediate size galena

(25–38 μm), with low surface area, was severely depressed by iron hydroxide at only 8% of an equivalent monolayer (Bandini et al. 2001). Since regrinding reduced the particle size to a fine or ultra-fine fraction, the iron oxidation species may have a more significant effect on mineral flotation after regrinding.

As discussed previously in section 2.3.1, galvanic interactions occur between steel grinding media and sulphide minerals, accelerating the oxidation of grinding media (Martin et al. 1991, Huang 2005), with simultaneous generation of more iron oxidation species. Adam and Iwasaki (1984) and Pozzo and Iwasaki (1989) observed that the more electrochemically active the grinding media and the longer the contact time, the higher the galvanic current and the lower the floatability of pyrite and pyrrhotite due to the formation of iron hydroxide on the surface determined by XPS analysis. The same conclusions were also made from the grinding of other sulphide minerals (Yelloji Rao and Natarajan 1988, Ahn and Gebhardt 1991, Huang 2005). Therefore, minimizing the galvanic interaction during grinding is beneficial to sulphide mineral flotation due to the reduced production of iron hydroxides (Huang and Grano 2006), which can be achieved by using more inert grinding media (e.g. stainless steel, ceramic media) or by reducing the dissolved oxygen concentration by purging inert gas into the grinding mill.

Overall, the flotation of sulphide minerals can be adversely affected by iron oxidation species from steel grinding media since these hydrophilic species can inhibit collector adsorption and decrease the surface hydrophobicity. It has also been found that fine particles are more susceptible to the iron contamination, which suggests that the control of grinding media oxidation may be more important during regrinding. Furthermore, the galvanic interactions play an important role in the oxidation of grinding media during grinding. A lower galvanic interaction may reduce the generation of iron oxidation species and therefore benefit the subsequent mineral flotation.

2.3.2.2 *Effect of pulp potential (Eh)*

The pulp potential (Eh) is an indicator of the oxidation-reduction environment, and is influenced by dissolved oxygen concentration, pH and also other species in the slurry. Different grinding media may produce different pulp potentials. Generally, the electrochemically active grinding media, such as mild steel, produce a reducing environment with a low Eh and DO value, due to the rapid consumption of oxygen in the slurry. However, the nobler grinding media, such as stainless steel,

usually produce a highly oxidizing environment with a high Eh value (Grano et al. 1990, Yuan et al. 1996a).

As discussed in section 2.2, both hydrophilic and hydrophobic oxidation species can be formed on sulphide mineral surfaces. During grinding, the pulp potential in the slurry can influence the surface oxidation, and then change the surface hydrophobicity. It is well-known that chalcopyrite can be floated in the absence of collectors under oxidizing conditions, but cannot be floated under a reducing environment (Heyes and Trahar 1977). As discussed in section 2.2.2.1, the collectorless flotation of chalcopyrite is mainly due to the formed hydrophobic sulphur-rich surfaces under a mildly oxidizing condition (Guy and Trahar 1985, Chander 1991, Fairthorne et al. 1997). However, extensive oxidation may result in a production of high quantities of hydrophilic metal hydroxides or sulphates on the mineral surface, decreasing chalcopyrite flotation recovery (Senior and Trahar 1991, Gonçalves et al. 2003, Hirajima et al. 2014).

Unlike chalcopyrite, pyrite and chalcocite only exhibit minimal self-induced flotation under normal operation conditions, although some laboratory studies managed to get a high recovery without any collector by controlling the solution chemistry (Walker et al. 1984, Ekmekçi and Demirel 1997). The main reason for the low pyrite and chalcocite collectorless flotation is the major oxidation product being hydrophilic with only a small amount of hydrophobic species (Hamilton and Woods 1981, Buckley and Woods 1987, Mielczarski and Suoninen 1988).

In addition to the effect on mineral surface oxidation, the pulp potential of the grinding product can be passed on to the subsequent flotation and influence the pulp potential in the flotation stage (Yuan et al. 1996a). The pulp potential plays an important role on the interaction of xanthate collectors with sulphide minerals in the flotation. As shown in Figure 2.7, Richardson and Walker (1985) found that the ethyl xanthate-induced flotation of each mineral (chalcocite, bornite, chalcopyrite, and pyrite) was markedly dependent on electrochemical potential, with the recovery changing from zero to 100% in potential intervals of approximate 0.2 V. Grano et al. (1990) studied the flotation of copper and lead-zinc sulphide ore from Mt. Isa over a range of grinding and flotation Eh conditions, and also found that the flotation of both ores with collector showed a strong dependency on Eh. The mechanism of chalcopyrite-xanthate interaction was studied by Mielczarski et al. (1998). They found that only under oxidizing conditions, the uptake of collector by chalcopyrite was possible, by forming dixanthate or Cu^+ -xanthate on chalcopyrite surfaces. Under reducing conditions, the uptake

of xanthate on chalcopyrite was minimal. Similar mechanisms for the pyrite-xanthate interaction were proposed by Janetski et al. (1977).

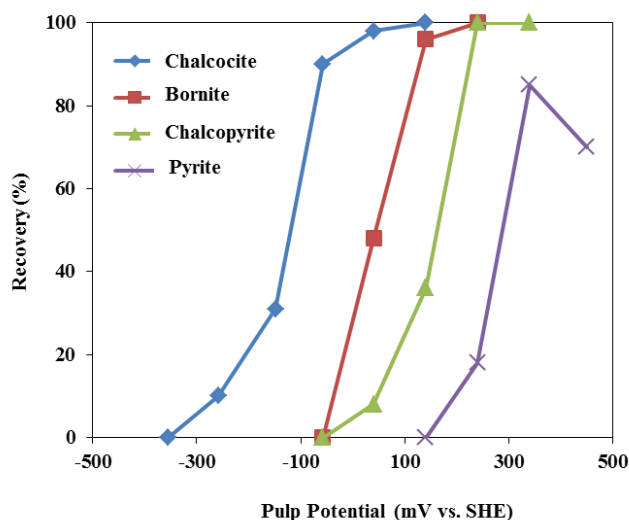


Figure 2.7 Relationship between flotation recovery and conditioning potential for chalcocite, bornite, chalcopyrite, and pyrite in modified Hallimond cell in nitrogen purged borate solution in the presence of ethyl xanthate concentration (Adapted from Richardson and Walker (1985)).

Overall, grinding media has a significant influence on pulp potential during grinding, which can affect the oxidation of mineral surfaces and grinding media and the adsorption of collectors. In addition, due to the strong electrochemical reactions and relatively long grinding time required for regrinding to produce fine particles, the pulp potential may have a more significant effect on subsequent flotation compared with primary grinding.

2.3.2.3 Effect of grinding media on separation of different sulphide minerals

The effect of grinding media on separation of different minerals has also been studied. Different sulphide minerals have different electrochemical properties, and hence may respond differently to the iron contamination and pulp chemistry generated by the grinding media, resulting in a selective separation between these minerals.

Wang and Xie (1990) observed that better flotation selectivity could be achieved in the separation of chalcopyrite, galena and sphalerite from pyrite when the ore or the mineral mixture was ground in porcelain and stainless steel mills rather than in an iron mill. With ceramic or stainless steel

media, the more active sulphide mineral, such as chalcopyrite, galena or sphalerite, was oxidized initially to form a sulphur rich surface, thus exhibiting good flotation response. Due to the galvanic interaction between different minerals, oxygen reduction took place on the nobler sulphide mineral such as pyrite and its surface then showed less affinity to collector xanthate due to a reducing surface state. This hypothesis was confirmed by some later research results. Peng et al. (2003a) observed that 30 wt% chromium grinding media produced higher chalcopyrite flotation and lower pyrite flotation than mild steel media, benefitting the separation of chalcopyrite from pyrite. Apart from the electrochemical explanation by Wang and Xie (1990), another important reason suggested by Peng et al. (2003a) is that the pyrite activation was prohibited under an oxidizing environment during grinding with 30 wt% chromium medium. Peng et al. (2003b) also studied the effect of grinding media on the separation of galena from pyrite. They found that the grinding condition with 30 wt% chromium medium and oxygen purging produced an amount of iron oxidation species which depressed pyrite flotation significantly but depressed galena flotation only slightly, resulting in the highest galena selectivity against pyrite. A similar conclusion was also made by Huang (2005) in the study of the copper–lead–zinc sulphide ore from Newmont’s Golden Grove Operation. It was found that the enhanced selectivity of chalcopyrite against sulphide gangue minerals was achieved by using both high chromium grinding media and low oxygen content during grinding, and that mild steel grinding media depressed the flotation of all the sulphide minerals due to the high amounts of iron oxidation species.

However, the inert grinding media does not always produce better flotation than the forged steel. Some experimental results indicated that mineral selectivity can be reduced when the minerals were ground in an oxidizing environment provided by stainless steel or ceramic medium, but was improved after grinding in a reducing environment provided by mild steel media (Van Deventer et al. 1991, Yuan et al. 1996b, Leppinen et al. 2000). Kinal et al. (2009) investigated the effect of grinding media on lead-zinc flotation in a lead cleaner circuit. Interestingly, iron hydroxide surface coatings from forged steel grinding media were effective depressants for sphalerite, and the use of high chrome media was potentially detrimental to lead cleaner flotation due to the difficulty in depressing sphalerite. It was also found that a 1% chrome alloy produced the desired pulp chemistry to yield an increase in lead concentrate grade through the rejection of sphalerite. This study indicates that the selection of grinding media should depend on the specific ore properties and operation conditions, and the composition of grinding media can be adjusted to provide the most suitable grinding chemistry for the subsequent mineral flotation.

Moreover, the effect of grinding media on the separation of different minerals has also been found to be highly dependent on the subsequent flotation conditions. Yuan et al. (1996a) investigated the copper-zinc selectivity after grinding with both stainless steel media and mild steel media, and various gases were used in subsequent flotation. It was found that stainless steel media always gave good copper flotation regardless of the flotation conditions. However, Cu/Zn selectivity showed a strong dependence on the flotation gases after grinding with mild steel media. Similar results were also found in the Cu/Fe selectivity (Yuan et al. 1996b).

Overall, past studies have demonstrated that grinding media can influence subsequent mineral flotation and separation of different minerals through the production of iron contamination species and the generation of different pulp chemistry. After regrinding, as most of the particles are reduced to a fine or ultra-fine fraction, it will be more difficult to separate the valuable minerals from gangue minerals, and the loss of fine particles into flotation tailings is becoming one of the biggest challenges in many mineral processing plants. In addition, the galvanic interactions between the grinding media and the fine particles may become stronger due to the larger particle surface area. Therefore, it is more important to tailor the regrinding chemistry of the system to achieve the best metallurgical performance by correct selection of grinding media.

2.3.3 Effect of grinding pH on flotation

The floatability of sulphide minerals is highly dependent on the pH during flotation. For example, lime is usually used to create a high alkaline condition during flotation to depress pyrite. Although there are still some debates on the depression mechanism, it is generally agreed that the depression is related to the formation of a mixed film of $\text{Fe}(\text{OH})_3$, $\text{FeO}(\text{OH})$, CaSO_4 or CaSO_3 on pyrite surfaces, which reduces the pyrite floatability by preventing collector adsorption (Bulatovic 2007). However, a high pyrite flotation recovery can be achieved at a pH value of 4 to 5 (Leppinen 1990, Zhang et al. 1997). Generally, the dependency of mineral floatability on pH is due to the different surface species formed at different pH values which not only influence the mineral surface hydrophobicity but also affect the collector adsorption (Cases et al. 1993).

During grinding, fresh mineral surfaces are produced, and the pH has a significant effect on the formation of surface species. In addition, the oxidation of steel grinding media is pH dependent. Therefore, the grinding pH may have a significant influence on subsequent flotation. Ahn and Gebhardt (1991) observed that the chalcopyrite floatability was highly related to grinding pH. For

grinding with high carbon steel in a nitrogen-purged atmosphere, low grinding solution pH was detrimental to chalcopyrite recovery at constant flotation pH, and chalcopyrite floatability was enhanced during grinding at higher pH values as a result of lower galvanic interactions resulting from the passivation of steel media at higher pH. However, when the minerals were ground with high-carbon steel in the presence of air, chalcopyrite flotation was not significantly affected by grinding pH. This was consistent with polarization measurements of chalcopyrite and high-carbon steel electrodes which were not significantly affected by pH changes in the presence of air.

The effect of grinding pH on chalcopyrite flotation was also studied by Peng (2003) by using a Magotteaux Mill[®] which allowed the pulp chemical environment to be monitored and manipulated during grinding in a rod mill (Greet et al. 2004). It was found that the chalcopyrite recovery increased slightly with pH increasing from 7 to 11 after grinding with mild steel, however, the recovery decreased slightly after grinding with 30% chromium steel medium. The same trend was found in the chalcopyrite-pyrite mixture test. Similar to the previous study by Ahn and Gebhardt (1991), it was suggested that the effect of pH on chalcopyrite flotation was related to the amount of iron oxidation species produced during grinding. EDTA extraction tests showed that, with an increase in grinding pH, the production of iron oxidation species increased when using 30 wt% chromium medium, but decreased when using mild steel medium. In summary, as studied by Ahn and Gebhardt (1991) and Peng (2003), the grinding pH mainly influences the flotation of chalcopyrite through the oxidation of grinding media which produces iron oxidation species and contaminates the mineral.

Peng (2003) studied the effect of different grinding pH on pyrite flotation. It was observed that the pyrite recovery was low after grinding without copper activation with either mild steel or stainless steel media, and the recovery just slightly decreased with pH increasing from 7 to 11. After being mixed with chalcopyrite, the pyrite recovery was significantly increased after grinding at pH 7 and 9, however, the recovery almost dropped to 0 after increasing grinding pH to 11. According to the analysis of surface species by EDTA extraction, it was proposed that most Cu^{2+} deposited on the pyrite surface in the form of copper hydroxide at pH 11, which depressed the pyrite floatability rather than activated pyrite due to the hydrophilic nature of these species. The same trend was found in galena-pyrite mixture tests and the pyrite recovery after grinding at pH 7 with 30% chromium medium was significantly higher than that at other pH values. Therefore, the presence of other minerals should be considered when studying the effect of grinding chemistry on the floatability of one particular mineral.

Since grinding pH can influence the formation of surface species, the collector adsorption in the subsequent flotation may be also affected. Cases et al. (1992) studied the effect of grinding pH (from 4.0 to 12.5) on the floatability of finely ground galena. At low collector concentrations, galena flotation recovery increased with grinding pH up to a pH value of 11.0 and then decreased with further increase in pH values. However, at high collector concentrations, the trend was reversed. The authors proposed that the effect of grinding pH on galena flotation was dependent on the oxidation species formed on the galena surface which influenced the adsorption and abstraction of the xanthate collector. The conclusion was further confirmed by infrared measurements which suggested that mineral surface oxidation during grinding led to the formation of PbS_2O_3 in acidic conditions, and PbS_2O_3 and basic lead carbonate in neutral or alkaline conditions. Peng (2003) also observed an increase of iron oxidation or lead oxidation species after grinding galena at higher pH, resulting in a slightly decreased flotation recovery.

In summary, the literature review indicates the importance of grinding pH on the formation of various surface species and on the collector adsorption which have a direct influence on mineral floatability. During regrinding, as particles are reduced to fine and ultra-fine fractions and the surface area has a significant increase, the pH may play a more important role in the electrochemical reactions occurring in the grinding mill. Furthermore, some surface species are carried to grinding mill from the flotation concentrates and, therefore, the regrinding pH will affect not only the surface oxidation but also the interaction of these species with the mineral surfaces, and finally more significantly influence the mineral surface hydrophobicity.

2.3.4 Effect of gas purging during grinding on flotation

Gas purging during grinding is not a common practice in mineral processing plants, however, its effect on mineral flotation has been widely investigated in the laboratory. Oxygen, air and nitrogen are the three most used gases in laboratory studies. Gas purging mainly changes the dissolved oxygen concentration and the pulp potential in the slurry, and then affect the sulphide mineral oxidation, grinding media corrosion and also collector adsorption in the subsequent flotation.

As discussed previously, the self-induced flotation of chalcopyrite is highly dependent on the pulp potential, and it only occurs under mild oxidizing conditions due to the formation of hydrophobic sulphur rich surfaces. Dissolved oxygen can affect pulp potential to a great extent and then influence the mineral floatability. Ahn and Gebhardt (1991) purged air and nitrogen during grinding

and studied the effect of grinding atmosphere on the self-induced flotation of chalcopyrite. At the same flotation conditions for both stainless steel and high carbon steel grinding media, the floatability of chalcopyrite was markedly higher after grinding in an air-purged mill than in a nitrogen-purged mill. The result is consistent with the collectorless flotation of chalcopyrite under mildly oxidizing conditions in the conditioning and flotation stage as discussed in previous section.

Gas purging not only affects the mineral surface properties but also influences the grinding media corrosion. As discussed in section 2.3.1, air purging can increase the galvanic interaction during grinding, and correspondingly accelerate the oxidation of steel grinding media. Yelloji Rao and Natarajan (1988) demonstrated that the presence of oxygen caused more iron species from grinding media to be present on the chalcopyrite surface and therefore reduced chalcopyrite recovery in flotation. However, Peng et al. (2003a) found that gas purging had little effect on chalcopyrite flotation after grinding with both mild steel and 30 wt% chromium grinding media. They suggested that this effect was closely associated with the presence of hydrophilic iron oxidation species and hydrophobic sulphur rich species present on the chalcopyrite surface. The increased oxygen concentration not only increased iron oxidation species from grinding media but also increased the presence of sulphur rich species. As a result, the purging gas had little effect on chalcopyrite surface hydrophobicity.

Peng (2003) also investigated the effect of gas purging on pyrite flotation after grinding with high chromium grinding media. It was found that nitrogen purging produced a slightly higher pyrite recovery than oxygen purging, and the reduced iron oxidation species should be responsible for this effect. However, Huang (2005) found that, after grinding with mild steel media, the pyrite recovery with nitrogen purging was much lower than that with air and oxygen purging. This may be caused by the extremely low pulp potential under nitrogen purging inhibiting the interaction of xanthate collector with pyrite surfaces in the subsequent flotation. This study indicates that gas purging during grinding can also influence the pulp chemistry in the subsequent flotation.

The effect of gas purging during grinding on mineral separation has also been studied. Yuan et al. (1996b) used an air-purging mild steel mill to test the influence of air content in grinding on Cu/Fe sulphide separation. The results showed that air grinding gave no advantage in chalcopyrite selectivity against pyrite compared with ordinary closed mild steel grinding. However, the flotation atmosphere was more important after grinding with mild steel media and the selectivity was significantly enhanced when using air as a flotation gas. The ineffectiveness of air purging in mill

was explained by the low gas dissolution and diffusion rates in the pulp during grinding caused by the high pulp density and viscosity in the mill and the formation of a surface film of metal oxides/hydroxides, therefore, the purged air cannot effectively react with minerals. Similar results were also reported by Peng et al. (2003a) who found that the purging gas did not influence the separation of chalcopyrite from pyrite during grinding with both stainless steel and mild steel media. However, Peng et al. (2003b) observed that the galena selectivity against pyrite was significantly influenced by purging gases. The grinding condition with 30 wt% chromium medium and oxygen purging produced an amount of iron oxidation species which depressed pyrite flotation significantly but depressed galena flotation only slightly, resulting in the highest galena selectivity against pyrite. In a copper–lead–zinc sulphide ore study by Grano and Huang (2006), the enhanced selectivity of chalcopyrite against sulphide gangue minerals was achieved by using both high chromium grinding media and nitrogen purging during grinding. The authors suggested that nitrogen purging inhibited chalcopyrite and galena oxidation, and then reduced copper/lead activation of pyrite, improving the selectivity.

Overall, the gas purging during grinding has a significant influence on the mineral surface oxidation, grinding media corrosion, and the pulp chemistry in both grinding and flotation stage, which all play important roles in the subsequent flotation and the separation of different minerals,

2.3.5 Effect of grinding chemistry on flotation of fine particles

This thesis study will focus on regrinding and cleaner flotation, which mainly deal with fine and ultra-fine particles. For example, the mineral industry has commenced processing low grade ores by regrinding the composite particles to P_{80} values less than 10 μm in order to achieve sufficient liberation of the contained valuable minerals (Johnson 2006), such as, the McArthur River concentrator in the Northern Territory (Nihill et al. 1998), the Mount Isa lead zinc concentrator in North Queensland (Young and Gao 2000), and the Century Zinc concentrator in north-west Queensland (Burgess et al. 2003). It is well known that the floatability of particles is highly dependent on their size. The fine particles are usually more difficult to be recovered by flotation, which was believed to be primarily caused by the low particle-bubble collision efficiency. In addition, recent studies have demonstrated that the fine particles are more strongly affected by the grinding chemistry than the intermediate and coarse particles and therefore can be more easily oxidised or contaminated, which may play a more important role in the low floatability of fine

particles (Bruce 1976, Grano et al. 1994, Cullinan et al. 1999, Huang et al. 2006, Johnson 2006, Grano 2009, Peng and Grano 2010a).

A study by Grano et al. (1994) on a copper ore at plant scale indicated that the recovery of fine (-8 μm) chalcopyrite was much lower after grinding in a conventional plant ball mill with mild steel media than in a fully autogenous plant mill due to the iron hydroxide present in the system. However, the recoveries of intermediate and coarse particles were not influenced by the different grinding conditions. Therefore, it was suspected that the iron oxidation species may preferably adsorb on fine particles, or the floatability of the fine particles was more significantly influenced by these hydrophilic species. Huang et al. (2006) also found that fine particles of arsenopyrite (-10 μm) were more adversely affected by iron hydroxides emanating from grinding media sources than intermediate (-40 + 20 μm) sized particles. Fully inert grinding media, such as ceramic beads, have been used in stirred mills for fine grinding purpose. Grano (2009) observed that the ceramic media was more beneficial to the flotation of fine chalcopyrite than the mild steel media, and the fine chalcopyrite was affected to a greater extent than the other size fractions. Several case studies in the plant from different ore bodies have also shown that the flotation rate of fine particles were significantly improved after using inert grinding media (Pease et al. 2006a, Pease et al. 2006a). Grano (2009) attributed the detrimental effect of iron hydroxide on fine particles to the decreased particle-bubble attachment due to the reduced surface hydrophobicity. At a critical coverage of iron hydroxide on fine particles, bubble attachment no longer took place and the fine particles reported to the tailings as a non-floating component. In addition, De F. Gontijo et al. (2007) observed that fine chalcopyrite particles (-10 μm) required a higher critical contact angle to affect their attachment to bubbles when compared with intermediate sized particles. Thus the floatability of fine particles was more affected by the coverage of iron hydroxide.

A recent comprehensive study by Peng and Grano (2010a) further confirmed the critical influence of grinding chemistry on the flotation of fine particles and the mechanisms were investigated by applying advanced surface analysis techniques. Figure 2.8 shows the effect of different grinding conditions on the flotation of galena and chalcopyrite on a particle size basis. It is obvious that fine galena and chalcopyrite (-10 μm) were affected by different grinding media and gas purging to a much greater extent than intermediate size fractions (+10-53 μm). Mechanisms were investigated by rest potential measurement, ToF-SIMS analysis, mineral dissolution study and zeta potential measurement. It was found that fine particles were more easily oxidised than intermediate particles resulting in a higher concentration of metal oxidation species on the surface, enhancing the

adsorption of iron oxidation species at pH 9 by electrostatic interactions. In addition, fine oxidized galena had a stronger affinity for iron oxidation species than fine oxidized chalcopyrite and therefore was more affected by the control of iron oxidation contamination.

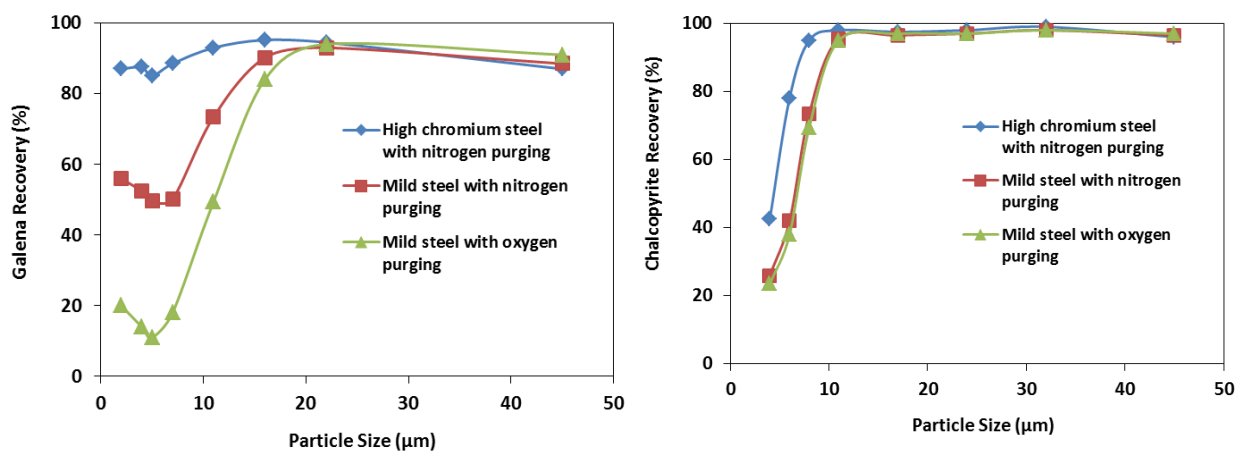


Figure 2.8 Galena and chalcopyrite flotation recovery on a size-by-size basis after grinding at different conditions (adapted from Peng and Grano (2010a)).

To sum up, past studies have shown that the floatability of fine particles could be more affected by various grinding conditions compared to the intermediate and coarse particles. Regrinding reduces most of particles to fine and ultra-fine fractions, therefore, it is anticipated that the regrinding chemistry may play a more important role in subsequent cleaner flotation than the primary grinding chemistry.

2.3.6 Effect of grinding chemistry on pyrite activation by copper ions

2.3.6.1 Pyrite activation mechanism by copper ions

Pyrite is often associated with copper sulphide minerals, such as, chalcopyrite and chalcocite. The Cu^{2+} ions can be dissolved from copper minerals during grinding or conditioning, and then activate the pyrite flotation, increasing the pyrite floatability (Finkelstein 1997). The activation mechanism has been widely studied for several decades. The first mechanism was proposed by Bushell and Krauss (1962), who suggested that the oxidation of pyrite by Cu^{2+} with the formation of elemental sulphur was responsible for this activation. However, this mechanism was questioned by Mellgren et al. (1974), because no heat of adsorption of Cu^{2+} on pyrite could be detected. Nicol (1984) suggested that Cu^{2+} caused a catalytic oxidation of pyrite surface leading to the formation of

elemental sulphur, inducing pyrite flotation. From cyclic voltammetry studies, Richardson et al. (1996) suggested that the formation of Cu_2S was responsible for the activation, and the reduction process may attribute to the formation of S^0 . XPS technique was also used to detect the activation species, and most of the studies showed a new Cu^+ sulphide species formed on the pyrite surface. However, the exact nature of this sulphide species is still in debate. Voigt et al. (1994) suggested that Cu^+ on pyrite was bonded in a CuS_2 or $(\text{Cu}, \text{Fe})\text{S}_2$ surface species. Laajalehto et al. (1999) demonstrated that the new phase on the copper activated pyrite was probably a chalcopyrite type (CuFeS_2), and the reduction of Cu^{2+} was compensated by the oxidation of iron when chalcopyrite was formed. Weisener and Gerson (2000) proposed that the reduction of Cu^{2+} to Cu^+ was accompanied by oxidation of S_2^{2-} to S_2^{1-} or S_n^{2-} , which was supported by the increased S_2^{2-} signal in the XPS spectrum.

The improved pyrite flotation by copper activation is mainly caused by the increased collector adsorption on activated pyrite surfaces. Without copper activation, the xanthates adsorb on pyrite surface via dixanthogen formation, especially at an acidic pH. This interaction involves the oxidation of xanthate to dixanthate with surface Fe^{3+} being reduced to Fe^{2+} (Leppinen 1990, Buckley 1994, Valdivieso et al. 2005). However, the adsorption of collector on un-activated pyrite surface is minimal at alkaline conditions. When Cu^{2+} ions are present, copper xanthate is formed on the pyrite surface (Zhang et al. 1997, Laajalehto et al. 1999), which is responsible for the increased pyrite floatability. Although both Cu^+ and Cu^{2+} adsorb on pyrite surface, using XPS, Voigt et al. (1994) demonstrated that there were no Cu^{2+} -xanthate species formed on pyrite surface after the treatment of copper-activated pyrite in xanthate solutions. They also proposed that Cu^+ -xanthate species on copper-activated pyrite could be formed from both Cu^+ and Cu^{2+} and the pH range of 6-9 was the most favourable for the adsorption of xanthate. Shen et al. (2001) studied the effect of copper concentration on the xanthate adsorption and reported that Cu^+ -xanthate was the only product when the ratio of them was 1:1. However, under other ratios, dixanthogen was produced, and if the copper concentration was higher, Cu^{2+} -xanthate was also detected.

In summary, the pyrite activation by copper ions can significantly improve the pyrite floatability. The schematic representation of pyrite activation by Cu^{2+} is shown in Figure 2.9. Although there are still some debates about the exact activation species, it is generally agreed that the activation is mainly due to the reduction of Cu^{2+} to Cu^+ on the surface and the formation of a new copper sulphide phase on the surface while S_2^{2-} is oxidized to S_2^{1-} or S_n^{2-} . Subsequently, the collector can adsorb on the copper sulphide phase, resulting an improved hydrophobicity.

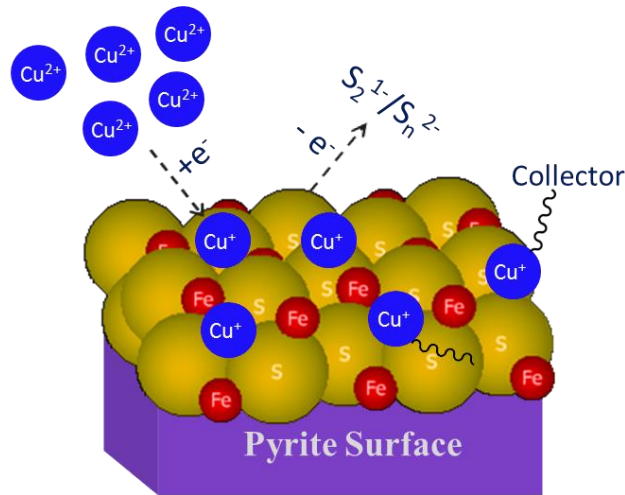


Figure 2.9 Schematic representation of pyrite activation by Cu^{2+} .

2.3.6.2 Effect of grinding chemistry on pyrite activation

Since the pyrite activation by copper ions is an electrochemical process, it can be influenced by grinding chemistry, such as the pulp chemistry (pH, Eh, and DO) and different grinding media.

Bushell and Krauss (1962) investigated copper activation by measuring the residual copper in cuprammonium solutions and concluded that in order to activate pyrite, the copper concentration and solution pH had to fulfil the following relation:

$$\text{LogCu}^{2+} + 2\text{pH} > 4.72 \quad (2.25)$$

Apparently, copper activation of pyrite is highly dependent on solution pH. Wang et al. (1989) investigated the adsorption of Cu^{2+} on pyrite in both acidic and neutral pH. It was found that the removal of Cu^{2+} by pyrite in acidic media was exceedingly slow. With an increase in solution pH, the copper adsorption rate increased. Voigt et al. (1994) also found that pH had a large effect on Cu^{2+} adsorption but had little effect on Cu^+ adsorption. As shown in Figure 2.10, the amount of Cu^{2+} adsorbed increased with solution pH to 9 and then decreased. After 30 min of reaction, a similar amount of Cu^+ was adsorbed at all pH values. Furthermore, they found that adsorption time influenced the interaction of Cu^{2+} with pyrite. A fast saturation of the pyrite surface with Cu^+ was observed at pH 5, whereas the Cu^+ uptake started only slowly at pH 8 and 10. Prolonged conditioning in alkaline solution resulted in a precipitation of Cu^{2+} hydroxy species, which was also observed by Weisener and Gerson (2000). Simultaneously, the amount of adsorbed Cu^+ increased

until the same Cu^+ level was reached as in acidic media. Different pH can also influence the collector adsorption on activated pyrite. Lai et al. (1990) studied the adsorption of xanthate on activated and non-activated pyrite at different pH. It was found that acidic pH favoured the adsorption of xanthate on non-activated pyrite, whereas the neutral pH range is most favourable for the xanthate adsorption on activated minerals. Further studies showed that copper activation significantly increased pyrite recovery within pH 6-10 (Leppinen 1990, Zhang et al. 1997, Dichmann and Finch 2001).

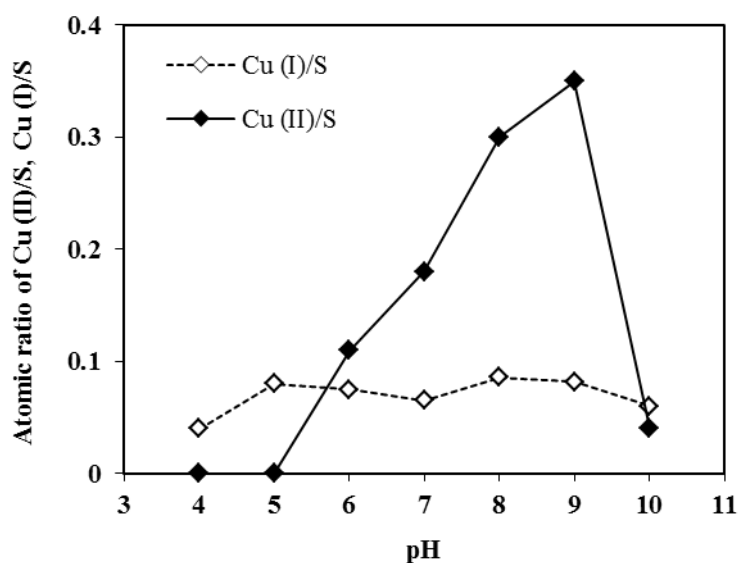


Figure 2.10 Atomic ratios of Cu(I)/S and Cu(II)/S taken from the Cu 2p and S 2p XPS spectra of pyrite after 30 min of copper activation at different solution pH (Adapted from Voigt et al. (1994)).

Pyrite activation by copper ions was also found to be strongly dependent on the redox potential of the activating solution. By using voltammetric techniques, Richardson et al. (1996) found that increases in oxidizing potential inhibited copper uptake while increases in reduction potential promoted copper uptake. This result is in agreement with Laajalehto et al. (1999) who studied the influence of electrode potential on activation of pyrite by copper ions using the XPS technique. Peng et al. (2012) adjusted the pulp potential during grinding by adding oxidizing or reducing reagents and studied its effect on the pyrite activation by copper ions. It was found that the reducing environment benefited the activation, while, the oxidation environment inhibited the activation process. This phenomenon was explained by the activation mechanism. A reducing potential favours the reduction of Cu^{2+} to Cu^+ and hence the formation of Cu^+ -sulphide, while an oxidizing potential inhibits this reaction and prohibits the activation process.

The dissolved oxygen concentration plays an important role in the electrochemical reactions and hence may also influence the pyrite activation. As studied by Wang et al. (1989), oxygen decreased copper adsorption especially in solutions with lower pH values. They pointed out that ferric hydroxides caused by pyrite oxidation inhibited copper adsorption but Cu^{2+} could diffuse from the solution through the hydroxide film into the inner surface. However, the study by Peng et al. (2003a) shows that different purging gases did not influence copper activation. This result was confirmed by the EDTA extraction and XPS tests which showed that the amount of copper hydroxides or copper sulphides on the pyrite surface was similar after grinding with oxygen or nitrogen purging.

The grinding media have a significant effect on pulp chemistry and the production of iron contamination species, as discussed in section 2.4.1. Therefore, the activation of pyrite by Cu^{2+} may also be influenced by different grinding media. Peng et al. (2003a) studied the effect of different grinding media on pyrite activation in the presence of copper ions. It was found that a higher pyrite recovery was achieved by using mild steel media than high chromium steel media. The copper activation was more effective during grinding with mild steel media, which was confirmed by EDTA extraction and XPS results, showing that grinding with mild steel media resulted in more copper sulphide species transformed. Although a large amount of iron oxidation species was produced during grinding with mild steel media, the flotation of copper activated pyrite was not depressed. The authors explained this by examining the surface electrical properties of minerals and metal hydroxides (Peng and Grano 2010a). The new copper sulphide phase formed during pyrite activation by Cu^{2+} was similar to chalcopyrite with its zeta potential being negative at pH 9.0. Iron hydroxide colloidal particles were also negatively charged at pH 9.0. Therefore, the iron oxidation species from grinding media was electrostatically repulsive with respect to copper-activated pyrite, and not likely to depress its flotation (Peng and Grano 2010a).

Overall, the pyrite activation by copper ions can significantly improve the pyrite floatability and was found to be dependent on grinding chemistry, such as pulp chemistry and grinding media. During regrinding, a large amount of fresh surfaces is produced, which can also be activated in the presence of copper ions. Therefore, it is important to further investigate the potential effect of regrinding conditions on pyrite activation.

2.4 Particle breakage mechanisms during regrinding and their effects on flotation

2.4.1 Particle breakage mechanisms during regrinding

A wide range of grinding mills is being used in mineral processing, such as, rod mill, ball mill, and high intensity stirred mill. Different mills not only have different energy efficiency but also present various particle breakage mechanisms. Generally, there are three types of particle breakage mechanisms: abrasion, compression, and impact, as illustrated in Figure 2.11 (Kelly and Spottiswood 1982). In practice, breakage mechanisms do not occur in isolation, but with one normally dominating. Gao and Forssberg (1995) proposed that compression was more related to crushers, impact to tumbling mills and abrasion to stirred mills.

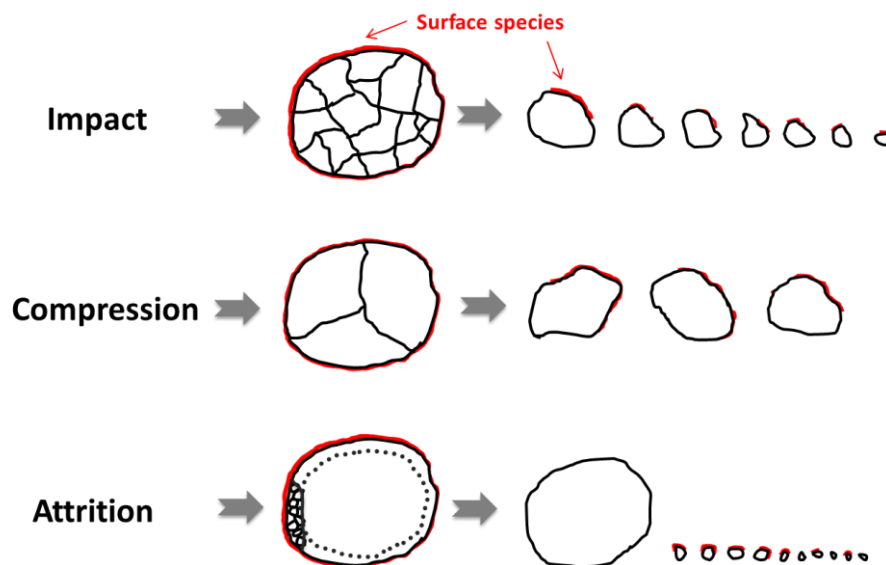


Figure 2.11 Representation of three particle breakage mechanisms (adapted from Kelly and Spottiswood (1982)).

Tumbling mills, such as rod mills and ball mills, are widely used in mineral processing for coarse-grinding in which particles between 5 and 250 mm are reduced in size to between 40 and 300 μm . Tumbling mills are large cylindrical vessels that rotate on their axes at a reasonable speed and the motion is imparted to the charge via the mill shell. The grinding medium is lifted along the rising side of the mill by the action of the mill shell and lifter system until a position of dynamic equilibrium is reached. Then the grinding medium cascades and cataracts down the free surface of the other grinding medium and ore samples. So, it is generally accepted that there are two main size reduction processes: impact and attrition. Impact breakage largely occurs at the toe of the charge

where lifted grinding media fall under the influence of gravity, while, attrition breakage occurs within the bed of grinding media due to relative motion (Wills and Napier-Munn 2006).

As grinding is the single largest energy consuming process in mineral processing plant, the development of energy efficient mills is always of high interest in the industry. For some fine grained ores, fine (15 – 40 μm) and ultra-fine (< 15 μm) grinding become necessary to liberate the valuable minerals from gangue minerals, with more energy consumed. With regards to size reduction efficiency, the recently developed stirred mills are much more efficient than tumbling mills (Jankovic 2003), and have been extensively used for fine and ultra-fine grinding (Young and Gao 2000, Gao et al. 2002, Pease et al. 2006a). In contrast to tumbling mills, where motion is imparted to the charge via the rotating mill shell, in stirred mills the mill shell with either a horizontal or a vertical orientation is stationary and motion is imparted to the charge by the movement of an internal stirrer. Therefore, it has been assumed that the movement of the stirrer through the bed of grinding media, and the sliding/rolling motion that this imparts to the charge itself, provides a solely attrition breakage environment. However, recent studies suggest that impact breakage mechanisms may also exist in stirred mills, and the proportion of impact and attrition varies from case to case (Kwade and Schwedes 2002, Yue and Klein 2005, Roufail and Klein 2010).

Different particle breakage mechanisms significantly influence the particle size distribution, particle shape, liberation and particle surface properties. All of them play an important role in the subsequent flotation, which will be discussed in the following section.

2.4.2 Effect of particle breakage mechanisms on flotation

2.4.2.1 Particle size distribution and its effect on flotation

It has been well known that the particle size is one of the most important factors affecting the mineral floatability. Typical mineral recovery as a function of particle size is shown in Figure 2.12, and the maximum recovery is typically between 20 - 150 μm (Trahar 1981, Pease et al. 2006a). The low floatability of coarse particles is mainly due to the particle-detachment from bubbles as a result of turbulence within the pulp and upon hitting the pulp-froth interface (Schulze 1977, Crawford and Ralston 1988, Vera et al. 1999, Seaman et al. 2006). In addition, increasing the particle size may result in longer induction times that affect attachment efficiency and a commensurate deterioration in floatability (Feng and Aldrich 1999). Moreover, it has been shown that, per unit surface area,

coarse particles require more adsorbed collector compared to intermediately sized particles in order to be recovered (Crawford and Ralston 1988).

The main focus of this thesis study is the flotation of the fine particles produced after regrinding, which also present a lower floatability as shown in Figure 2.12. The most important reason that fine particles are usually difficult to be recovered by flotation is the low particle-bubble collision. Additionally, as discussed in the section 2.3.5, the fine particles are more susceptible to the grinding chemistry. For example, the iron hydroxides prefer to coat on fine particles rather than intermediate and coarse particles. Moreover, it was found by Crawford and Ralston (1988) that the fine particles required more surface coverage of collector in order to float compared to intermediate particles. Johnson (2006) also observed that fine particles were more easily to be lost in tailings due to the insufficient collector addition, which is often necessary to depress the flotation of sulphide gangue.

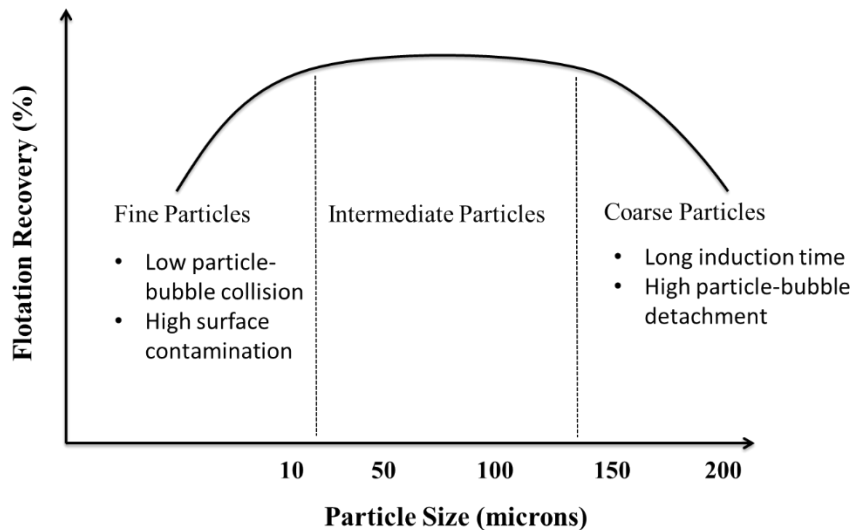


Figure 2.12 Mineral recovery as a function of particle size.

Since the particle size can significantly influence mineral floatability, the particle size distribution after grinding for a target P_{80} may also have an effect on the subsequent flotation recovery. The particle size distribution of minerals after grinding strongly depends on the particle breakage mechanisms. Abrasion tends to give a narrow size distribution, impact a broad one and compression an intermediate one (Kelly and Spottiswood 1982). Gao and Forssberg (1995) investigated size distribution differences between ball mill grinding and stirred mill grinding. In ball mill grinding, as the process proceeded, the amount of fine particles accumulated gradually. The product size distributions overlapped each other based on grinding times or the level of energy input. However,

in stirred mill grinding, the discretised size distributions from different grinding times had a similar form and moved forward to the finer end. The disappearance of particles larger than the median size and the creation of particles smaller than the median size take place continuously (Gao and Forssberg 1995). The specially designed stirred mill such as Isamill has a separator which keeps the media and coarse particles inside the mill allowing only the fine product to exit. This special design together with the attrition mechanism makes the Isamill to provide a much sharper size distribution benefiting the flotation recovery of the fine particles in the plant operation (Bruce 1976, Pease et al. 2006a, Pease et al. 2006a).

Ye et al. (2010a) compared the particle size distributions of pyrrhotite after regrinding using the Magotteaux Mill and the Isamill. It was observed that the Magotteaux Mill always produced a broader size distribution and more fine particles than the Isamill, especially for the finer regrinding (P_{80} of 20 and 10 μm). The BET surface area of Isamill product was a little higher than that of Magotteaux Mill product, which was attributed to the aggregation of ultra-fine particles produced by Magotteaux Mill. The reduced production of fine particles with Isamill grinding increased the overall recovery. Pease et al. (2006a) also suggested that grinding technology which minimised the production of fine particles would assist with improving recovery and selectivity. The effect of size distribution after regrinding on flotation and separation will be addressed in this study by using tumbling mill and stirred mill, respectively.

2.4.2.2 Particle shapes and their effects on flotation

A number of studies have shown that the shape properties of various materials can be influenced by different comminution methods due to their different particle breakage mechanisms (Ulusoy et al. 2003, Ulusoy et al. 2004, Yekeler et al. 2004). Andreatidis (1995) investigated the shape properties of rougher concentrates from Mt. Isa and McArthur River lead-zinc ores after grinding by a ball mill and a stirred mill, respectively. It was found that the general particle shape was governed by the ore matrix with surface roughness dependent upon ore grain texture. The breakage mechanisms only seemed to affect the degree of particle rounding (removing of edges) and the size of the breakage fragments produced. Ball milling with iron balls provided a system which was dominated by an impact grinding mechanism. It was found that a wide range of particle shapes with sharper, angular surface features were produced. The stirred mill exhibits an attrition mechanism independent of particle size. It was found that the attrition of particles, by surface erosion or chipping at edges or corners, was more likely to cause rounding of particles although the small

fragments removed were quite irregular in shape. The process also seems to grind particles of high aspect ratio (columnar/acicular particles) at a greater rate (Andreatidis 1995).

The particle shape also has implications for downstream flotation. Anfruns and Kitchener (1977) found that the flotation collection efficiencies of angular quartz were higher than those of spherical ballotini particles. Similar trends were also reported recently by Koh et al. (2009), as shown in Figure 2.13. The angular particles present a higher floatability than spherical particles at all size fractions resulting from a faster rate of film thinning and rupture at rough surfaces. In another study by Verrelli et al. (2014), the induction period for attachment was directly measured by using Milli-Timer apparatus to directly observe the process of particle-bubble interaction and attachment by means of a magnified, high-speed video recording. The results were consistent with previous studies, with angular particles exhibiting induction periods that were an order of magnitude lower than those of spheres, further illustrating the importance of particle shape on induction period. However, the materials used in these studies are either highly spherical or highly angular, which cannot represent the products generated by practical grinding methods.

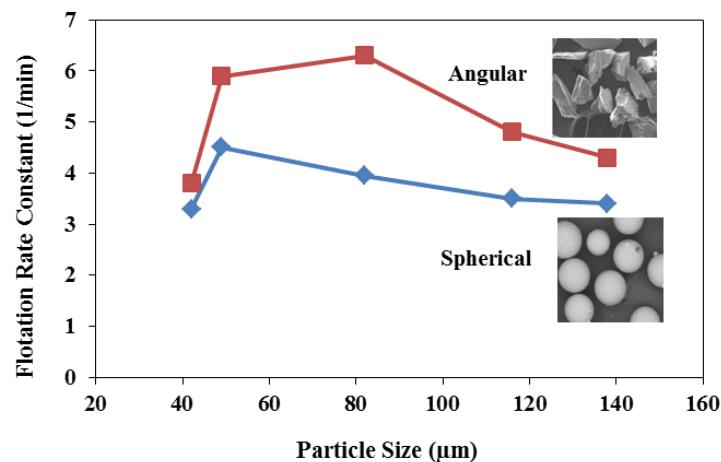


Figure 2.13 Flotation rate as a function of particle size for angular and spherical particles and SEM micrographs of both particles (Adapted from Koh et al. (2009)).

Another important study regarding the effect of particle shapes on flotation has been conducted by Vizcarra (2010) in a condition similar to that in the practical application. The particle angularity properties of sized chalcopyrite concentrates from a micro-flotation cell were quantified by using a Mineral Liberation Analyzer (MLA). When floated in the absence of collector, angular chalcopyrite particles floated faster than comparatively round particles when the feed material was characterized

with a distribution of particle angularities. However, when the floatability of chalcopyrite was high (following conditioning with PAX), no relationship was found between shape properties, surface chemistry and the rates at which particles reported to the concentrate. This could possibly indicate that the contribution of shape properties towards particle floatability may only be significant for weakly hydrophobic minerals.

Overall, different particle breakage mechanisms during grinding may generate different particle shape properties which can more or less affect their flotation behaviour depending on the ore type and flotation condition.

2.4.2.3 Mineral liberation and its role in flotation

Liberation of valuable minerals from surrounding host rock is the most important objective of grinding process. It is impossible to selectively recover valuable minerals into concentrate unless they are well liberated, and the degree of liberation is dependent on the ore type and grind size. For the low grade and fine-grained ores, fine and ultra-fine grinding is becoming a normal practice to increase the liberation. However, the liberation rate is not only dependent on the particle size after grinding but also related to the different particle breakage mechanisms provided by different grinding mills. Andreatidis (1995) studied the liberation differences of McArthur River LGM rougher concentrate after regrinding with stirred mill and ball mill, respectively. It was found, for the very fine size fraction ($P_{80}=8\ \mu\text{m}$), the liberation of both the non-sulphide gangue mineral and sphalerite improved after regrinding with stirred mill. The author suggested that the improvement in liberation was due to both the increased liberation of these minerals in the fine size fractions and the greater proportion of ultra-fine solid produced from stirred milling. The improved liberation in the fine size fraction was attributed to the attrition grinding mechanism predominant in the stirred mill which used low energy breakage and gave fine daughter fragments which were close to the non-sulphide gangue grain size. However, in another study of Mount Isa LGM (low-grade-middling) rougher concentrate, there was no significant difference observed after grinding in different mills, which indicates the effect of particle breakage mechanisms on liberation is highly dependent on the ore compositions.

Mineral liberation properties also have a significant influence on the floatability of particles. It has been demonstrated by Gaudin (1939) that composite particles are recovered more slowly than fully liberated ones. Sutherland (1989) demonstrated the kinetic rate constant k was dependent not only

on the identity of a phase of interest, but also on the associated minerals in the particle, which was also verified by Lamberg and Vianna (2007). The authors also stated that particles that could be floated only needed to be composed of small proportions of hydrophobic minerals (ca. 10% by mass), and that even small amounts of gangue (ca. 5-20% by mass) were deleterious to the floatability of particles when compared to fully liberated minerals (Sutherland 1989). These observations were supported by the results of flotation recovery as a function of percentage liberation for a given size fraction (Bartlett and Mular 1974, Vianna 2004, Savassi 2006). Recovery increased with increasing the particle liberation, and the gradient was much sharper at both ends of the distribution.

The development of liberation measurement techniques, such as the QEMSCAN and MLA, has enabled the easy measurement of the surface liberation of a population of particles, and can be used to determine the particle size and liberation class of particles in the feed and concentrate, and accordingly, their effect on the flotation recovery or rate constant. Jameson (2012) studied the effect of surface liberation and particle size on flotation rate constants by using the experimental results for the flotation of galena particles. k/k_{max} , the ratio of the rate constant at a given particle size and liberation class, to the rate constant for fully-liberated particles of the same size, was calculated. It was found that the rate constant ratio as a function of liberation was essentially the same for each particle size, and the line of best fit is shown in Figure 2.14. This study indicates that partial surface liberation affects the rate constants of all particles in the same way, independently of particle size.

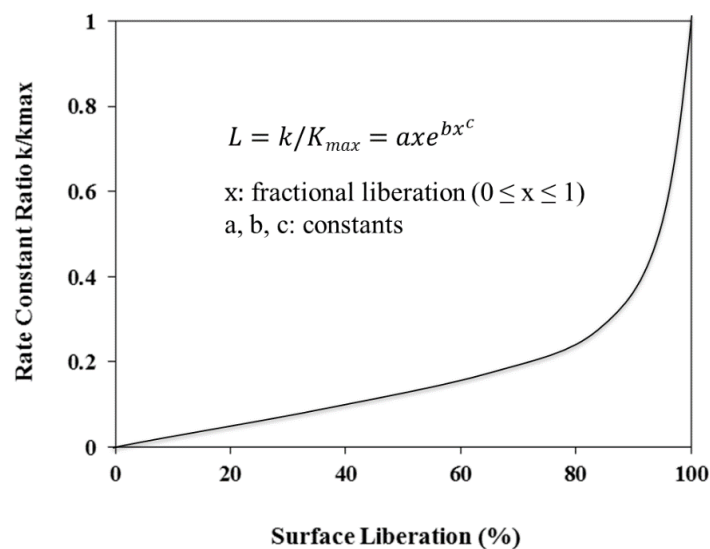


Figure 2.14 Ratio of the rate constant k to the maximum rate constant K_{max} as a function of the liberated class (Adapted from Jameson (2012)).

Overall, the different particle breakage mechanisms provided by different mills can influence the mineral liberation, which plays an important role in flotation, especially the separation of different minerals. In the plant operation, this must be considered when designing and optimizing the regrinding process. However, this thesis study mainly focused on the change of surface chemistry during regrinding, therefore, the liberation will not be considered and will be ruled out by using single minerals.

2.4.2.4 Particle surface and its effect on flotation

As the particle size reduces during regrinding, a large amount of new surface area is created. As shown in Figure 2.11, there are two different types of surfaces produced after regrinding. One is the surface covered by the species carried from primary grinding and rougher flotation, such as the collectors and activation species. The other type of surface is the freshly produced surface. The particle breakage mechanisms obviously have a significant influence on the distribution of surface species. As studied by Ye et al. (2010a), breakage mechanisms in regrinding, may have significant effects on mineral particle surface properties. It is hypothesized that the impact particle breakage mechanism in tumbling mill produces mineral particles partially covered with species from the original particle surface in the initial stage of regrinding. However, as stirred mill employs a comminution mechanism combining the compressional and torsional stresses, it enables a product in the submicron size range to be produced (Gao and Forssberg 1995). It is hypothesized that, in the initial stage of regrinding, stirred mill regrinding produces fine particles with most of the surface species from the original feed particles and intermediate particles with new surface area (clean surfaces). During stirred milling, the abrasion between mineral particles and grinding media may have a great effect on surface cleaning. Huang et al. (2006) observed the increased arsenopyrite recovery after grinding in a stirred bead mill with ceramic media, which was principally accounted by decreased surface contamination from surface oxidation species. Except for the reduced iron contamination by employing ceramic media, the authors suggested that the attrition removed the surface oxidation products from the particle surfaces. Ye et al. (2010b) also reported the surface cleaning action of stirred milling on the surface of chalcocite. It was found that improvement in chalcocite recovery after attrition was dependent on the level of surface contamination and was mainly evident in coarse particle size fractions, while the recovery in fine size ranges was not increased. A trend of hydrophilic species migrating from coarse to fine particles during attrition was revealed by XPS.

Overall, the past studies have revealed that the different particle breakage mechanisms might influence the mineral floatability by the production of different particle surface properties. However, complex changes of surface properties occur during regrinding, such as the generation of new surfaces, the surface oxidation and contamination, and the distribution of various surface species, which all play important roles in subsequent flotation. Therefore, it is important to isolate these factors and to investigate the effect of each factor individually. In this study, the effect of different particle breakage mechanism on the evolution of surface species will be further studied, and ToF-SIMS can be used to obtain more details of this surface difference on a size-by-size basis.

2.5 Conclusions

The conclusions of this literature review can be summarized as follows:

- Pyrite and copper sulphides can be oxidized during grinding due to their semi-conductive nature and the surface oxidation may promote or depress the mineral floatability depending on the mineral properties and oxidizing conditions. Therefore, it is important to comprehensively investigate the mineral surface oxidation during regrinding and their effects on the cleaner flotation in this thesis study.
- During grinding, strong galvanic interactions occur between steel grinding media and sulphide minerals or between different sulphide minerals, which significantly increases the electrochemical reaction rate inside the grinding mill and change the mineral surface properties. The grinding chemistry, such as different grinding media, pH and Eh, has a significant influence on the subsequent flotation and can also affect the pyrite activation by copper ions. In addition, the fine and ultra-fine particles are more susceptible to the grinding chemistry than the intermediate and coarse particles. Although most of the past studies in the literature focused on primary grinding and rougher flotation, these research methodologies and theoretical mechanisms are important in understanding the role of regrinding chemistry in the subsequent cleaner flotation which is one main focus of this thesis study.
- Different grinding mills used for regrinding (e.g. tumbling mill, stirred mill) present different particle breakage mechanisms. The breakage mechanisms have a significant effect on particle size distribution, particle shape, liberation and particle surface properties, all of which play important roles in the mineral flotation. The overview of these factors provides

the theoretical basis for this thesis study on the effect of particle breakage mechanisms on subsequent cleaner flotation.

2.6 Research gaps and hypotheses

As indicated in the above literature review, intensive studies have been carried out over last few decades to understand the effect of grinding conditions on the subsequent flotation. However, most of the previous studies focused on primary grinding and rougher flotation, and the effect of various regrinding conditions on the subsequent cleaner flotation has not been studied to a great extent, especially in the aspect of fundamental understanding, such as the change of particle surface properties and the complex electrochemical reactions and galvanic interactions occurring during regrinding.

In addition, there are some differences between primary grinding and regrinding. First of all, unlike primary grinding producing relatively coarse particles, regrinding reduces most particles to fine and ultra-fine fractions. In some mineral processing plants treating fine grained ores, mineral liberation can only be achieved at less than 10 μm regrind size (Johnson 2006). It has been reported that the flotation of fine and ultra-fine particles is more affected by grinding conditions than the flotation of intermediate and coarse particles (Johnson 2006, Grano 2009, Peng and Grano 2010a). Secondly, the electrochemical reactions during regrinding will be much stronger than during primary grinding due to the larger surface areas of these fine particles. It is therefore anticipated that different regrinding conditions have a more significant effect on the subsequent mineral flotation. Another difference is the high sulphide content of the regrinding feed compared to the primary grinding feed because a majority of non-sulphide gangue minerals have been rejected in the rougher flotation (Johnson 2006, Kinal et al. 2009). This makes galvanic interactions between sulphide minerals and grinding media much stronger during regrinding than during primary grinding. Moreover, the particle surfaces of regrinding feed are covered by some species carried from primary grinding and rougher flotation, such as collectors and oxidation species. As illustrated in Figure 2.15, there are two types of surfaces existing after regrinding: the remaining surfaces carried over from the regrinding feed, and the fresh surfaces generated during regrinding. Both of them are important for subsequent cleaner flotation and their changes during regrinding need to be investigated.

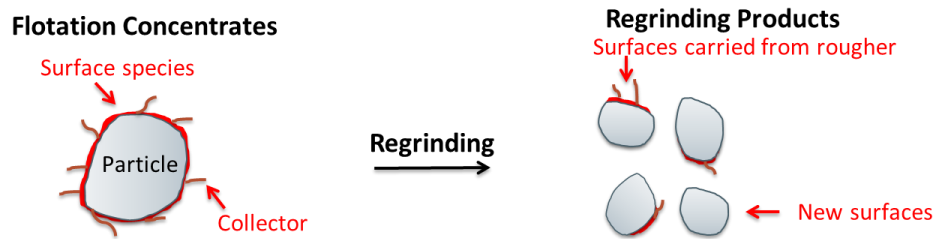


Figure 2.15 The change of particle surfaces after regrinding.

Furthermore, different grinding mills are being used at the regrinding stage, including traditional tumbling mill and energy efficient stirred mill. Different mills providing different particle breakage mechanisms, which has been proved to influence the particle size distribution, particle shape and liberation. These parameters may play a role in the subsequent flotation. Recent studies have suggested that different grinding mills may also affect the subsequent flotation through the change of surface properties (Ye et al. 2010a, Ye et al. 2010b). Therefore, it is important to further investigate the effect of particle breakage mechanisms on mineral floatability by considering and isolating all the factors, especially for fine regrinding.

The research gaps identified together with the research objective have led us to formulate the following hypotheses to be tested in this study:

Hypothesis one: Regrinding chemistry has a more significant influence on mineral floatability compared to primary grinding chemistry, because regrinding produces more fine and ultra-fine particles with a larger surface area for various electrochemical reactions to occur.

Hypothesis two: The separability of chalcopyrite and chalcocite from pyrite will be different after regrinding, because the two copper minerals have different electrochemical properties. This may not only influence the flotation of copper minerals but also affect the pyrite floatability through the galvanic interaction and copper activation.

Hypothesis three: Pulp chemistry can be significantly changed during regrinding rougher concentrates with a high content of sulphides because of the large amount of reactive fresh surfaces created during regrinding, and the pulp chemistry can be optimized by different methods to improve the subsequent flotation.

Hypothesis four: Different flotation behaviour can be observed after regrinding in a tumbling mill and stirred mill, because these two mills provide different particle breakage mechanisms which can affect the mineral surface properties of the grinding product and hence influence the mineral floatability.

Chapter 3 Experimental

3.1 Introduction

The experiments in this thesis were designed and conducted to fundamentally investigate the effect of regrinding chemistry and particle breakage mechanisms on subsequent cleaner flotation. The test work is composed of flotation tests and surface analysis. In each study, flotation tests were conducted firstly. Where different flotation behaviours were observed, surface analysis methods were used to examine the mineral surface species of the regrinding products and flotation concentrates/tailings to understand the mechanisms responsible for the different mineral floatability.

Since this project was conducted in the context of commissioning and optimizing the regrinding process in Newcrest's Telfer gold mine in Western Australia, pyrite and copper sulphide minerals which are the major base metal sulphides in Telfer ore were selected as the main target minerals of this study. Single minerals were used in most of test work because they were more reliable to study the mineral surface properties and the mineral liberation did not need to be considered. In addition, by using single mineral samples, there were no impurities to affect the flotation tests and surface analysis, which may occur if plant samples are used. When the pulp chemistry which was linked with the plant situation was studied, ore samples collected from the Telfer plant were used.

Following are the experimental details including the mineral samples and reagents, the grinding and flotation procedures, and surface analysis.

3.2 Mineral samples and reagents

3.2.1 Single minerals

Pyrite, chalcopyrite and chalcocite single mineral samples were purchased from GEO Discoveries, Sydney and originated from Peru. XRD analysis indicated that the pyrite sample was very pure without detecting any impurity. The chalcocite sample also has a high purity with a minor amount (<2%) of iron sulphide impurity. The purity of the chalcopyrite sample was slightly lower with about 95% chalcopyrite and 5% pyrite. These samples were crushed through a jaw crusher and a

roll crusher, and then screened to collect -3.35+0.71mm particle size fractions. The processed samples were sealed in polyethylene bags and then stored in a freezer at a temperature of -20 °C to minimise further surface oxidation.

3.2.2 Pyrite concentrates from Telfer

A sample of pyrite concentrate was collected from the feed of the regrind mill at Newcrest's Telfer gold mine. The concentrate was filtered, and then frozen immediately at -18 °C. The chemical compositions of the sample are shown in Table 3.1.

Table 3.1 Chemical compositions of the pyrite concentrate supplied from Telfer.

Elements			
Cu	Fe	S	Au
0.44%	39.5%	44.7%	4.38 ppm

3.2.3 Reagents

For the single mineral studies, potassium amyl xanthate (PAX) and Interfroth 56 were used as a collector and frother, respectively. These reagents were of industrial grade and were used as received. The pH was adjusted by the addition of a NaOH solution instead of lime as used in the plant to eliminate the effect of Ca^{2+} on flotation and on the surface analyses by XPS (Hu et al. 2000). Copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was added as a source of aqueous copper ions during pyrite grinding and regrinding to activate the pyrite. Both NaOH and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were of AR grade. De-ionized water was used in all experiments. All chemical solutions were made fresh daily.

For the study of regrinding pyrite concentrates, the reagents used in this work include thionocarbamate-based RTD11A collector from Tall Bennet, and DSF004A from Orica as a frother. These reagents were supplied directly by the Telfer plant. Lime was used to adjust pH during regrinding and flotation. Three oxidizing agents, namely hydrogen peroxide (H_2O_2), potassium permanganate (KMnO_4), and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were used in this study to adjust the pulp chemistry during regrinding. Hydrogen peroxide was a 30% (w/w) solution in H_2O , while potassium permanganate and potassium dichromate are solids with a purity $\geq 99\%$.

3.3 Grinding and flotation experimental details

3.3.1 Particle size distribution analysis

The size distribution of the regrinding product was determined by laser diffraction with a Malvern MasterSizer (Malvern Instrument Ltd., U.K.). This instrument calculates particle size based on the diffraction of laser light by particles. It is fast and gives very reproducible results and therefore has been widely used by both researchers and plant engineers (Wills and Napier-Munn 2006). The size results given by Malvern sizer tend to appear coarser than other methods (e.g. sieving, Warman Cyclosizer) due to different mechanisms. However, since the purpose in this study is to compare the size distribution of different regrinding and flotation products, the results from different methods will not influence the conclusion. In addition, the Malvern sizer generate more size data points, especially for fine particles, while the Cyclosizer can only generate C1-C5 five data points. Overall, it is more practical to use Malvern sizer in this study for the purpose of measuring and comparing the size distribution of fine and ultra-fine particles.

3.3.2 Single mineral study

Based on the conventional regrinding circuit configuration in the processing plant, an experimental process in laboratory has been designed to simplify the plant circuit and study the effect of various regrinding conditions on subsequent flotation, as shown in Figure 3.1. The procedure is detailed as follows.

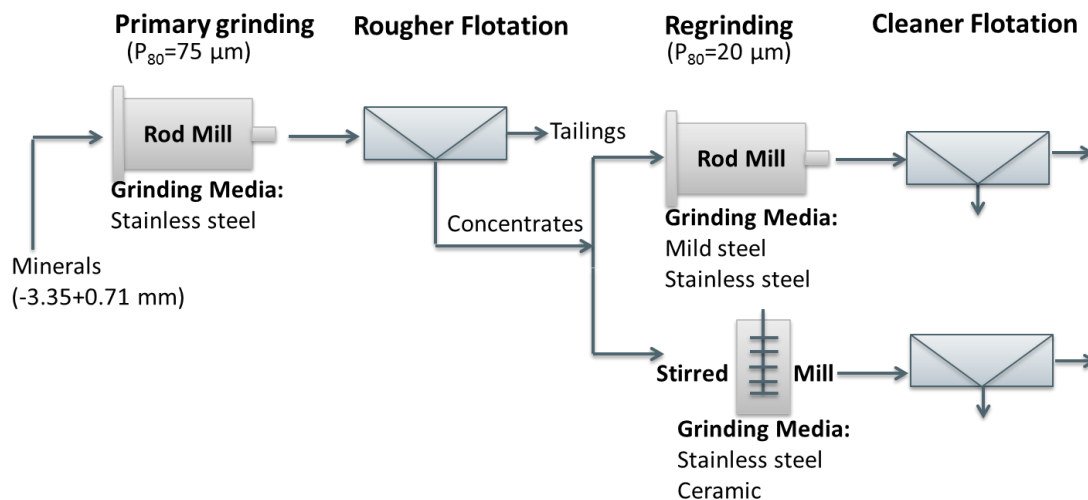


Figure 3.1 Schematic representation of the grinding, regrinding and flotation process in the laboratory.

The crushed minerals (100 g) were combined with 150 ml of de-ionized water, and ground in a stainless steel rod mill (Length: 260 mm, Diameter: 205 mm) using 4 stainless steel rods (3750 g) to achieve a P_{80} of 75 μm . An amount of 2.5% w/v sodium hydroxide solution was added in the feed before grinding to achieve pH 9.0 in the mill discharge.

After grinding, the pulp was transferred to the flotation cell (1.5 dm^3) for the initial rougher flotation. A JKMRC laboratory batch flotation cell with a bottom-driven agitator was used in this study, as shown in Figure 3.2. Collector (160 g/t) and frother (200 g/t) were added and 2 min of conditioning time was allowed for the conditioning of each reagent. During flotation, the pH was maintained at 9.0 by adding a sodium hydroxide solution (2.5% w/v). The froth was scraped every 10 sec, and four concentrates were collected after cumulative times of 0.5, 2.0, 4.0 and 8.0 min. The air flow rate was 1.5 dm^3/min during the first 0.5 min, and then increased to 3.0 dm^3/min thereafter. The flotation time for this batch rougher test was chosen to provide the recovery value from the laboratory test which was comparable with the plant rougher recovery.



Figure 3.2 JKMRC batch flotation cell used in the laboratory tests.

The four rougher flotation concentrates were combined and mixed with additional water to achieve a pulp density of 18%, and then reground. Either a rod mill or a stirred mill was used for the regrinding, as shown in Figure 3.3. The target particle size of the regrinding product was $P_{80}=20 \mu\text{m}$. For regrinding by the rod mill, 10.3 kg stainless steel or mild steel rods were used, and the desired particle size of $P_{80}=20 \mu\text{m}$ was achieved after grinding for a certain time. The stirred mill used in this study was a vertical bead mill with a disc-type agitator, and the volume of the grinding chamber was 1.5 L. Two different types of grinding media, specifically stainless steel beads and ceramic beads, were used in the stirred mill. The diameter of both media was 2.5 mm,

and 1 L of media was added during regrinding. The rotational speed of the stirrer was 1200 RPM. The target product particle size is also $P_{80}=20 \mu\text{m}$. When N_2 was applied during regrinding, the regrinding feed was firstly purged by N_2 to reduce the DO to zero before transferring it into the mill. Then the mill was purged again with N_2 for 10 min to expel the air. A sodium hydroxide solution (2.5%) was used to maintain pH 9.0 in the regrind mill discharge.

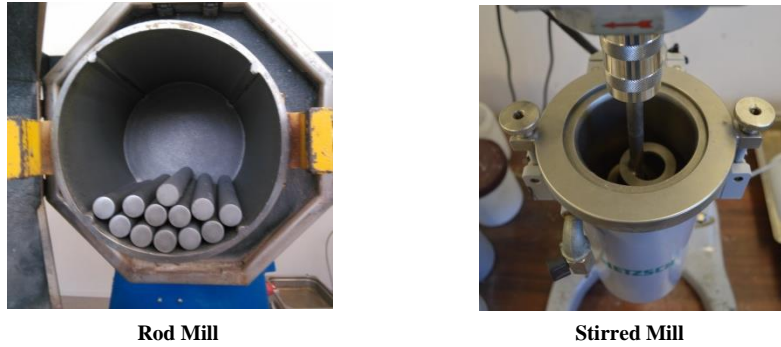


Figure 3.3 Rod mill and stirred mill used in the laboratory tests.

After regrinding, the pulp was transferred to a 1.5 dm^3 flotation cell for a cleaner flotation stage. Frother (200 g/t) was added during the conditioning time of 2 min. For some tests, more collector was added, the specific amount of collector are detailed in the results chapter. The cleaner flotation procedure was the same as used in the rougher flotation after primary grinding.

In this single mineral study, the size-by-size recovery was calculated by using the mass of each flotation concentrate and tailings and the size distribution of each flotation concentrate and tailings measured by Malvern Sizer. Although the laser diffraction theory reports the size as a volume equivalent sphere diameter, it is still possible to compare the size difference of the concentrate samples and tailings. Under this experimental condition, the Warman Cyclosizer can only separate the particles above $7.8 \mu\text{m}$, and therefore, cannot be used in this study where a great amount of $<7.8 \mu\text{m}$ occurred. Following is the formula used to calculate the recovery of particles from different size fractions:

$$R_i = \frac{M_{c1} * S_{c1i} + M_{c2} * S_{c2i} + M_{c3} * S_{c3i} + M_{c4} * S_{c4i}}{M_{c1} * S_{c1i} + M_{c2} * S_{c2i} + M_{c3} * S_{c3i} + M_{c4} * S_{c4i} + M_t * S_{ti}}$$

where R_i is the recovery of particles in the size fraction i ; M_{c1} , M_{c2} , M_{c3} , M_{c4} , and M_t is the mass of flotation concentrate 1, concentrate 2, concentrate 3, concentrate 4 and tailing. S_{c1i} , S_{c2i} , S_{c3i} , S_{c4i} , and S_{ti} is the percentage of particle retained in the size fraction i in the flotation concentrate 1 to 4

and flotation tailing. Although the particles over 53 μm is less than 0.5% in most samples, the recovery can be still calculated based on the size distribution data.

3.3.3 Regrinding and flotation of Telfer plant pyrite concentrates

For each test, 1 kg sample of pyrite concentrate was combined with 500 g tap water, and ground in a stainless steel rod mill to achieve a P_{80} of 25 μm . Lime was added before grinding to adjust the slurry pH to 9.5. To simulate the plant pulp chemistry after regrinding, the slurry was purged with nitrogen during regrinding to reduce the concentration of dissolved oxygen in the slurry. To adjust the regrinding chemistry, some oxidising agents were added in the mill.

After regrinding, the slurry was transferred to a 3L JKMRC flotation cell. Collector RTD11A (60 g/t) and frother DSF004A (45 g/t) were added. A conditioning time of 2 min was allowed for the conditioning of each reagent. During flotation, the pH was fixed at 10.5 by adding lime. Flotation concentrates were scraped from the cell every 10 s, and four concentrates were collected after cumulative times of 0.5, 2.0, 4.0, and 8.0 min. The flotation concentrates and tailings were filtered, and dried. A representative sub-split of each sample was sent for the assay of Cu, Au, Fe and S.

The flotation rate constant k of copper mineral, pyrite and Au was calculated from the following first-order flotation model:

$$R=R_{max}(1-e^{-kt}) \quad (3.1)$$

R is the recovery at the cumulative time t , R_{max} is the total recovery at infinite flotation time, and k is the rate constant for the floatable component. The flotation recovery of copper mineral is calculated from the Cu assay by assuming that the chalcopyrite is the main copper mineral present (Zheng and Manton 2010). The pyrite recovery is calculated from the S assay by assuming that pyrite is the only sulphide gangue mineral (Seaman et al. 2012). The flotation rate of Au is used in this study to indicate the overall flotation kinetics of both free gold and gold associated with other minerals (e.g. pyrite, copper mineral).

3.3.4 The reproducibility of the flotation tests

In the flotation tests conducted in this thesis, although standard operating procedures were strictly followed in all the test work to minimise the error, certain sources of error were inevitably involved in these experiments, including the errors associated with sampling, grinding, regrinding, flotation and assaying processes, combined with operator and random errors. The reproducibility of the mineral flotation tests was analysed by using the flotation of pyrite single minerals as the example. Both rougher flotation and cleaner flotation after regrinding with stainless steel were replicated four times. Results are shown in Figure 3.4. For the rougher flotation tests, the relative recovery error is 2.0% with 95% confidence interval. For the cleaner flotation tests, the relative recovery error is 3.8% with 95% confidence interval. Overall, good reproducibility was achieved in both rougher flotation and cleaner flotation.

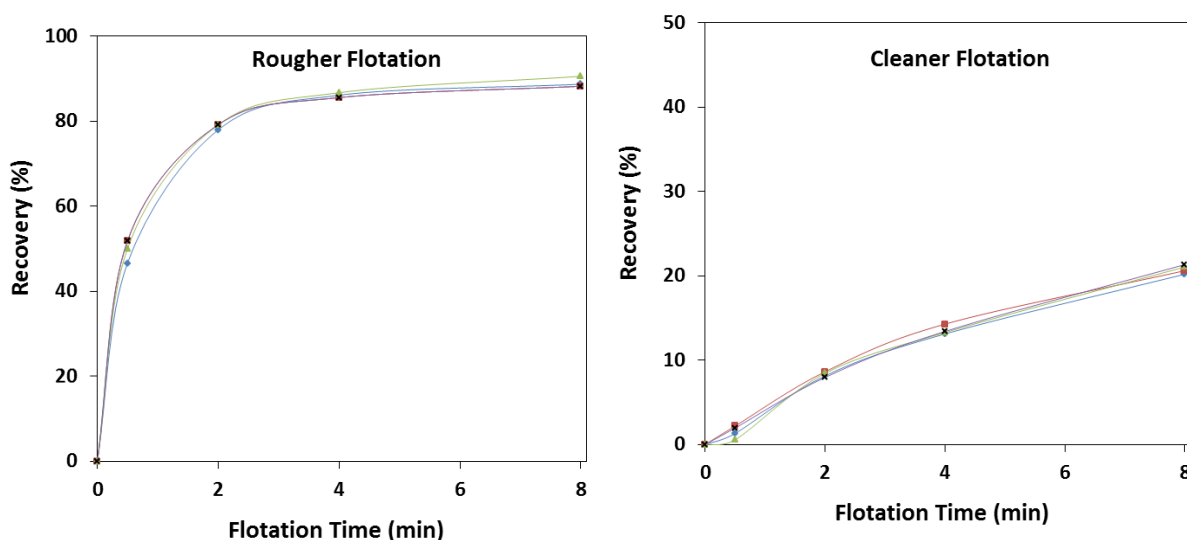


Figure 3.4 The replicated tests of pyrite rougher flotation and cleaner flotation.

3.4 Surface analysis

Samples for the surface analysis (about 10 ml of slurry) were subsampled from selected mill discharges and flotation concentrates/tailings. The slurry samples were immediately frozen in liquid nitrogen (-196 °C) to deoxygenate and avoid surface oxidation.

3.4.1 Surface area analysis

The surface area of the grinding and regrinding products was measured using the Brunauer–Emmett–Teller (BET) method using a Tristar 3000 analyser. BET surface area measurement is a technique based on the physical adsorption of gas molecules on a solid surface (Brunauer et al. 1938). Nitrogen is used in this study as the adsorption gas. The samples were degassed at 100 °C for 180 mins and analysed at bath temperature of -195.9 °C.

3.4.2 EDTA extraction

Ethylene diamine-tetra acetic acid (EDTA) has the ability to solubilise metal oxidation products (e.g. metal oxides, hydroxides, carbonates and sulphate) rather than the metal sulphide, and therefore can be used to determine the amount of oxidation species from minerals and grinding media (Rumball and Richmond 1996). In this study, a 3 wt% solution of AR grade ethylene diamine-tetra acetic acid disodium salt (EDTA) was made up and the pH was adjusted to 7.5 by adding sodium hydroxide solution. 95 cm³ of the EDTA solution was placed in a vigorously-stirred reaction vessel and continuously purged with nitrogen for 10 min to eliminate oxygen in the solution. Then the sample was added to the EDTA solution, and leached by EDTA for 10 min while nitrogen was continuously purged through the system. The slurry was then filtered through a 0.45 µm Millipore filter. Filtrate and dry solids were both weighed and analysed by ICP. The sample dry weight was used to calculate the mass of metal oxidation species per unit mass of solid or unit area of solid surface.

3.4.3 XPS analysis

XPS measurements were carried out with a KRATOS Axis Ultra (Kratos Analytical, Manchester, United Kingdom) with a monochromatic Al X-ray source operating at 15 kV and 10 mA (150 W). The analysis spot size was 300 × 700 µm. The frozen slurry samples were defrosted just prior to the analysis. The solids were placed on a stainless steel bar and immediately loaded into the introduction chamber of the spectrometer. The samples were analysed at a pressure of 9×10⁻¹⁰ Torr at room temperature. Each analysis started with a survey scan from 0 to 1200 eV using a pass energy of 160 eV at steps of 1 eV with one sweep. High resolution spectra of O 1s, C 1s, S 2p, and Cu 2p were collected at 20 eV pass energy at steps of 100 meV with two or three sweeps. Binding energies were charge-corrected by referencing to adventitious carbon at 284.8 eV.

3.4.4 ToF-SIMS analysis

Time of flight secondary ion mass spectrometry (ToF-SIMS) was used to study the distribution of collector species on particles of different size fractions after regrinding. The instrument used in this work is a PHI TRIFT V nanoTOF equipped with a pulsed liquid metal ^{79+}Au primary ion gun (LMIG), operating at 30 kV energy. “Unbunched” beam settings were used to optimize spatial resolution. Surface analyses, in positive and negative SIMS modes, were performed at a number of locations typically using a $75 \times 75 \mu\text{m}$ raster area. For the purposes of statistical interrogation, approximately 25 particles of interest were imaged per sample to collect representative data. Region-of-interest analyses were performed on the collected raw image data, which involved the extraction of mass spectra specifically from within the boundaries of the particles of interest. Resulting spectra in each polarity were calibrated using WincadenceN software (Physical Electronics Inc.) and peaks were selected based upon previously identified species of interest. Integrated peak values of the selected ions were normalised to the total selected secondary ion intensities, to correct for differences in total ion yield between analyses and samples. The resulting data were then compared qualitatively by preparing plots of average normalised counts (with 95% confidence intervals) for the collector species.

3.5 Polarization of mineral electrodes

Carefully selected high-purity chalcopyrite and chalcocite were cut by using an Isomet4000 Precision Saw into $3 \text{ mm} \times 3 \text{ mm} \times 10 \text{ mm}$ dimension. The electrodes were prepared by attaching the mineral specimen to copper wires with a conductive silver based electric conductive adhesive (RS Component Pty Limited), and then mounting them into non-conductive epoxy resin with the $3 \text{ mm} \times 3 \text{ mm}$ side exposed. Before each experiment, the mineral electrode was treated with a grade 600 then a grade 1200 silicon carbide paper, further polished with grit 100,000 diamond paste ($0.25 \mu\text{m}$ in diameter), rinsed in an ultrasonic bath and then thoroughly washed with de-ionized water. The polarization experiments were conducted by using a standard three-electrode system composed of the chalcopyrite or chalcocite mineral electrode, a platinum counter electrode with a surface area of 31.4 mm^2 and a saturated calomel reference electrode (SCE). The three-electrode system was linked to a Voltalab potentiostat/galvanostat (Model PGZ-100) controlled by a PC with Voltmaster 4 software. The polarization experiments were conducted in 0.1 M KCl solution at pH 9.0. The potential sweep was positively directed and at the rate of 10 mVs^{-1} . Before each

experiment, the open circuit potential (OCP) was recorded for 300 s. The potential recorded was against SCE.

Chapter 4 The Effect of Regrinding Chemistry on Pyrite Cleaner Flotation in the Presence of Copper Ions

4.1 Introduction

The objective of this study is to investigate the effect of regrinding chemistry on pyrite cleaner flotation and pyrite activation by copper ions. Pyrite is a sulphide gangue mineral but often associated with valuable minerals, such as copper and gold minerals. For example, at Newcrest's Telfer Gold Mine, a large amount of gold and copper minerals with a small grain size are locked in pyrite (Seaman et al. 2012). The pyrite flotation concentrates are reground to liberate the contained copper and gold minerals which are recovered in the subsequent flotation. However, the pyrite depression has been difficult in some operating plants, especially for the fine particles produced after regrinding and in the presence of copper ions. Therefore, it is important to understand the effect of different regrinding conditions on pyrite flotation and copper activation.

As indicated in the literature reviewed in Chapter 2, earlier researchers observed that the grinding chemistry during primary grinding, such as different types of grinding media, had a significant effect on the mineral flotation (Adam et al. 1984, Peng et al. 2003a, Peng et al. 2003b, Greet et al. 2004, Bradshaw et al. 2006, Grano 2009, Kinal et al. 2009, Bruckard et al. 2011), and can also affect the pyrite activation by copper ions (Peng and Grano 2010a, Peng et al. 2012). However, most of past studies focused on primary grinding and rougher flotation which deal with coarse and intermediate particles. In comparison, regrinding reduces most of the particles to fine and ultra-fine fractions, resulting in a larger surface area available for various reactions to occur. In addition, various species (e.g. collectors, activating ions and oxidation products) are carried from rougher flotation concentrate and redistributed on the freshly produced particles during regrinding, which may also play an important role in the subsequent cleaner flotation.

In this study, the effect of regrinding chemistry on copper activation of the pyrite surface and subsequent pyrite flotation in the cleaner stage was investigated. Pyrite was activated by copper

ions during primary grinding and recovered in rougher flotation. The rougher flotation concentrate was reground in a tumbling mill prior to the cleaner flotation stage. The regrinding conditions were manipulated by using either stainless steel or mild steel grinding media. The modification of the existing and newly created surfaces after regrinding was monitored by surface analysis techniques and correlated with pyrite activation and flotation. The further activation of pyrite by copper ions during regrinding under different conditions was also investigated.

4.2 Results and discussions

4.2.1 Primary grinding and rougher flotation

In order to replicate the pyrite flotation behaviour in the rougher stage in the Telfer concentrator, a 90 wt% pyrite recovery was achieved in the laboratory batch rougher flotation by increasing the collector dosage to 160 g/t and adding 150 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as the activator. Figure 4.1 shows the pyrite flotation recovery as a function of flotation time, with stainless steel grinding media in the primary grinding stage. In the absence of copper ions, pyrite displayed very poor floatability, and the recovery was around 23 wt% at the completion of 8 min of flotation. When 150 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added during grinding, the pyrite recovery significantly increased to about 90 wt%, due to the copper activation on the pyrite surface. This result is consistent with the studies reported in the literature showing that, without activation, pyrite flotation is depressed in alkaline solutions, and that copper ions significantly increase pyrite recovery within the pH 6-10 range (Leppinen 1990, Finkelstein 1997, Zhang et al. 1997). In the subsequent tests, copper ions were added during primary grinding to simulate those emanating from copper minerals and 90 wt% recovery was achieved from the rougher flotation. This rougher flotation concentrate was reground under different condition and the effects of the regrinding condition on surface properties and pyrite flotation in the cleaner stage were studied as described in the following section.

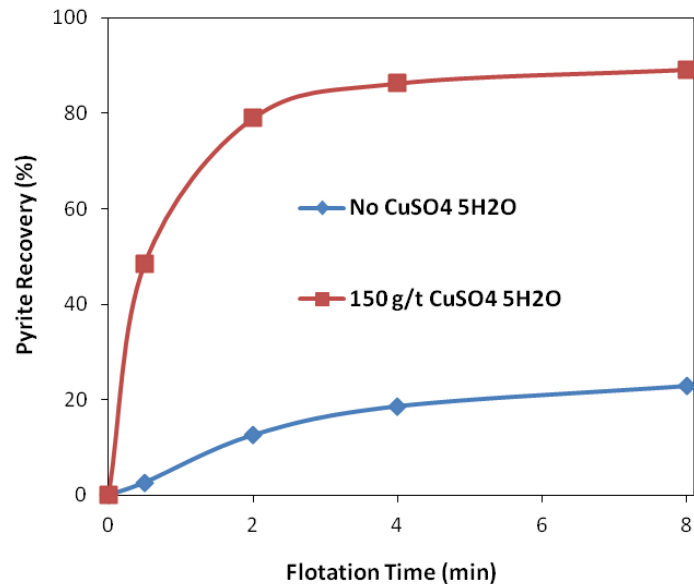


Figure 4.1 Pyrite recovery as a function of rougher flotation time in the absence and presence of copper ions during primary grinding with stainless grinding media (PAX dosage: 160g/t).

4.2.2 Pyrite flotation after regrinding with different grinding media

The rougher flotation concentrate (consisting of about 90 g pyrite) was reground in the rod mill with one of the two types of grinding media tested, either stainless steel or mild steel. The cleaner flotation results without additions of copper ions during regrinding and without the addition of collector in the cleaner flotation are shown in Figure 4.2. Regardless of grinding media type, the pyrite flotation was strongly depressed without the additional collector and copper ions. With mild steel media the recovery was about 6 wt% in 8 min of flotation. With stainless steel media, the pyrite recovery was higher, at about 20 wt%.

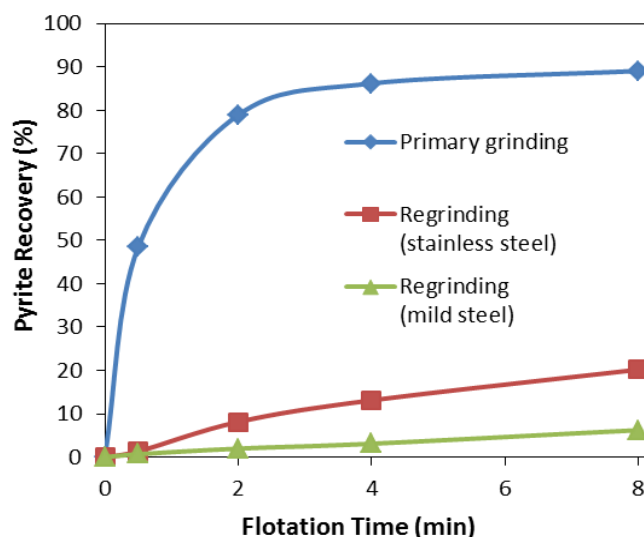


Figure 4.2 Pyrite recovery as a function of flotation time in the cleaner stage after regrinding with different grinding media.

Since the particle P_{80} of the pyrite concentrate decreased from 75 μm to 20 μm after regrinding, the reduced particle size may be one of the contributing factors to the lower pyrite recovery after regrinding due to the lower bubble-particle collision efficiency (Trahar 1981). However, a number of studies indicated that particles at 20 μm still showed maximum flotation (Pease et al., 2010, Peng and Grano, 2010; Peng and Grano, 2010a). The low pyrite flotation after regrinding in this study may be mainly associated with the altered surface properties.

The surface area of the pyrite concentrate before regrinding was 0.087 m^2/g but increased to 0.549 m^2/g after the regrinding with stainless steel media, which indicates that a large amount of new surface was generated during regrinding. In order to detect the surface species and their changes before and after regrinding, the regrinding feed and products were examined by XPS. The XPS-measured atomic concentrations normalized to oxygen, sulphur, iron, and copper on the pyrite surfaces are given in Table 4.1. The oxygen concentration was increased significantly from 26.0 at% on the regrinding feed to 41.2 at% and 50.6 at% after regrinding with stainless steel and mild steel media, respectively. The high oxygen concentration on the regrinding products suggests a high amount of oxidation species. Mild steel media produced a higher oxygen concentration than stainless steel media, which may be due to more iron oxidation species emanating from the mild steel media. As shown in Table 4.2, regrinding with mild steel media produced a much higher amount of EDTA extractable iron. This is also consistent with the higher atomic concentration of iron on the pyrite surface when mild steel media was used during regrinding as shown in Table 4.1.

After regrinding with stainless steel media, the amount of EDTA extractable iron slightly increased compared to the regrinding feed (Table 4.2), but the atomic concentration of iron decreased significantly (Table 4.1). This is due to the increased surface area of pyrite particles after regrinding. The surface concentrations of sulphur and copper also decreased after regrinding. In particular, the copper concentration was 4.8 at% on the regrinding feed, but decreased to 1.9 at% when it was reground with stainless steel media. When the regrinding feed was reground with mild steel media, copper species could not be detected. This is mainly caused by the increased pyrite surface area after regrinding, whilst the amount of the carried copper ions from the rougher flotation to regrinding was the same. The reason why copper species could not be detected after regrinding with mild steel media may be due to the masking of copper species by the significantly increased iron oxidation products.

Table 4.1 XPS derived surface concentrations (atomic % normalized to Fe, S, O and Cu) on pyrite surfaces before and after regrinding with different grinding media.

Samples	Atomic concentration of element (at%)			
	O	Fe	S	Cu
Regrinding Feed	26.0	22.3	46.9	4.8
Regrinding Product, Stainless Steel	41.2	17.1	39.8	1.9
Regrinding Product, Mild Steel	51.0	26.2	22.9	0*

*Cu cannot be detected in the survey scan.

Table 4.2 EDTA extractable iron of the pyrite regrinding feed and regrinding products with different grinding media.

	Regrinding Feed	Regrinding Product Stainless Steel	Regrinding Product Mild Steel
Extracted Fe (mg/g solid)	0.5	0.6	85.1

The S 2p XPS spectra from pyrite surfaces before and after regrinding with different grinding media are shown in Figure 4.3. These spectra were fitted using the 2p_{1/2} and 2p_{3/2} doublet with a fixed 1:2 intensity ratio and 1.18 eV energy separation. The doublet with the S 2p_{3/2} binding energy at the range of 161.5 to 161.7 eV can be attributed to the monosulphide S²⁻ and the doublet at 162.4-162.7 eV is from disulphide S₂²⁻ (Nesbitt, 1998; Schaufuß et al., 1998; Smart et al. 1999). An energy loss (EL) feature has been fitted at approximately 164.5 eV, which is associated with S 3p to Fe eg excitation (Schaufuß et al., 1998; Peng et al. 2012). Another doublet with the S 2p_{3/2} binding energy

at 163.4 eV was fitted in the spectra of the sample with stainless steel regrinding, which was attributed to the polysulphide S_n^{2-} (Smart et al. 1999). The broad peak at 168.9 eV represents the sulphate SO_4^{2-} . The binding energy of the major peaks for the mild steel regrinding sample shifted to a lower value, which may be due to the rather reducing sample preparation environments (Peng et al. 2012), or caused by the slight shift of the carbon reference peak. As calculated from the S 2p spectra, 92.6% of S was present as S^{2-} and S_2^{2-} in the regrinding feed, and no SO_4^{2-} species were detected. This indicates a very low level of surface oxidation of the regrinding feed, or the rougher flotation concentrate. After regrinding with stainless steel media, the proportion of S^{2-} and S_2^{2-} was decreased to 67.5% S, while 10.9% S occurred in the form of SO_4^{2-} . Obviously, the regrinding feed was strongly oxidized after regrinding with stainless steel media due to the oxidizing grinding environment produced with the Eh value of 220 mV (vs SHE) and DO value of 4.13 ppm at the end of grinding. Regrinding with mild steel media produced a reducing grinding environment with an Eh value of -230 mV (vs SHE) and DO value of 0 ppm, corresponding to low pyrite surface oxidation. As shown in Figure 4.3, no SO_4^{2-} species was detected when mild steel media was used during regrinding. This is consistent with Peng et al. (2003a) who found that less polysulphide and sulphate species were produced on the chalcopyrite surface after primary grinding with mild steel media than with high chromium media.

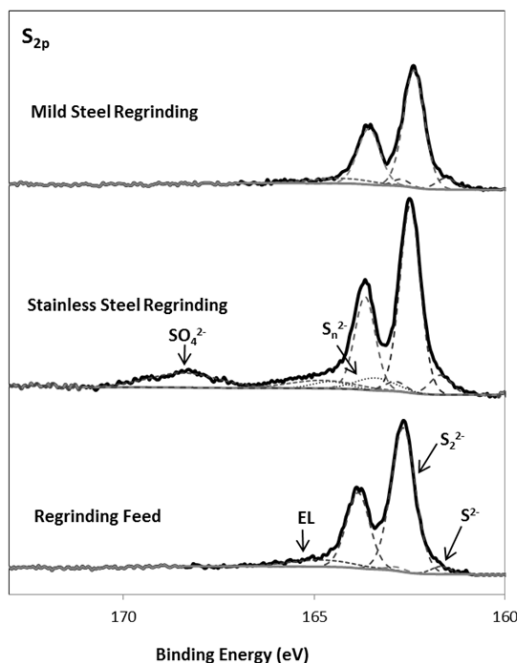


Figure 4.3 S 2p XPS spectra from pyrite surfaces before and after regrinding with different grinding media.

The Fe 2p XPS spectra from pyrite surfaces before and after regrinding with different grinding media are shown in Figure 4.4. Fe²⁺ in the pyrite bulk is represented by a narrow single peak with a binding energy of 707.1 eV, and Fe²⁺ on the surface appears as a tail with about 0.5 eV higher binding energy (Buckley and Woods 1987, Nesbitt 1998, Schaufuß et al. 1998). The broad peak centred at 710.8 eV is attributed to Fe³⁺-O/OH species (Buckley and Woods 1987, Schaufuß et al. 1998). 72.1% of Fe on the pyrite surface after regrinding with mild steel was in the form of Fe³⁺-O/OH. This is much higher than that on the regrinding feed (30.4%) and after regrinding with stainless steel (28.3%). The amount of iron in the form of Fe³⁺-O/OH obtained by XPS is in line with the amount of EDTA extractable iron in Table 4.2. Previous studies indicated that mild steel media produced a much higher amount of iron oxidation species than high chromium or stainless steel media, depressing the flotation (Peng et al. 2003a, Peng et al. 2003b). Ye et al. (2010a) proposed that iron contamination from stainless steel media after regrinding depressed pyrrhotite flotation. However, in this study, stainless steel media did not cause iron contamination on the pyrite surface after regrinding as indicated in Table 4.2.

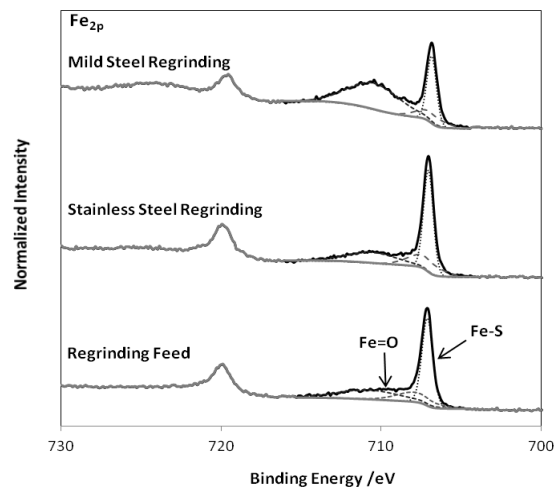
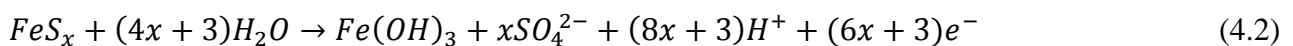


Figure 4.4 Fe 2p XPS spectra from pyrite surfaces before and after regrinding with different grinding media.

According to the surface analysis by XPS and EDTA, the main chemical reactions occurred on pyrite surfaces during regrinding with stainless steel media were the oxidation of sulphide to polysulphide and sulphate. The following reactions are proposed:



During regrinding with mild steel media, the surface oxidation of pyrite was minimal due to the strong reducing condition. The main reaction in the system was the oxidation of iron from mild steel media:



The Cu 2p XPS spectra from pyrite surfaces before and after regrinding with different grinding media are shown in Figure 4.5. The Cu⁺ Cu 2p_{3/2} component was identified at about 932.2 eV, similar as that observed for Cu⁺-S minerals and compounds (McIntyre and Cook, 1975; Deroubaix and Marcus, 1992). A second component in the Cu 2p_{3/2} at about 934.3 eV is attributable to Cu²⁺-hydroxyl species (Weisener and Gerson, 2000). The percentage of Cu⁺ to the overall Cu for the regrinding feed and the product after regrinding with stainless steel media is 73.0 and 79.0% Cu, respectively. However, on the pyrite surface, the atomic concentration of Cu⁺ for the regrinding feed and the product after regrinding with stainless steel media is 3.5 and 1.5 at%, respectively. The reduced atomic concentration of Cu⁺ may be attributed to the increased surface area after regrinding. A clear Cu 2p XPS spectrum was not detected on the product after regrinding with mild steel media. Again, this may be due to the masking of Cu species by the iron oxidation products.

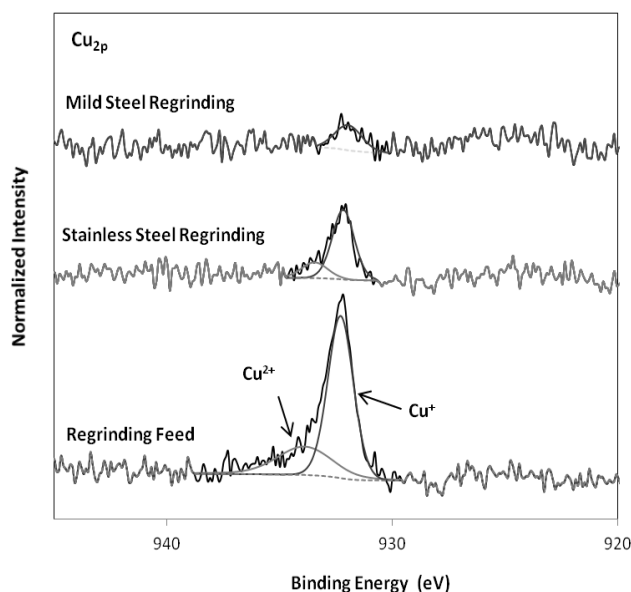


Figure 4.5 Cu 2p XPS spectra from pyrite surfaces before and after regrinding with different grinding media.

The XPS analysis correlates well with pyrite flotation after regrinding. Without additional amounts of the collector and copper ions, the concentration of copper ions, in particular Cu⁺ ions carried

from the rougher flotation concentrate on the pyrite surface was reduced significantly after regrinding. As most of the xanthate adsorbed on copper activation species by forming dixanthogen or Cu-xanthate (Bruckard et al., 2011), the concentration of xanthate species can be also greatly reduced, which may be the major contributing factor to the low pyrite flotation after regrinding. Regrinding with stainless steel media also promoted more mineral surface oxidation. It is not distinguishable whether the oxidation occurred on the carried Cu-activated pyrite surface or new created pyrite surface. It is known that the Cu-activated pyrite behaves like copper sulphide products (Leppinen 1990, Voigt et al. 1994), and the copper sulphide minerals are more electrochemically active than pyrite (Cheng and Iwasaki 1992). It is therefore anticipated that the carried Cu-activated pyrite surface which necessitates the pyrite flotation was more oxidized during regrinding resulting in the further depression of pyrite flotation in the cleaner stage. Regrinding with mild steel media produced a much higher amount of iron oxidation species. Again it is not distinguishable whether the iron oxidation species were adsorbed on the carried Cu-activated pyrite surface or new created pyrite surface. The un-detectable Cu species on the pyrite surface suggest that the iron oxidation species were adsorbed on the carried Cu-activated pyrite surface and further depressed pyrite flotation.

4.2.3 Pyrite flotation with an additional amount of collector in the cleaner stage

In order to restore pyrite flotation after regrinding, an additional amount of collector was added in the cleaner flotation without adding copper ions during regrinding. The flotation results are shown in Figure 4.6. For both stainless steel and mild steel media, pyrite flotation recovery increased as collector dosage increased and reached the maximum at 640 g/t collector. This is consistent with Ye et al. (2010a) showing that an additional amount of collectors improved pyrrhotite flotation by increasing the collector concentration on the increased surface after regrinding. However, this may not explain the increased pyrite flotation after regrinding in this study. Although the collector concentration was increased in relation to the increased surface, the concentration of copper ions which necessitate pyrite flotation was not increased. Without further activating pyrite, an additional amount of the collector may not improve pyrite flotation. Therefore, it is more likely that the additional amount of collector mitigated the hydrophilic oxidation products on the pyrite surface. Once the carried Cu-activated pyrite surface was exposed, pyrite flotation was increased. This is consistent with Mielczarski et al. (1998) showing that a higher amount of collectors improved the flotation by removing the hydrophilic oxidation products. However, pyrite recovery increased more markedly after regrinding with stainless steel media than mild steel media. For example, the pyrite

recovery increased from 20 to 60 wt% at the completion of 8 min of flotation after the addition of 640 g/t collector with stainless steel media but only increased from 7 to 29 wt% with mild steel media. Obviously, the restoration of pyrite flotation is more difficult after regrinding with mild steel media. This may be due to the very high amount of iron oxidation species produced from the oxidation of mild steel media which play a dominant role in depressing the mineral flotation (Adam et al. 1984, Johnson 2002, Peng and Grano 2010a) .

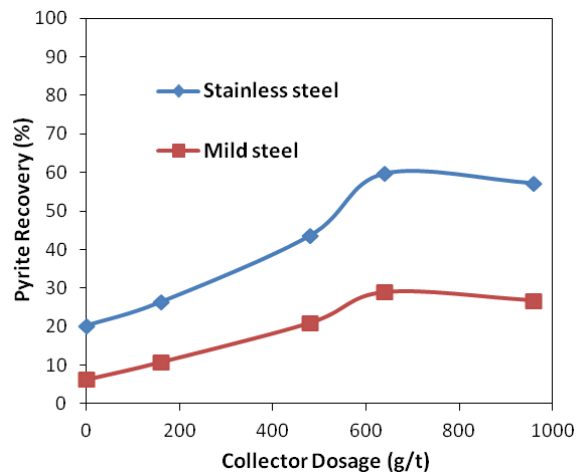


Figure 4.6 Pyrite recovery after regrinding as a function of collector dosage without additional copper ions.

It is interesting to observe that pyrite flotation could not be restored completely after regrinding even with stainless steel media which only produces a small amount of iron oxidation products. It seems that the copper concentration or the activated pyrite surface carried from the rougher flotation concentrate may not be sufficient in relation to the increased surface area after regrinding. To further increase pyrite flotation, additional copper ions may have to be added during regrinding to activate the newly generated pyrite surface, and this is discussed below.

4.2.4 Pyrite flotation with additional Cu^{2+} added during regrinding

Pyrite flotation in the cleaner stage as a function of the dosage of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ added during regrinding is shown in Figure 4.7. 640 g/t PAX collector was added in the cleaner flotation. Interestingly, as the dosage of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ increased, pyrite flotation was increased when mild steel media was used in regrinding, but decreased when stainless steel media was used. For example, after adding 600 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, pyrite recovery was increased from 29 to 50 wt% with mild steel media but decreased from 60 to 42 wt% with stainless steel media. It was noted that froth

in the flotation coalesced when copper ions were added during regrinding with stainless steel media. The water recovery which is an indicator of froth stability was measured at each dosage of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ added during regrinding. As shown in Figure 4.8, with the addition of copper ions, the water recovery decreased linearly with stainless steel media, but increased and then stabilized with mild steel media. Apparently, the addition of copper ions during regrinding decreased the froth stability with stainless steel media but increased the froth stability with mild steel media. In fact, a similar observation was found by Bradshaw et al. (2006) and Ekmekci et al. (2006) who investigated the effect of different grinding media on the flotation of Merensky ores in the presence of copper sulphate. O'Connor et al. (1988) also found that copper sulphate reduced the maximum froth height in pyrite flotation. They proposed that hydrophobic Cu-xanthate colloids formed in the pulp, attached onto air bubbles and promoted coalescence of air bubbles.

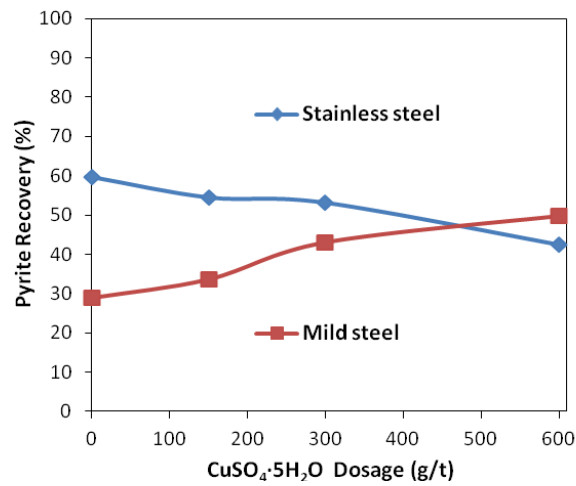


Figure 4.7 Pyrite recovery as a function of the dosage of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ added during regrinding with 640 g/t collector added in the cleaner flotation.

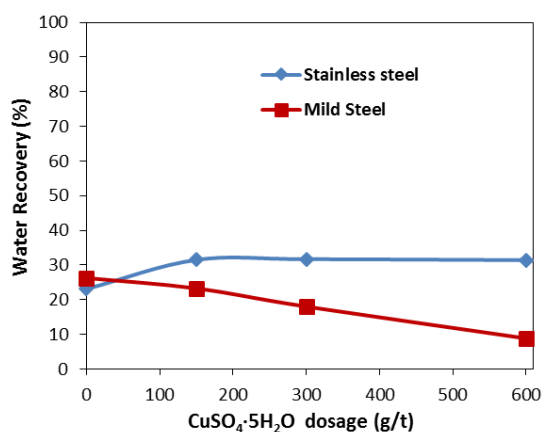


Figure 4.8 Water recovery as a function of the dosage of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ added during regrinding with 640 g/t collector added in the cleaner flotation.

To identify the change of the pyrite surfaces after the addition of copper ions during regrinding, the regrind mill discharges were subjected to surface analysis using XPS. The measured atomic concentrations of O, Fe, S and Cu on the pyrite surfaces are shown in Table 4.3. Compared to the previous results in Table 4.1, the concentrations of O, Fe and S did not change significantly after the addition of 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during regrinding with stainless steel media, while, the concentration of Cu increased from 1.9 to 2.5 at%. Figure 4.9 shows the related Cu 2p XPS spectra. After decoupling Cu^+ from Cu^{2+} , the concentration of Cu^+ without and with the addition of 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during regrinding was increased from 1.5 to 2.2 at%. Given the small atomic concentration of Cu^+ required to activate pyrite flotation, this increase in Cu^+ concentration on the pyrite surface indicates some further activation when 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added during regrinding with stainless steel media.

A more pronounced change occurred on the pyrite surface after the addition of 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during regrinding with mild steel media. Firstly, copper species were clearly detected with the addition of 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with 2.2 at% Cu and with 88.0% of the copper occurring in the form of Cu^+ . This indicates that the pyrite surfaces were further activated by copper ions. Secondly, the atomic concentration of Fe on the pyrite surface was decreased significantly from 26.2 to 21.1 at% without and with the addition of 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during regrinding. The atomic concentration of S also increased accordingly. After decoupling the Fe 2p XPS spectra shown in Figure 4.10, the atomic concentration of Fe in the form of $\text{Fe}^{3+}\text{-O/OH}$ decreased from 18.9 to 12.3 at% after the addition of 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during regrinding. Obviously, the addition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during regrinding with mild steel media decreased the amount of iron oxidation

products. EDTA extraction also indicated that the amount of EDTA extractable iron decreased from 85.14 mg/g solid (Table 4.2) to 57.40 mg/g solid (Table 4.4) after the addition of 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during regrinding with mild steel. As discussed, the Cu-activated pyrite behaves like copper sulphide products (Leppinen 1990, Voigt et al. 1994), and the copper sulphide minerals are more electrochemically active than pyrite (Cheng and Iwasaki 1992). The galvanic interaction between mild steel media and the Cu-activated pyrite is weaker than that between mild steel media and pyrite resulting in less oxidation of the media and generation of less iron oxidation products. This may explain the reduced amount of iron oxidation products present when 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added during regrinding with mild steel media.

Table 4.3 XPS derived surface concentrations (atomic % normalized to Fe, S, O and Cu) on pyrite surfaces after regrinding in the presence of 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with different grinding media.

Samples	Atomic concentration of element (at%)			
	O	Fe	S	Cu
Stainless Steel, CuSO_4 300g/t	40.82	16.21	40.43	2.54
Mild Steel, CuSO_4 300g/t	49.57	21.13	27.15	2.15

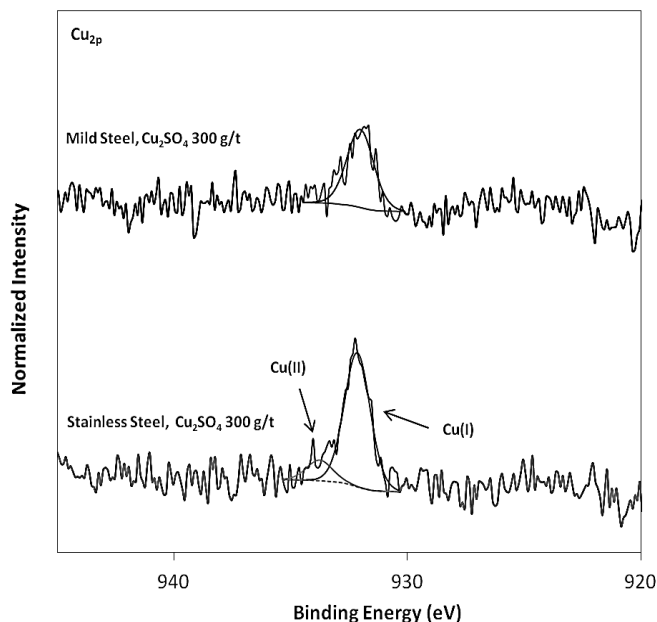


Figure 4.9 Cu 2p XPS spectra from pyrite surfaces in the presence of 300g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during regrinding with different grinding media.

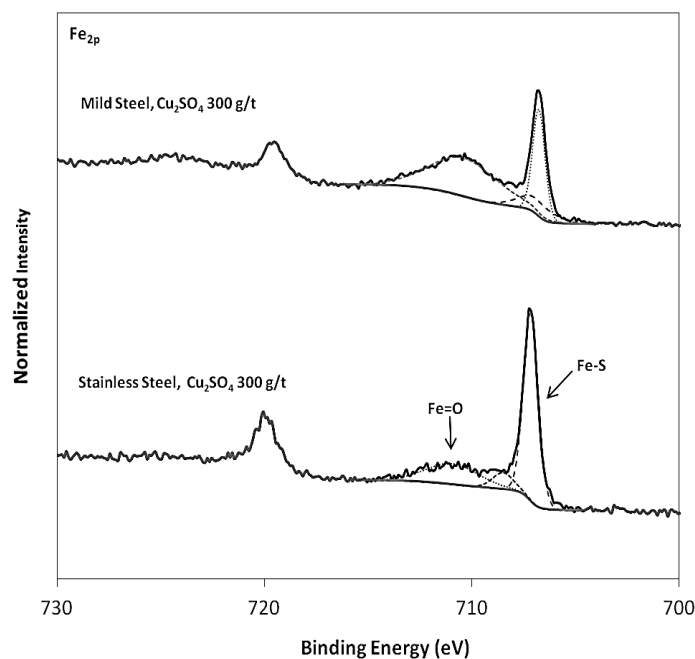


Figure 4.10 Fe 2p XPS spectra from pyrite surfaces in the presence of 300g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ during regrinding with different grinding media.

Table 4.4 EDTA extractable iron of the pyrite after regrinding in the presence of 300 g/t $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with different grinding media.

	Stainless Steel Regrinding + CuSO_4 (300g/t)	Mild Steel Regrinding + CuSO_4 (300g/t)
Extractable Fe (mg/g solid)	0.49	57.40

Pyrite flotation with additional Cu^{2+} ions during regrinding together with the XPS analysis and EDTA extraction indicates that mild steel and stainless steel media have a different effect on the further pyrite activation by copper ions and the subsequent pyrite flotation. As found previously, the mild steel media produced a reducing grinding condition and promoted pyrite activation, whilst stainless steel media produced an oxidizing grinding condition and inhibited pyrite activation (Peng and Grano, 2010b; Peng et al., 2012). XPS measurements in this study showed further copper activation on the pyrite surface with the increased atomic concentration of Cu^+ after the addition of copper ions during regrinding especially with mild steel media. With mild steel media, pyrite flotation increased steadily with the amount of copper ions. Another evidence of further activation on the pyrite surface with mild steel media is the reduced galvanic interaction between mild steel media and pyrite as indicated by the significantly reduced amount of iron oxidation species which

were detected by the XPS analysis (Figure 4.10) and EDTA extraction (Table 4.4). Regrinding with stainless steel media also induced pyrite activation on the new created surface but to a much smaller extent with an additional amount of copper ions. More copper ions stayed in the pulp, destabilized the froth by Cu-xanthate compounds and depressed pyrite flotation.

4.3 Conclusions

The current study indicates the important effect of regrinding conditions on copper activation of the pyrite surface and on subsequent pyrite flotation in the cleaner stage. Regrinding with stainless steel and mild steel media has a different effect on the properties of carried Cu-activated and newly created surfaces with and without an additional amount of collector and copper ions, resulting in different pyrite flotation response in the cleaner stage. Without an additional amount of the collector and copper ions, pyrite flotation in the cleaner was significantly depressed especially after regrinding with mild steel media. The dilution of collector and copper concentrations and the adsorption of the hydrophilic oxidation products on the pyrite surface were identified as the main contributing factors. An additional amount of the collector increased pyrite flotation for both stainless steel and mild steel media probably due to the mitigation of the hydrophilic oxidation products on the carried Cu-activated pyrite surface. A further additional amount of copper ions increased pyrite flotation after regrinding with mild steel media through the significant activation on the newly created pyrite surface. Regrinding with stainless steel media also induced some copper activation although to a lesser extent but the significant froth destabilization in this case reduced pyrite flotation with the additional copper ions. The results and mechanisms proposed in this study can provide guidelines for the plant operation to understand pyrite flotation behaviour in the cleaner flotation and optimize the regrinding chemistry to achieve a better flotation performance.

Chapter 5 The Separation of Chalcopyrite and Chalcocite from Pyrite in the Cleaner Flotation after Regrinding

5.1 Introduction

The objective of this study is to investigate the separation of different copper sulphide minerals from pyrite in the cleaner flotation after regrinding. In processing plants treating low grade copper/gold ores, it is often necessary to regrind the copper concentrates or pyrite concentrates to further liberate the valuable copper/gold minerals, such as the copper and pyrite regrind circuit at Newcrest's Telfer operation (Seaman et al. 2012). However, it is usually difficult to effectively separate the fine copper sulphides from pyrite in the subsequent cleaner flotation, even though the valuable minerals have been well liberated. In addition, with the depletion of primary copper sulphide dominant ores, more and more secondary copper sulphide dominant ores with a high pyrite content need to be treated. As discussed in the literature reviewed in Chapter 2, different copper sulphide minerals have different electrochemical properties, which play important roles in their oxidation and flotation. Moreover, there is a general industrial observation that secondary copper ores are more difficult to treat in particular in cleaner flotation after regrinding (Bulatovic 2007, Wightman et al. 2011, Seaman et al. 2012). However, limited studies have been undertaken to understand the fundamental aspect of this industrial problem.

In this study, the separation of chalcopyrite and chalcocite from pyrite in the cleaner flotation after regrinding was investigated. Chalcopyrite and chalcocite are the two most common copper sulphide minerals and also the two main copper minerals in Telfer ore. The first part of this study focused on investigating the different electrochemical properties of copper minerals and the influences of these on the flotation of the copper minerals and pyrite after regrinding in the cleaner flotation. Stainless steel media were used in both primary grinding and regrinding to provide a clean and mildly oxidizing grinding environment. As studied in Chapter 4, the different regrinding chemistry manipulated by different grinding media had a significant influence on pyrite flotation and copper

activation, therefore, in the second part of this study, mild steel grinding media was also used to provide different grinding chemistry and their effects on the separation of copper minerals from pyrite were tested in both primary grinding and regrinding. The mechanisms underpinning these phenomena were investigated by a range of techniques including polarization of mineral electrodes, EDTA extraction and XPS analyses.

5.2 *Results and discussion*

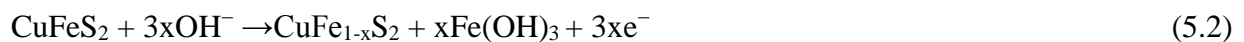
5.2.1 **Electrochemical properties of chalcopyrite and chalcocite**

The electrochemical properties and surface oxidation of copper sulphide minerals play a critical role in their flotation, and also influence the floatability of other minerals (e.g., pyrite) through galvanic interactions and copper activation. The electrochemical behaviour of chalcopyrite and chalcocite was firstly studied by the polarization of mineral electrodes following the method described in section 3.5. Figure 5.1 shows the resulting polarization curves of chalcopyrite and chalcocite mineral electrodes. The corrosion potential (or open circuit potential, OCP) of chalcopyrite and chalcocite is about -20 mV and -90 mV, respectively, in the same aqueous solution. As a result, chalcocite is more electrochemically active than chalcopyrite. During polarization, the anodic corrosion process is controlled by the dissolution (or oxidation) of the mineral, while the reduction of dissolved oxygen is the main cathodic process. On the two mineral electrodes, the cathodic reaction, oxygen reduction is the same:

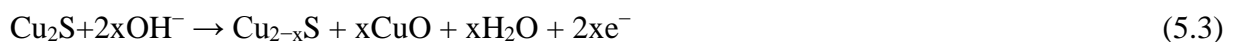


However, the anodic reaction, mineral oxidation is different.

The anodic oxidation of chalcopyrite is (Buckley and Woods 1984):



While the anodic oxidation of chalcocite is (Steger and Desjardins 1980):



Obviously, reaction 5.3 is stronger than reaction 5.2 since the anodic current density (the right part of the polarization curve at more positive potentials from the OCP) on chalcocite was much higher than that on chalcopyrite. The corrosion current density obtained by extrapolating the linear Tafel regions of the polarization curve to the corrosion potential is an indication of the corrosion rate (Baboian 2005). The corrosion current density of chalcopyrite and chalcocite was about $10^{-6.3}$ and $10^{-4.8}$ A cm⁻², respectively. Obviously the corrosion rate of chalcocite was greater than the corrosion rate of chalcopyrite based on the polarization curves. In other words, the oxidation rate of chalcocite was greater.

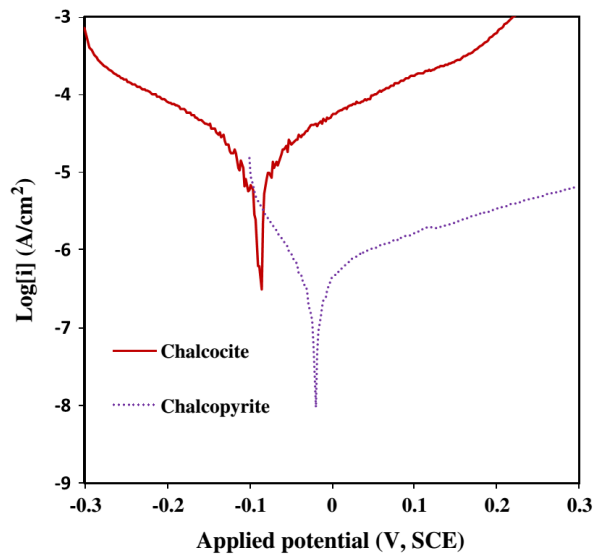


Figure 5.1 The polarization curves of chalcopyrite and chalcocite electrodes.

During regrinding of the mixed mineral system, a galvanic interaction occurs between minerals due to their different rest potential, which can cause a net current through the surface, and significantly influence the reduction of cathode and oxidation of anode (Martin et al. 1991). It is generally agreed that pyrite is more electrochemically noble than chalcopyrite and chalcocite with higher rest potential as indicated by Chmielewski and Kaleta (2011). Moreover, the rest potential difference between chalcopyrite and pyrite is smaller than that between chalcocite and pyrite, with a weaker galvanic interaction. This may affect mineral flotation differently, which was further investigated.

5.2.2 Flotation of chalcopyrite and chalcocite and their separation from pyrite after regrinding with stainless steel media

Before studying the separation of chalcopyrite and chalcocite from pyrite, the floatability of single copper minerals in the absence of pyrite was investigated. In order to simulate normal flotation circuits in plant, in this study, the chalcopyrite and chalcocite recovery were maximized in the rougher flotation by using stainless steel media in primary grinding and adding collector in the flotation stage. The rougher flotation concentrate was reground from P₈₀ 75 µm to 20 µm, and then subjected to cleaner flotation.

5.2.2.1 Flotation of chalcopyrite

As shown in Figure 5.2, approximately 91% chalcopyrite recovery was achieved in 8 min of flotation in the rougher stage. The rougher concentrate was reground from P₈₀ 75 µm to 20 µm. Chalcopyrite recovery after regrinding is shown in Figure 5.3. Without additional collector added to the cleaner, 71% recovery of chalcopyrite in 8 min of flotation was achieved. As the particle size was reduced during regrinding, some existing surfaces with adsorbed collectors were carried from rougher flotation while fresh surfaces were generated. From the BET surface area measurement as shown in Table 5.1, the specific surface area was increased from 0.686 m²/g to 1.392 m²/g after regrinding. About half of the surface may be carried forward from the rougher stage to the cleaner stage, covered by collector, and contribute to chalcopyrite recovery in the cleaner flotation even without additional collector. As shown in Figure 5.3, chalcopyrite recovery was increased after the addition of extra collector. Maximum recovery of 95% was achieved after the addition of 160 g/t collector. However, further addition of collector above 160 g/t decreased chalcopyrite recovery.

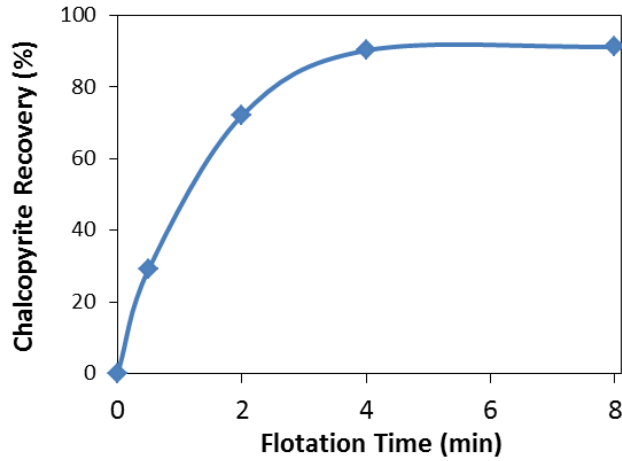


Figure 5.2 Chalcopyrite recovery as a function of flotation time in rougher flotation after primary grinding.

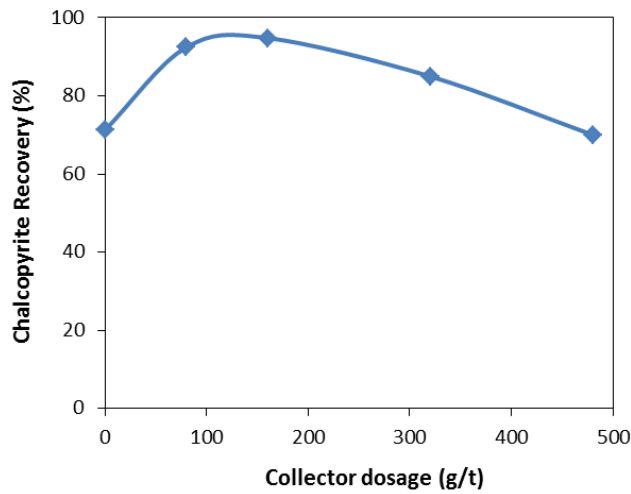


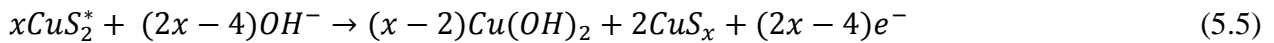
Figure 5.3 Chalcopyrite recovery in cleaner flotation as a function of collector dosage after regrinding.

Table 5.1 Specific surface area of regrinding feeds and products (m²/g)

Sample	Regrinding Feed	Regrinding Product
Chalcopyrite	0.686	1.392
Chalcocite	0.192	1.317
Pyrite/Chalcopyrite	0.760	1.340
Pyrite/Chalcocite	0.144	1.272

During grinding and regrinding in an oxidizing environment with stainless steel media, the chalcopyrite surface should have been oxidized to some extent, which affects its flotation. To detect chalcopyrite oxidation species, the regrinding feed and product were examined by XPS. The S 2p XPS spectra from mineral surfaces before and after regrinding are shown in Figure 5.4. These

spectra were fitted using the $2p_{1/2}$ and $2p_{3/2}$ doublet with a fixed 1:2 intensity ratio and 1.18 eV energy separation. The doublet with the S $2p_{3/2}$ binding energy at 161.1 eV is attributed to S^{2-} from $CuFeS_2$. The doublet at 162.1 eV is due to S_2^{2-} from the metal-deficient sulphide (CuS_2) caused by oxidation of chalcopyrite. The doublet at 162.7 eV can be attributed to the formation of polysulphide from the oxidation of both sulphide minerals (Buckley and Woods 1984, Smart et al. 1999). An energy loss (EL) feature has been fitted at approximately 164.1 eV, which is associated with S 3p to Fe 3d excitation (Harmer et al. 2004, Acres et al. 2010). Based on the type of surface oxidation species, the following reactions on chalcopyrite surfaces are proposed:



The quantification of the regrinding feed and product was summarized in Table 5.2. The percentage of monosulphide was increased after regrinding, which was due to the fresh surface generated. Although some polysulphide was present in both regrinding feed and product, no sulphate product was observed, which suggests that chalcopyrite surfaces in both regrinding feed and product were only mildly oxidized. The metal-deficient sulphide and polysulphide from mild oxidation of chalcopyrite surfaces are hydrophobic, and contribute to the collectorless flotation of chalcopyrite (Gardner and Woods 1979, Buckley and Woods 1984, Zachwieja et al. 1989).

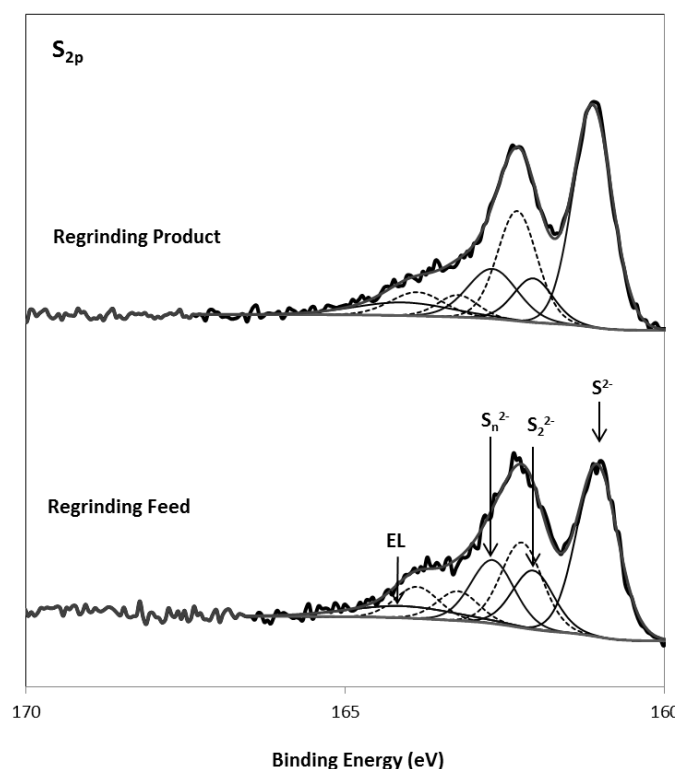


Figure 5.4 S 2p XPS spectra from mineral surfaces of regrinding feed and product of chalcopyrite mineral.

Table 5.2 S 2p quantification for the regrinding feed and product of chalcopyrite mineral

Sample	Species	2p _{3/2} position	Area contribution (%)
Regrinding Feed	Monosulphide	161.1	53.8
	Disulphide	162.1	18.6
	Polysulphide	162.7	21.1
	Energy loss	164.1	6.5
Regrinding Product	Monosulphide	161.1	63.0
	Disulphide	162.1	12.7
	Polysulphide	162.7	18.1
	Energy loss	164.1	6.2

EDTA extraction was conducted after primary grinding and regrinding of chalcopyrite to study the surface oxidation of chalcopyrite by measuring copper and iron ion production. As shown in Table 5.3, the amounts of EDTA extractable iron and copper ions from chalcopyrite are relatively low. The amount of extracted ions is slightly higher in the regrinding product than in the regrinding feed, which may be due to the further oxidation of the fresh surfaces.

Table 5.3 EDTA extractable iron and copper ions of the regrinding feed and product of the chalcopyrite mineral.

	Chalcopyrite	
	Feed	Product
Fe (mole/m ² mineral)	4.46×10^{-6}	5.18×10^{-6}
Cu (mole/m ² mineral)	7.66×10^{-6}	9.69×10^{-6}

In summary, the results show that mild oxidation occurred on the chalcopyrite surface during regrinding. The metal-deficient and polysulphide oxidation products, together with collector carried from rougher flotation, provided surface hydrophobicity, contributing to high chalcopyrite recovery in cleaner flotation even without additional collector. More fresh surfaces were created by regrinding, requiring more collector for further improving the recovery.

5.2.2.2 Flotation of chalcocite

The flotation of chalcocite without mixing with pyrite was also studied. As shown in Figure 5.5, at the rougher stage, 84% recovery was achieved after 8 min flotation. The rougher concentrate was reground and floated in the cleaner stage. Chalcocite recovery as a function of collector dosage is shown in Figure 5.6. Chalcocite recovery of 59% was achieved without additional collector in cleaner flotation. After adding extra collector, the recovery was further improved. At 200 g/t collector, the recovery was about 82% and increased only slightly with a further addition of collector. Chalcocite recovery was lower than chalcopyrite recovery in both rougher and cleaner flotation stages. This may be associated with the more electrochemically active nature of chalcocite.

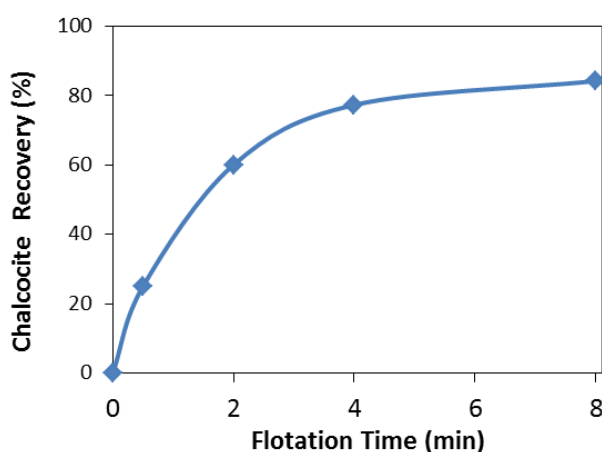


Figure 5.5 Chalcocite recovery as a function of flotation time in rougher flotation after primary grinding.

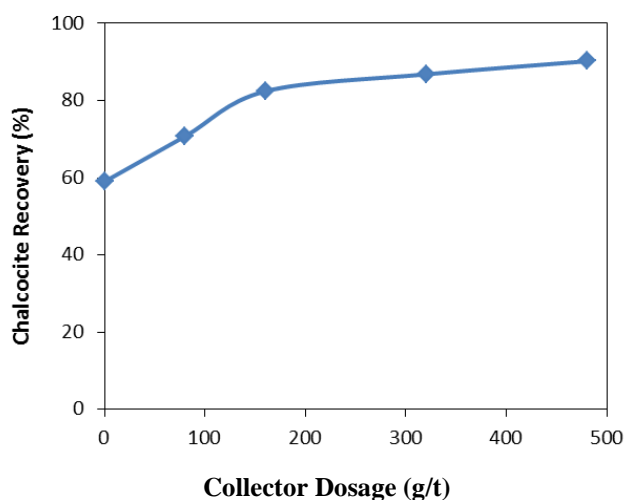


Figure 5.6 Chalcocite recovery in cleaner flotation as a function of collector dosage after regrinding.

To identify the species on the chalcocite surface, the regrinding feed and product of chalcocite were examined by XPS. The S 2p XPS spectra from the mineral surfaces before and after regrinding are shown in Figure 5.7. The doublet at 161.8 eV is assigned to S^{2-} from Cu_2S (Buckley and Woods 1984). The broad peak observed at 167.7 eV is attributed to sulphate SO_4^{2-} . An energy loss (EL) peak was also fitted at 164.0 eV. The quantification of regrinding feed and product was summarized in Table 5.4. In the regrinding feed, 79.2 at% of S is present as S^{2-} , while, in the regrinding product, 80.5 at% is present as S^{2-} . Therefore, the speciation of S did not change significantly after regrinding in the chalcocite single mineral system. Sulphate species are present in both regrinding feed and product and since these are hydrophilic they may decrease chalcocite floatability.

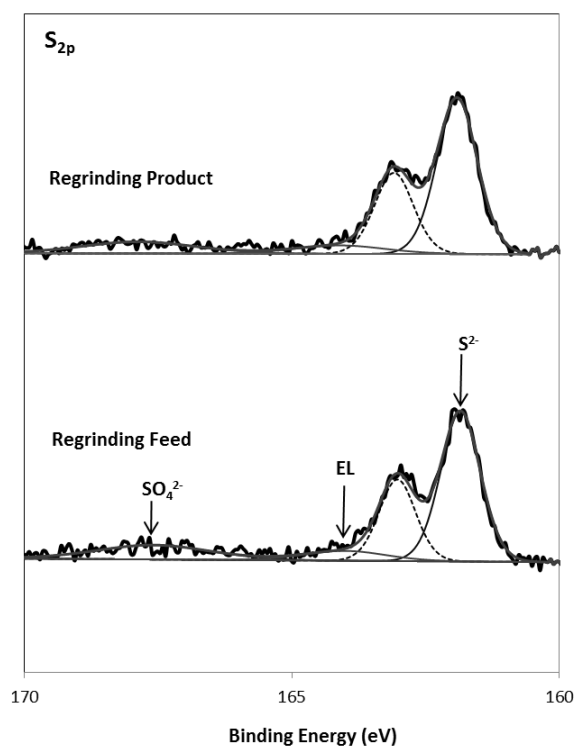


Figure 5.7 S 2p XPS spectra from mineral surfaces of regrinding feed and product of chalcocite mineral.

Table 5.4 S 2p quantification for the regrinding feed and product of chalcocite mineral

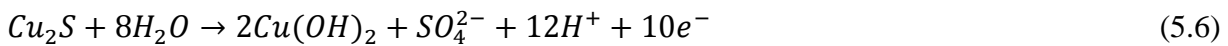
Sample	Species	2p _{3/2} position	Area contribution (%)
Regrinding Feed	Monosulphide	161.8	78.5
	Energy loss	164.0	7.1
	Sulphate	167.6	14.3
Regrinding Product	Monosulphide	161.9	81.8
	Energy loss	164.1	6.6
	Sulphate	167.9	11.6

EDTA extraction of the chalcocite after primary grinding (P₈₀, 75 µm) and regrinding (P₈₀, 20 µm) was also conducted to quantify metal oxidation products. As the EDTA extraction results in Table 5.5 show, chalcocite produced a greater amount of extractable Cu than chalcopyrite. This is in line with the polarization study, showing that chalcocite is more active than chalcopyrite. The extracted Cu ion should be in the form of Cu-hydroxide at pH 9 (Finkelstein 1997), which is hydrophilic and may decrease the chalcocite flotation. The amount of extracted Cu ions is lower in the regrinding product than in the regrinding feed, due to the greater surface area generated after regrinding.

Table 5.5 EDTA extractable iron and copper of the grinding and regrinding product of the chalcocite single mineral.

Chalcocite		
	Feed	Product
Fe (mole/m ² mineral)	8.93×10^{-6}	3.57×10^{-6}
Cu (mole/m ² mineral)	3.19×10^{-4}	1.52×10^{-4}

Based on the analysis of surface oxidation species by XPS and EDTA, the oxidation pathway of chalcocite was proposed as follows:



The presence of sulphate species and a higher amount of copper oxidation species on chalcocite indicates that stronger oxidation occurred during both primary grinding and regrinding of chalcocite compared to primary grinding and regrinding of chalcopyrite. This may explain lower chalcocite recovery in both rougher and cleaner flotation.

5.2.2.3 *The separation of chalcopyrite from pyrite*

The separation of chalcopyrite from pyrite was studied by using a 1:1 mixture of these two minerals. Figure 5.8 shows chalcopyrite recovery as a function of pyrite recovery in rougher flotation after primary grinding. Both chalcopyrite and pyrite displayed high floatability with more than 90% recovery at the completion of 8 min flotation. Pyrite flotation is usually depressed in alkaline solutions. However, in this system, high pyrite recovery occurred due to surface activation by copper ions emanating from copper minerals during grinding and conditioning (Leppinen 1990, Finkelstein 1997). This test was designed to simulate industrial flotation circuits which are operated to float some pyrite in rougher flotation and further reject pyrite in cleaner flotation (e.g. Telfer copper flotation circuit).

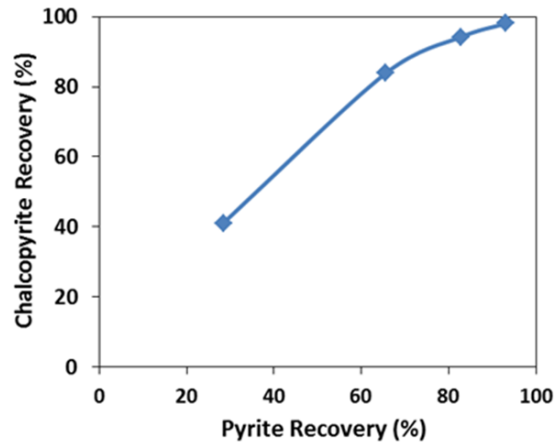


Figure 5.8 Chalcopyrite recovery as a function of pyrite recovery in rougher flotation after primary grinding.

The rougher concentrate was reground from P₈₀ 75 μm to 20 μm and then subjected to cleaner flotation to study the separation of chalcopyrite from pyrite. Figure 5.9 shows chalcopyrite and pyrite recovery from cleaner flotation as a function of the collector addition. 89% chalcopyrite recovery was achieved in 8 min flotation without additional collector, which is higher than that from the flotation of single chalcopyrite shown in Figure 5.3. It suggests that the presence of pyrite enhances chalcopyrite flotation. This may be caused by the galvanic interaction and surface oxidation, and will be further discussed. With the addition of extra collector, chalcopyrite recovery was increased slightly and then decreased, which is similar to the behaviour shown in the flotation of single chalcopyrite flotation shown in Figure 5.3. However, pyrite flotation was strongly depressed with 10% recovery in 8 min flotation regardless of the collector addition.

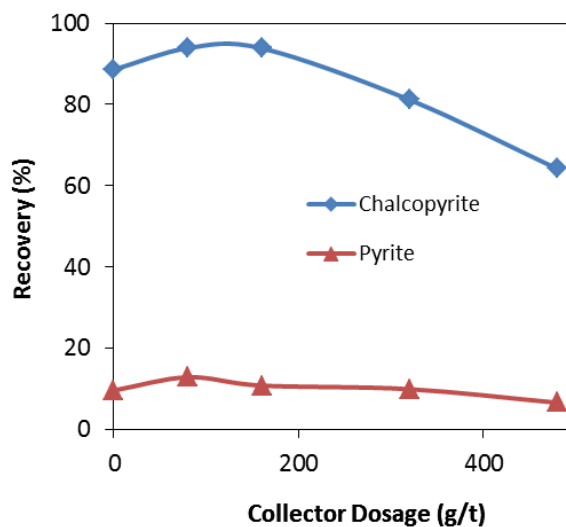


Figure 5.9 Chalcopyrite and pyrite recovery from cleaner flotation as a function of collector dosage.

To understand the surface species on both chalcopyrite and pyrite, the regrinding feed and product were examined by XPS. The S 2p XPS spectra from mineral surfaces before and after regrinding are shown in Figure 5.10. The spectra were fitted with only two doublets. The peak at 161.3 eV is attributable to S^{2-} from chalcopyrite or pyrite. The other doublet at 162.5 eV should be due to a combination of S_2^{2-} from pyrite, S_2^{2-} from chalcopyrite, and S_n^{2-} from chalcopyrite. Since the positions of these peaks are very close, especially S_2^{2-} from pyrite with S_2^{2-} from chalcopyrite, it is difficult to further decouple them precisely (Smart et al. 1999). Furthermore, a broad peak was observed at 168.2 eV in the regrinding product, which is attributed to sulphate SO_4^{2-} (Buckley and Woods 1984). Since chalcopyrite is more electrochemically active than pyrite, the sulphate species should be primarily generated from chalcopyrite. The quantification of the regrinding feed and product was summarized in Table 5.6. Again, a greater monosulphide proportion occurred in the regrinding product probably due to the generation of new surfaces.

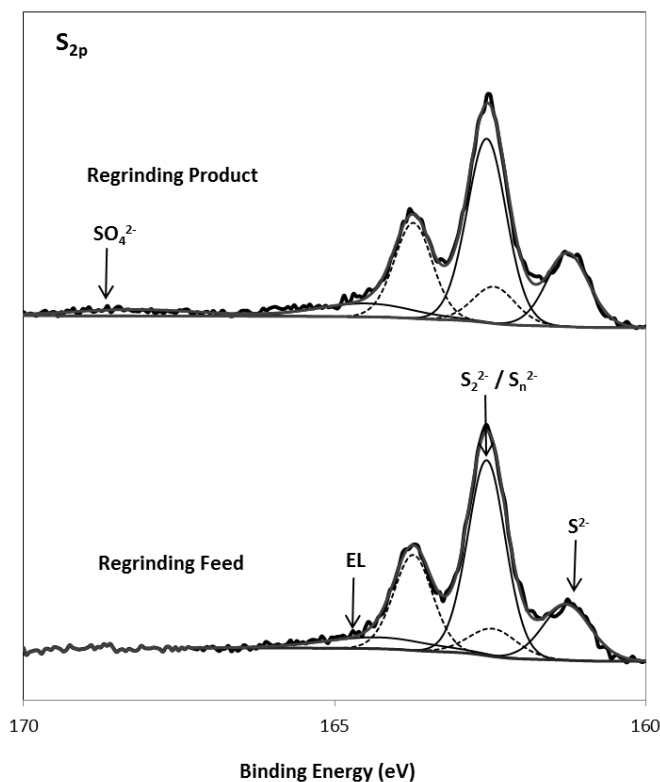


Figure 5.10 S 2p XPS spectra from mineral surfaces of regrinding feed and product for chalcopyrite-pyrite mixture.

Table 5.6 S 2p quantification for the regrinding feed and product for chalcopyrite-pyrite mixture

Sample	Species	2p _{3/2} position	Area contribution (%)
Regrinding Feed	Monosulphide	161.3	24.4
	Disulphide/Polysulphide	162.5	68.1
	Energy loss	164.3	7.5
Regrinding Product	Monosulphide	161.2	26.4
	Disulphide/Polysulphide	162.5	61.5
	Sulphate	168.2	4.8
	Energy loss	164.4	7.3

The Cu 2p XPS spectra from mineral surfaces before and after regrinding are shown in Figure 5.11. The Cu⁺ Cu 2p_{3/2} component was identified at about 932.2 eV (McIntyre and Cook 1975, Deroubaix and Marcus 1992). A second component in the Cu 2p_{3/2} at about 934.0 eV is attributable to Cu²⁺-hydroxyl species (Weisener and Gerson 2000). The percentage of Cu⁺ to the overall Cu for the regrinding feed and product is 78.9% and 84.0%, respectively. The slight increase of Cu⁺ after regrinding may be due to the generation of fresh chalcopyrite surfaces. However, for both regrinding feed and product, Cu²⁺ ions (oxidation products) are the minor copper species.

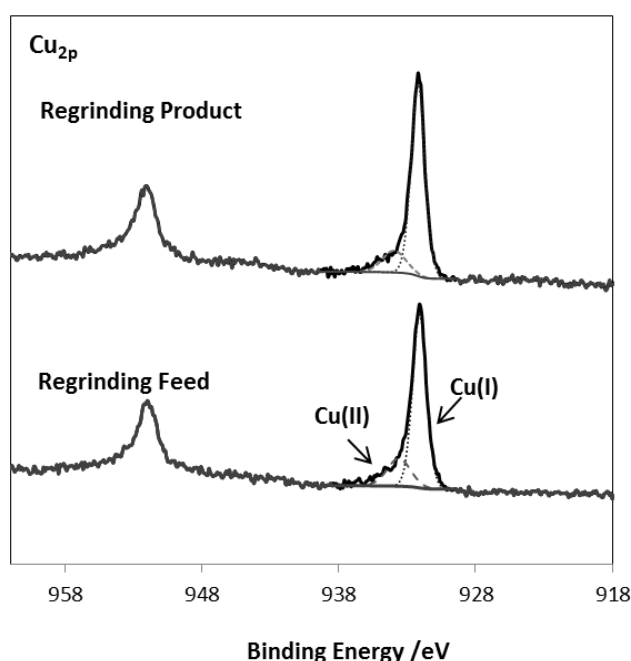


Figure 5.11 Cu 2p XPS spectra from mineral surfaces on regrinding feed and regrinding product for chalcopyrite-pyrite mixture.

Pyrite flotation in the cleaner stage was strongly depressed when the pyrite was in a mixture with chalcopyrite. As studied previously, pyrite flotation is depressed in alkaline solutions, but the addition of copper ions significantly increases pyrite recovery within the pH 6-10 range by activating the pyrite surface (Leppinen 1990, Finkelstein 1997, Zhang et al. 1997). The result of the pyrite single mineral experiment in Chapter 4 demonstrated that the effect of regrinding with stainless steel media on pyrite flotation at pH 9 was mainly governed by available copper ions and surface oxidation. As discussed in the previous section, the oxidation of chalcopyrite only produced a small amount of copper ions, which may not sufficiently activate pyrite in cleaner flotation. The amount of Cu ions per unit surface area after primary grinding and regrinding of chalcopyrite mixed with pyrite was estimated by assuming that the Cu ion production by chalcopyrite is the same with and without the addition of pyrite. The Cu ion per surface area is 9.21×10^{-6} mole/m² after primary grinding and significantly decreased to 4.06×10^{-6} mole/m² after regrinding. This decrease in copper ions may be associated with the increase in surface area after regrinding.

Figure 5.12 shows S 2p XPS spectra of flotation tailing with 96% pyrite and 4% chalcopyrite. Due to the predominant pyrite composition, the XPS spectra may illustrate the surface property of pyrite after regrinding in the presence of chalcopyrite. Figure 5.12 indicates a clear SO₄²⁻ peak at 168.2 eV, suggesting pyrite oxidation. As summarized in Table 5.7, 11.1 at% S occurs in the form of SO₄²⁻ which may limit pyrite activation by copper ions. Pyrite oxidation also indicates the weak galvanic interaction between chalcopyrite and pyrite with some oxidation occurring on cathodic pyrite.

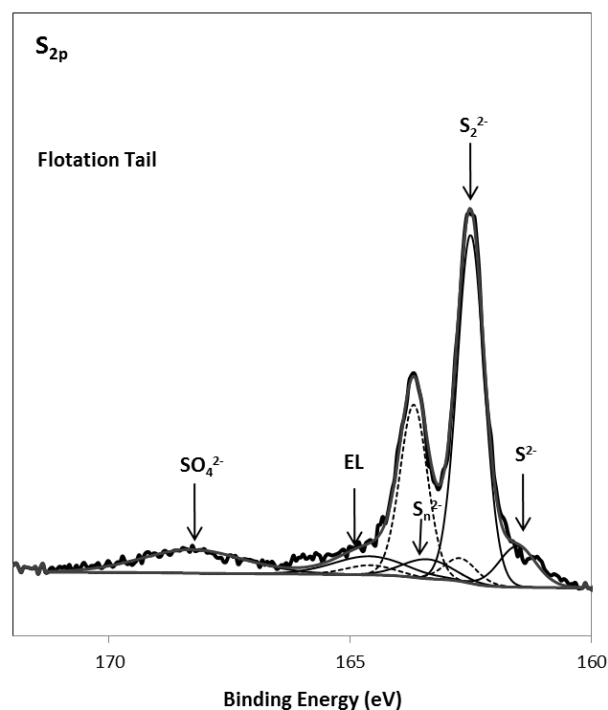


Figure 5.12 S 2p XPS spectra from mineral surfaces on the tailing consisting of 96% pyrite and 4% chalcopyrite from the cleaner flotation of chalcopyrite mixed with pyrite.

Table 5.7 S 2p quantification for the tailing from cleaner flotation of chalcopyrite mixed with pyrite (160 g/t collector).

Sample	Species	2p _{3/2} position	Area contribution (%)
Flotation Tail	Monosulphide	161.5	10.5
	Disulphide	162.5	65.6
	Polysulphide	163.4	6.6
	Energy loss	164.5	6.2
	Sulphate	168.3	11.1

In summary, the strong depression of pyrite in the flotation of chalcopyrite mixed with pyrite in the cleaner stage may be caused by insufficient copper ions originating from chalcopyrite and some surface oxidation on pyrite.

5.2.2.4 Separation of chalcocite from pyrite

The separation of chalcocite from pyrite was also investigated using a mixture of pure mineral samples. Figure 5.13 shows chalcocite recovery as a function of pyrite recovery in rougher flotation

after primary grinding. Both chalcocite and pyrite recovery were high, more than 90% at the completion of 8 min flotation. The high pyrite recovery was due to the activation by copper ions emanating from chalcocite. The presence of pyrite also slightly increased chalcocite flotation, which may be caused by the decrease of surface oxidation species. In addition, after mixing with pyrite, chalcocite flotation was slightly lower than chalcopyrite flotation, while pyrite flotation was slightly better in the presence of chalcocite than in the presence of chalcopyrite in rougher flotation with all flotation conditions being the same.

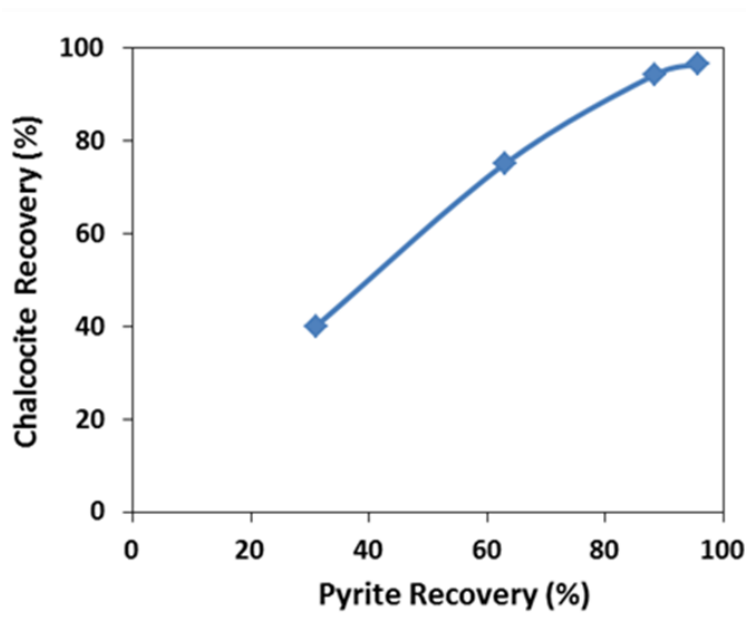


Figure 5.13 Chalcocite recovery as a function of pyrite recovery in rougher flotation after primary grinding.

After regrinding, chalcocite separation from pyrite without and with the addition of collector in the cleaner flotation stage is shown in Figure 5.14. Without the addition of collector, both chalcocite and pyrite flotation were reduced significantly. Chalcocite recovery was 42.8% in 8 min flotation, which is much lower than that in the single chalcocite flotation. With no collector addition, pyrite recovery was 24.8%. With the collector addition, chalcocite recovery increased significantly to 78% at 160 g/t collector and then increased slightly with further collector addition. Pyrite recovery increased in a similar way with the collector amount but at lower value than chalcocite recovery.

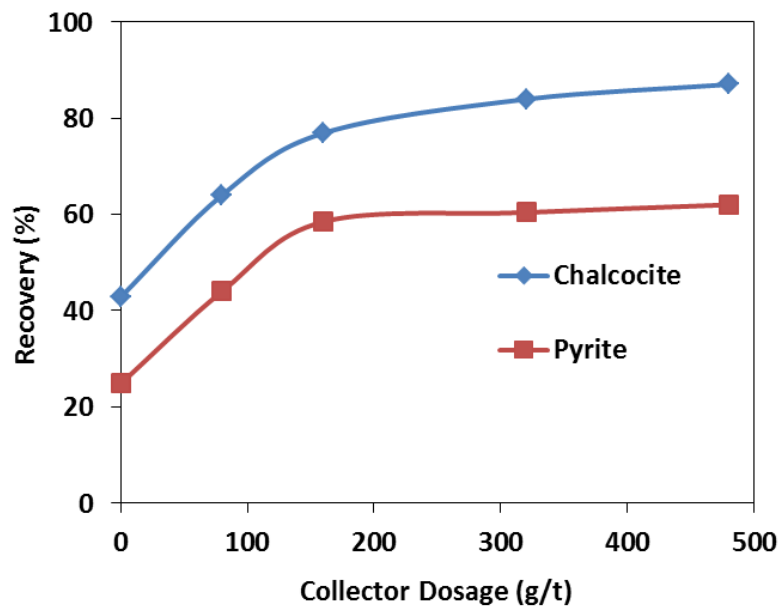


Figure 5.14 Chalcocite and pyrite recovery from cleaner flotation as a function of collector dosage.

The surface species on regrinding feed and product when chalcocite was mixed with pyrite were examined by XPS. The Cu 2p XPS spectra from mineral surfaces before and after regrinding are shown in Figure 5.15. The Cu⁺ Cu 2p_{3/2} component was identified at about 932.6 eV (McIntyre and Cook 1975, Deroubaix and Marcus 1992). A second component in the Cu 2p_{3/2} at about 934.2 eV is attributable to Cu²⁺-hydroxyl species (Weisener and Gerson 2000). The broad peak at about 943.3 eV is Cu²⁺-related shake-up satellite energy loss structure, which further confirms the presence of Cu²⁺. The percentage of Cu⁺ to the overall Cu for the regrinding feed and product is 79.4 and 61.9% Cu, respectively. It suggests that a greater amount of Cu-hydroxides were formed on regrinding product resulted from chalcocite oxidation. Compared to the XPS results of the chalcocite single minerals in the absence of pyrite, the presence of pyrite significantly accelerated the oxidation of chalcocite, which may due to a strong galvanic interaction between these two minerals as a result of a large difference in their rest potential.

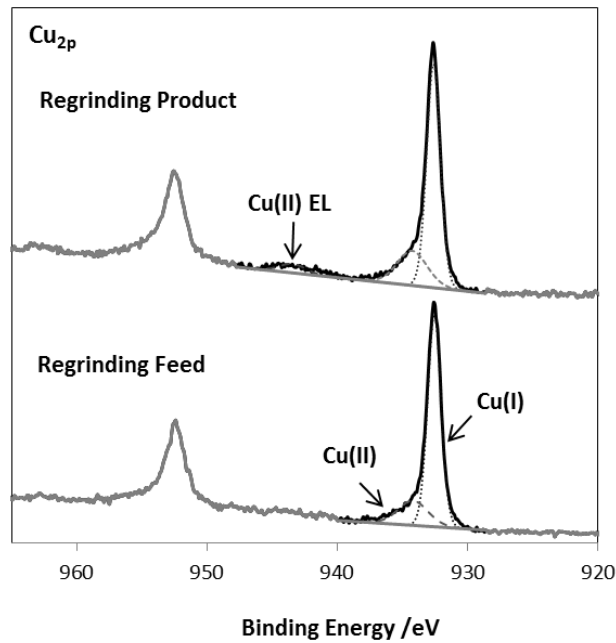


Figure 5.15 Cu 2p XPS spectra from mineral surfaces on regrinding feed and regrinding product for chalcocite-pyrite mixture.

The Cu ion per unit surface area after primary grinding and regrinding of chalcocite mixed with pyrite was estimated by assuming that the Cu ion production by chalcocite is the same with and without the addition of pyrite. After calculation based on the chalcocite single mineral data shown in Table 5.5, the Cu ion per unit surface area after primary grinding was about 4.25×10^{-4} mole/m². It decreased to 7.9×10^{-5} mole/m² after regrinding, still much higher than that produced from the chalcopyrite-pyrite mixture after primary grinding (9.21×10^{-6} mole/m²) where pyrite activation was evident. Therefore, chalcocite should be able to provide sufficient copper ions to activate pyrite after regrinding. Furthermore, a strong galvanic interaction occurs between chalcocite and pyrite, resulting in reduced oxidation on cathodic pyrite, which can also benefit the copper activation on pyrite.

5.2.3 Flotation of chalcopyrite and chalcocite and their separation from pyrite after regrinding with mild steel media

5.2.3.1 Flotation of chalcopyrite and chalcocite

In the previous study in 5.2.2, a high chalcopyrite and chalcocite recovery was obtained in the rougher flotation after primary grinding with stainless steel media, as shown in Figure 5.2 and

Figure 5.5, respectively. Mild steel grinding media was also used during primary grinding to investigate whether different grinding media during primary grinding can influence the mineral floatability at the rougher flotation stage. As shown in Figure 5.16, a high chalcopyrite and chalcocite flotation recovery can also be achieved in the rougher flotation after grinding with mild steel media with all other conditions remained unchanged. It indicates that, during primary grinding, different grinding media did not have a significant effect on the subsequent flotation performance of copper sulphides.

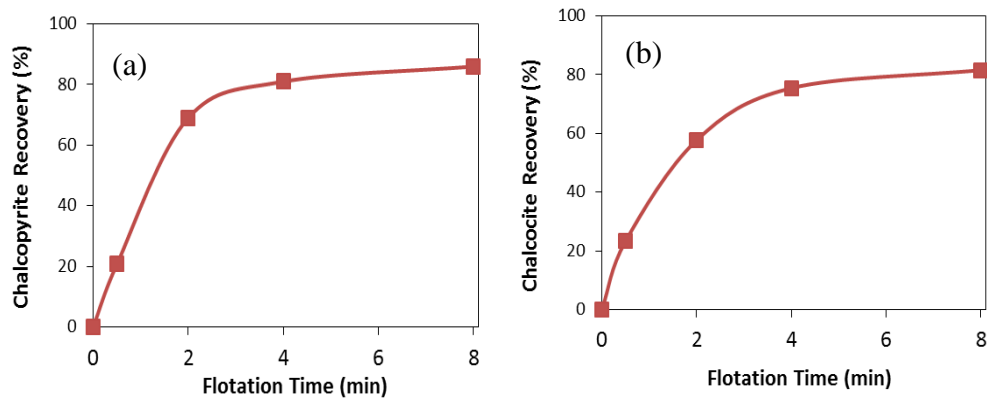


Figure 5.16 Chalcopyrite (a) and chalcocite (b) rougher flotation recovery after primary grinding with mild steel grinding media.

In order to study the effect of using mild steel grinding media during regrinding on the subsequent cleaner flotation, the rougher flotation concentrates were reground with mild steel grinding media after primary grinding with stainless steel grinding media and rougher flotation. The flotation behaviour of chalcopyrite and chalcocite after regrinding is shown in Figure 5.17. Without the additional collector, both the chalcopyrite and chalcocite flotation was strongly depressed with the recovery being just 5% and 7%, respectively. And the flotation recovery just slightly increased after the addition of more collectors. Thus, the restoration of flotation of copper sulphides was more difficult after regrinding with mild steel grinding media than with stainless steel media. This may be related to the high iron contamination from mild steel grinding media, which precipitated on mineral surfaces and prohibited the adsorption of collectors in the subsequent flotation.

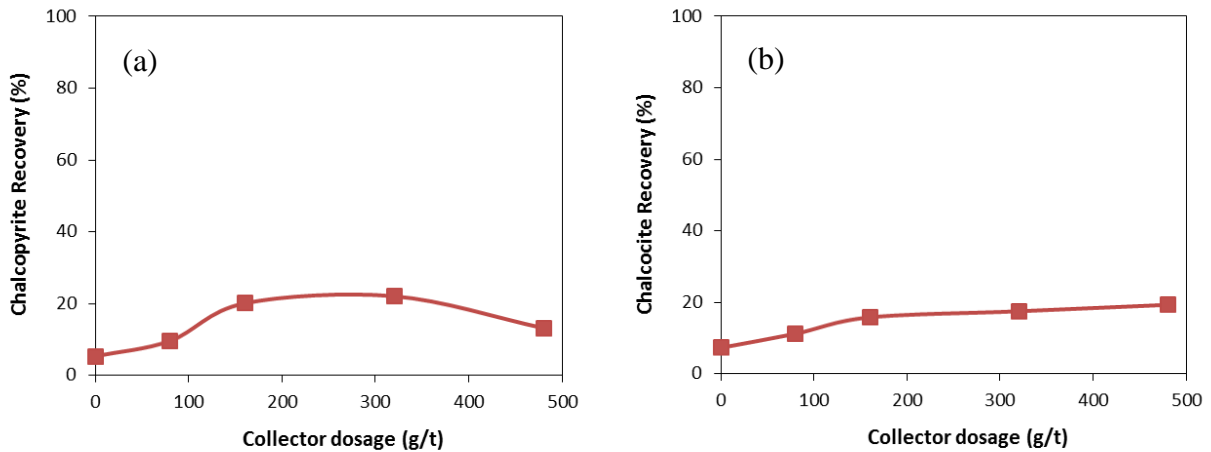


Figure 5.17 Chalcopyrite (a) and chalcocite (b) cleaner flotation recovery as a function of collector dosage after regrinding with mild steel grinding media.

The surface species on copper minerals after grinding and regrinding with mild steel media were examined by XPS and compared to the products ground with stainless steel media. The Fe 2p XPS spectra are shown in Figure 5.18. Fe²⁺ in the pyrite bulk is represented by a narrow single peak with a binding energy of 707.0 - 707.2 eV, and the broad peak centred at 710.3 - 710.9 eV is attributed to Fe³⁺-O/OH species. Table 5.8 shows the quantification of iron species on the chalcopyrite primary grinding and regrinding products. It is found that 89.2% of iron species were in the form of iron hydroxide after primary grinding with mild steel media, which was higher than that after grinding with stainless steel media (77.1%). For the chalcopyrite regrinding products, 95.6% of iron was in the form of iron hydroxide after regrinding with mild steel while the percentage dropped to 77.1% when stainless steel was used. In addition to XPS analysis, EDTA extraction of chalcopyrite after primary grinding and regrinding was also conducted to study the surface oxidation and contamination by measuring metal ion production. As summarized in Table 5.9, 5.17 mg/g Fe was extracted by EDTA after primary grinding with mild steel media while only 0.47 mg/g was extracted when using stainless steel media. For the regrinding product, the extracted Fe was 21.04 mg/g when using mild steel as grinding media, which was significantly higher than that of the primary grinding product, while only 0.41 mg/g Fe was extracted with stainless steel media which is similar to that of the primary grinding product. The EDTA extraction data clearly shows that mild steel media produced a higher amount of iron oxidation species than stainless steel, especially during regrinding. Although, from XPS analysis, most of the surface iron also presented in the form of iron hydroxides after grinding and regrinding with stainless steel media, the total amount of iron hydroxides produced by stainless steel was significantly smaller than that produced by mild steel

media according to the EDTA results. And most of these iron species on chalcopyrite surfaces may be from the oxidation of the mineral itself rather than the stainless steel media, because this media is relatively inert and does not produce much iron oxidation species and stainless steel generates an oxidizing grinding condition which increases the mineral surface oxidation. During grinding with mild steel media, most of the iron hydroxides should be from the corrosion of grinding media, because the mineral oxidation is weaker during grinding with mild steel media due to the more reducing condition it generated. It is generally agreed that these iron hydroxide species are hydrophilic and are detrimental to the flotation (Natarajan and Iwasaki 1984, Grano et al. 1997a, Grano et al. 1997b, Peng et al. 2003a, Peng et al. 2003b, Greet and Bartle 2008). However, these hydrophilic iron species did not depress the rougher flotation, which may be because these species were still not enough to generate a significant influence on surface hydrophobicity or because the floatability of coarse particles were not sensitive to the iron contamination species. Regrinding with mild steel media generated more iron species compared to primary grinding and the chalcopyrite flotation was strongly depressed in the subsequent cleaner flotation. It indicates these iron contamination species were playing an important role in the cleaner flotation of fine particles after regrinding.

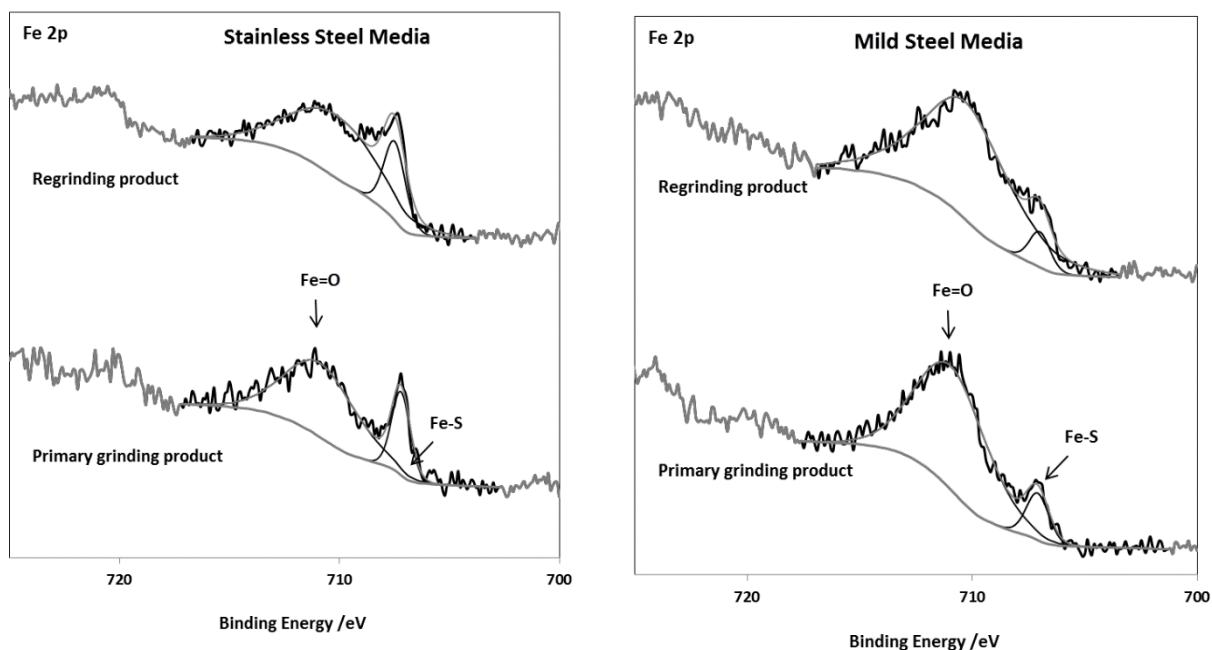


Figure 5.18 Fe 2p XPS spectra from mineral surfaces of regrinding product and primary grinding product of chalcopyrite mineral

Table 5.8 Fe 2p quantification for the grinding and regrinding product of chalcopyrite mineral

	Sample	Species	2p_{3/2} position	Area contribution (%)
Stainless steel	Primary grinding	Fe=O	710.9	76.6
	product	Fe-S	707.2	23.4
	Regrinding product	Fe=O	710.9	77.1
		Fe-S	707.2	22.9
Mild steel	Primary grinding	Fe=O	710.9	89.2
	product	Fe-S	707.1	10.8
	Regrinding product	Fe=O	710.3	95.6
		Fe-S	707.0	4.4

Table 5.9 EDTA extractable iron and copper ions of the grinding and regrinding product of the chalcopyrite mineral.

	Stainless steel		Mild steel	
	Primary grinding	Regrinding	Primary grinding	Regrinding
Extracted Fe (mg/g)	0.47	0.41	5.17	21.04
Extracted Cu (mg/g)	0.97	0.86	1.27	0.21

In addition to the iron contamination species, the sulphur oxidation species were critical to mineral floatability as well. From the XPS S 2p quantification shown in Table 5.10, only 49.3% of sulphur on chalcopyrite surface presented in its original monosulphide state after primary grinding with mild steel media and 37.3% after primary grinding with stainless steel media. Furthermore, there was 20.1% of sulphur presented in the form of sulphate when stainless steel was used as grinding media, and it dropped to 14.8% if mild steel was used during primary grinding. This indicates the chalcopyrite surfaces were oxidized and more oxidation occurred when using stainless steel media than using mild steel media. After regrinding, as more fresh surfaces were created, the percentage of monosulphide increased to 63% with stainless steel media and 67.9% with mild steel media. In addition, there was no sulphate species detected on the regrinding products. This suggests the oxidation was relatively weak during regrinding than during primary grinding. Among various oxidation species, some were hydrophobic, such as polysulphide, which can benefit the flotation, however, the sulphate species are hydrophilic and can depress the flotation. As discussed in previous section, the mild oxidation on chalcopyrite surfaces during regrinding with stainless steel significantly improved the chalcopyrite recovery due to the hydrophobic sulphur species. When using mild steel media, a more reducing condition was created inside the mill, therefore the

percentage of oxidised sulphur species is smaller compared with the products ground with stainless steel media.

Table 5.10 S 2p quantification for the regrinding feed and product of chalcopyrite mineral

	Sample	Species	2p_{3/2} position	Area contribution (%)
Stainless steel	Primary grinding Product	Monosulphide	161.1	37.3
		Disulphide	162.0	11.7
		Polysulphide	162.6	24.5
		Sulphate	169.1	20.1
		Energy loss	163.8	6.4
	Regrinding Product	Monosulphide	161.1	63.0
		Disulphide	162.1	12.7
		Polysulphide	162.7	18.1
		Energy loss	164.1	6.2
	Mild Steel	Primary grinding product	Monosulphide	160.9
Disulphide			161.9	8.1
Polysulphide			162.5	21.6
Sulphate			168.9	14.8
Energy loss			164.0	6.3
Regrinding Product		Monosulphide	160.7	67.9
		Disulphide	161.7	13.4
		Polysulphide	162.3	12.3
		Energy loss	163.8	6.3

The extracted copper ions from the primary grinding and regrinding products were also summarized in Table 5.9. During primary grinding, slightly more copper species were produced with mild steel media than with stainless steel media, which may be caused by a stronger galvanic interaction. It is noticeable that much less copper ions (0.21 mg/g) were extracted from the mild steel regrinding product. This may be caused by the strong reducing condition generated by mild steel media which prohibited the surface oxidation of chalcopyrite. The copper oxidation species may be not important for the flotation of chalcopyrite itself, however, they can activate some minerals presented in the system (e.g. pyrite) and then influence the separation of different minerals, which will be discussed in the following section.

5.2.3.2 Separation of chalcopyrite and chalcocite from pyrite

The studies in the last section, using chalcopyrite and chalcocite single minerals, indicated that the chalcopyrite and chalcocite could float well after primary grinding with mild steel media, however, their flotation was significantly depressed after regrinding with mild steel media and cannot be restored by additional collectors, which is obviously undesirable. As observed in section 5.2.2, if more than two sulphide minerals are present in one grinding system, galvanic interactions will occur between different minerals, which may influence the floatability of both minerals. Therefore, it is important to further study the effect of mild steel grinding media on the separation of copper minerals from pyrite.

In this study, the copper minerals and pyrite were mixed in a 1:1 ratio. Figure 5.19 shows that both copper minerals and pyrite can still float well at rougher flotation after primary grinding with mild steel grinding media, although the recovery was slightly lower than that after grinding with stainless steel media, which should be caused by the iron contamination from mild steel media. Similar to the copper single mineral study discussed in the last section, the results indicate that different grinding media during primary grinding did not have a significant influence on the separation of copper sulphides from pyrite in the rougher flotation.

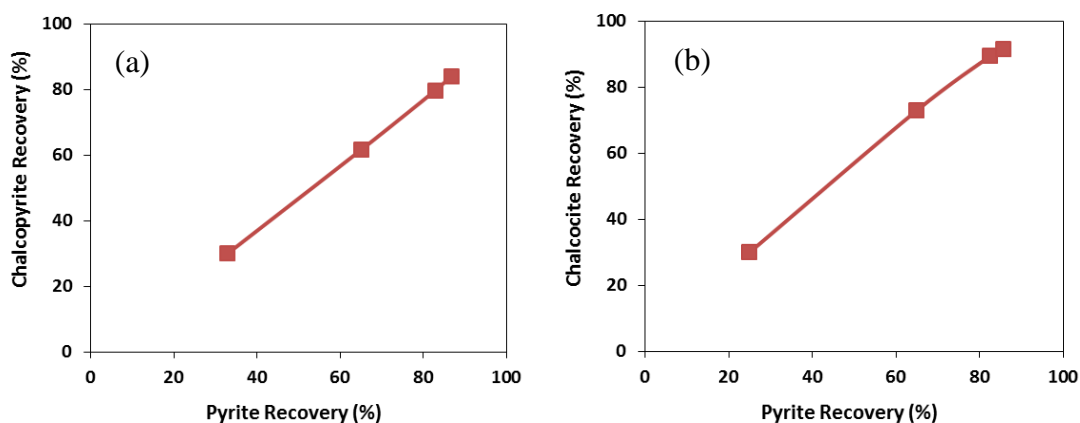


Figure 5.19 Chalcopyrite recovery as a function of pyrite recovery (a) and chalcocite recovery as a function of pyrite recovery (b) in the mixture after primary grinding with mild steel grinding media.

Although a high recovery can be achieved when using mild steel media in the primary grinding, the regrinding feed in the following study was also prepared by primary grinding with stainless steel media to keep consistent with the previous studies. After primary grinding and rougher flotation, the

rougher concentrates were reground with mild steel media. As shown in Figure 5.20, after regrinding with mild steel grinding media, the recovery of both copper minerals and pyrite were quite low and cannot be restored by additional collectors.

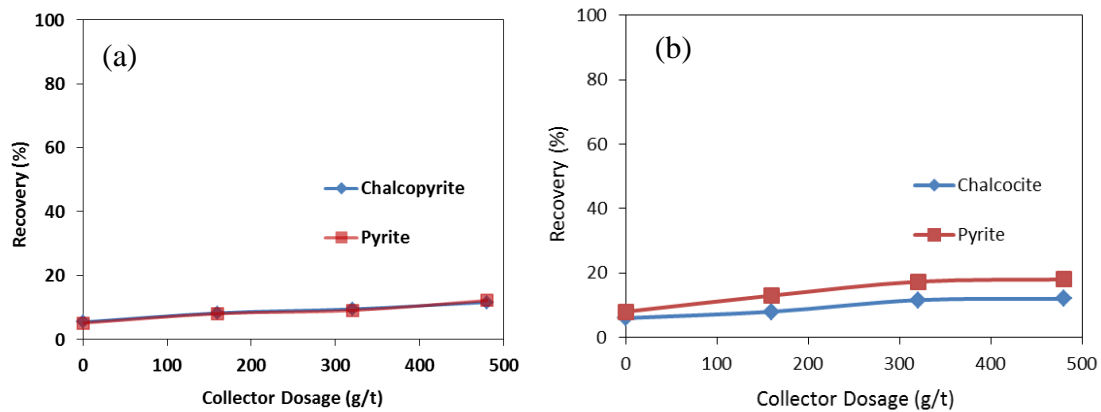


Figure 5.20 Chalcopyrite and pyrite recovery (a) and Chalcocite and pyrite recovery (b) as a function of collector dosage, after regrinding the mixture of both minerals with mild steel grinding media.

The overall trend of the flotation of copper minerals in the presence of pyrite is similar to the previous study of only copper single minerals. A high recovery was still achieved in rougher flotation but the flotation became poor in the cleaner. As discussed in the previous section, the large amount of iron hydroxides from mild steel media were detrimental to mineral flotation. And the iron contamination was more influential to the flotation of fine particles produced by regrinding than the flotation of coarse particles produced by primary grinding.

Furthermore, compared to the copper single mineral studies, the flotation of copper minerals after mixing with pyrite was more difficult to be increased by adding more collectors, which indicates that the presence of pyrite has some influence on the floatability of copper minerals. This may be caused by the galvanic interactions occurring between copper minerals and pyrite during regrinding (Martin et al, 1991). First of all, the corrosion of mild steel media may increase, which can depress the floatability of both minerals present in the system. In addition, because of the galvanic interaction of the two different minerals, the oxidation of copper mineral was increased while more O_2 was reduced to OH^- on pyrite surfaces. The OH^- can precipitate the metal ions and form hydrophilic metal hydroxides. Furthermore, it has been reported by Huang and Grano (2005) that the galvanic current increases with grinding time. So the galvanic interaction during regrinding with

a long grinding time will have a more significant effect on the surface reactions than that during primary grinding.

In this study, the copper species generated from the oxidation of copper minerals can activate pyrite surface and promote the pyrite flotation. The slightly higher pyrite recovery when mixed with chalcocite was caused by the more Cu activation. As discussed previously, the production of copper ions from chalcopyrite is quite low compared to chalcocite. However, during primary grinding, the amount of copper ions was enough to sufficiently activate pyrite to achieve a high pyrite flotation recovery. Compared to regrinding with stainless steel media, regrinding with mild steel media significantly reduced the production of copper species due to the reducing condition it generated. The low amount of copper ions may also contribute to the low pyrite flotation recovery.

5.3 Conclusions

The current study indicates the different flotation behaviour of chalcopyrite and chalcocite and their separation from pyrite in the cleaner stage after regrinding.

After regrinding with stainless steel media, a high chalcopyrite recovery was achieved due to the hydrophobic surface oxidation species formed in the oxidizing grinding condition, while the chalcocite flotation was depressed but can be further improved by additional collectors. The mixing of copper minerals with pyrite significantly changed the flotation behaviour of both minerals. When chalcopyrite was mixed with pyrite, a higher chalcopyrite recovery was achieved in the cleaner stage, whilst pyrite flotation was strongly depressed and could not be restored even at a high collector addition. Therefore, an efficient separation of chalcopyrite from pyrite can be achieved in the cleaner flotation after regrinding. When chalcocite was mixed with pyrite, both chalcocite and pyrite flotation decreased after regrinding, but the recovery of both minerals could be partly restored by additional collector. Therefore, the separation of chalcocite from pyrite was difficult in the cleaner flotation. These phenomena are governed by the electrochemical activity of chalcopyrite and chalcocite and their galvanic coupling with pyrite. The oxidation of chalcopyrite does not produce sufficient copper ions for activating pyrite but generates a hydrophobic sulphur rich surface. Chalcocite is more electrochemically active than chalcopyrite and therefore a stronger galvanic interaction occurs between chalcocite and pyrite than between chalcopyrite and pyrite. As a result, stronger oxidation occurs on chalcocite compared with chalcopyrite, producing a significant amount of hydrophilic oxidation species to depress its flotation, while providing a sufficient amount of

copper ions to activate pyrite. Furthermore, chalcopyrite and chalcocite do not affect pyrite flotation in such a way in the rougher flotation after primary grinding. This is because the galvanic interaction between minerals in both chalcocite-pyrite and chalcopyrite-pyrite systems is weak at coarse particle sizes with relatively small surface areas.

After regrinding with mild steel media, the flotation of both copper minerals were strongly depressed and cannot be restored by additional collectors, which was mainly caused by the high amount of iron oxidation species from mild steel media. After mixing with pyrite, the copper flotation was further depressed probably due to a stronger galvanic interaction which increased the generation of iron contamination from grinding media. The pyrite flotation recovery was also low mainly due to the iron contamination and may also be caused by the insufficient copper activation during regrinding with mild steel media which created a reducing condition and prevented the generation of copper ions from copper mineral oxidation. Compared to the regrinding and cleaner flotation, the use of mild steel media during primary grinding did not affect the mineral floatability in the rougher. It indicates that the iron contamination was more influential to the flotation of fine particles produced by regrinding than the flotation of coarse particles produced by primary grinding.

Chapter 6 Importance of Pulp Chemistry during Regrinding of Pyrite Flotation Concentrates at Telfer Gold Mine

6.1 Introduction

The objective of this study is to optimize the pulp chemistry during regrinding to improve the separation of copper/gold minerals from pyrite in the subsequent cleaner flotation. As described in Chapter 2, the pulp chemistry, such as pH, Eh and DO, plays an important role in the flotation of sulphide minerals. However, undesirable pulp chemistry is usually produced by the electrochemical reactions occurring in the pulp, such as the decrease of dissolved oxygen concentration due to the mineral or grinding media oxidation. Previous studies in Chapter 4 and Chapter 5 have proved that stronger galvanic interactions and electrochemical reactions occur during regrinding compared to primary grinding, which indicates that a greater change of pulp chemistry should be expected during regrinding. Another important feature of regrinding is that the sulphide content in the feed is usually high since the majority of non-sulphide gangue has been rejected during the previous rougher flotation. For example, in Newcrest's Telfer gold mine, the regrinding feed in the pyrite circuit contains almost 90% pyrite. The high sulphide content directly increases the intensity of chemical reactions inside the grinding mill and modifies the pulp chemistry to a greater extent. Therefore, it will be important to investigate the change of pulp chemistry during regrinding and then take proper measures to optimize it to enhance the subsequent flotation performance.

In this study, the pyrite regrinding-flotation process in Newcrest's Telfer gold mine shown in Figure 1.1 was taken as a case study to understand the effect of regrinding of rougher flotation concentrates on pulp chemistry and subsequent copper-gold flotation and pyrite depression. The pulp chemistry was measured in the plant to understand how regrinding affected the pulp chemistry and flotation at a plant scale. Then, the pyrite concentrate was collected directly from the Telfer processing plant for the regrinding and flotation tests in the laboratory. The plant chemistry and flotation performance were simulated in the laboratory experiments. The factors contributing to the change of pulp chemistry was investigated. A number of methods were tested to optimize the pulp

chemistry to improve the overall flotation performance with the mechanisms studied by surface analysis.

6.2 Results and discussion

6.2.1 Pulp chemistry at Telfer plant

At Telfer, the Eh and DO in the regrind mill discharge, flotation feed hatch, and flotation cells were measured as shown in Figure 6.1, and the results of these measurements are shown in Figure 6.2. The DO was almost zero after regrinding, and difficult to increase afterwards. The Eh (-200 mV) was quite low after regrinding as well, but it increased during flotation. The low DO and Eh after regrinding could be caused by the large amount of fresh pyrite surfaces produced after regrinding, quickly consuming all the oxygen in the slurry. This is a common phenomenon after regrinding of rougher flotation concentrates with a high content of sulphide minerals (Grano 2010). Despite aeration during flotation, the DO remained low indicating the high surface activity and rapid consumption of oxygen. However, the Eh measurement not only depends on dissolved oxygen but also on the ions present (e.g. Fe^{2+} , Cu^{2+}) and impinging mineral particles present in the slurry (Cheng and Iwasaki 1992). In addition, the copper sulphide minerals were recovered into the concentrates, leading to a gradual decrease of their percentage from cell 1 to cell 5. As a result, Eh increased from flotation cell 1 to cell 5 regardless of the low dissolved oxygen.

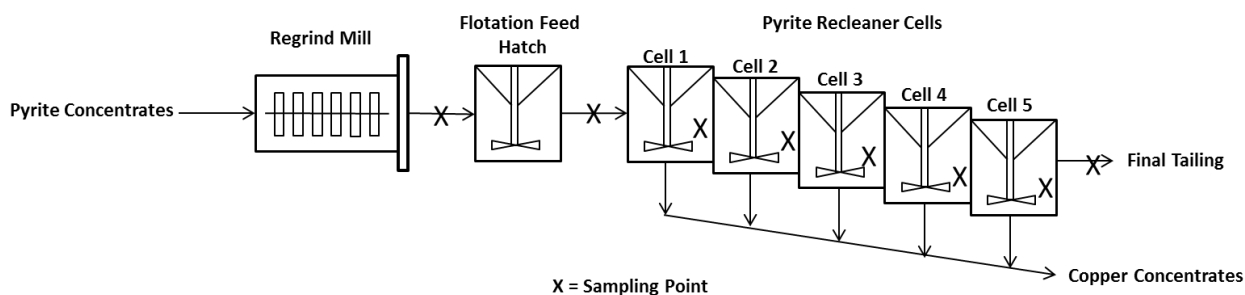


Figure 6.1 Detailed flowsheet of pyrite regrinding and flotation and the sampling points for Eh/DO measurement.

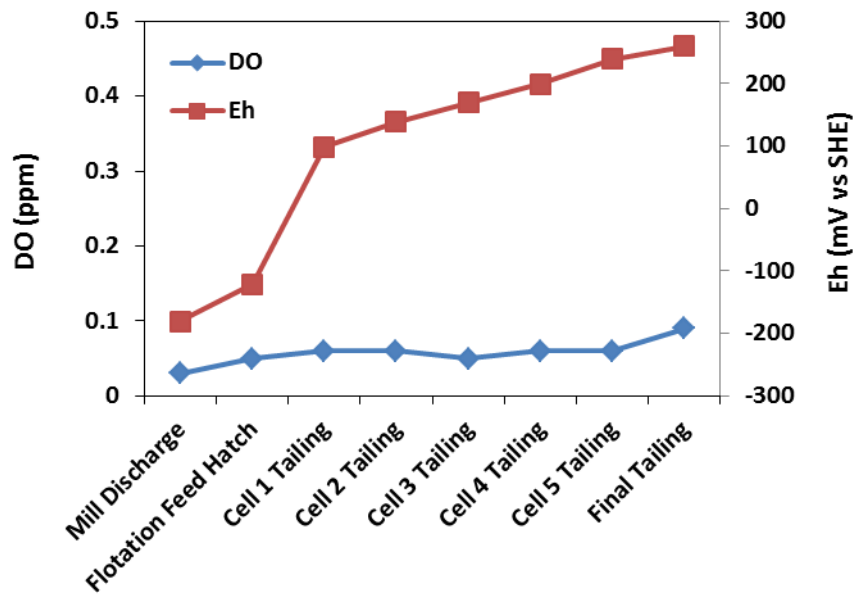


Figure 6.2 DO and Eh in the IsaMill discharge, pyrite recleaner feed hatch, and different stages of the flotation cell in Telfer pyrite regrinding circuit.

6.2.2 Matching plant performance in the laboratory

In the laboratory, nitrogen purging was used during regrinding in the rod mill to match the plant pulp chemistry after regrinding. The measured DO and Eh of the regrinding product were 0 ppm and -150 mV (SHE) respectively, similar to the value observed at Telfer as shown in Figure 6.2. The laboratory flotation results after regrinding are shown in Figure 6.3. The recovery of sulphur, copper and gold is 20%, 58%, and 45%, respectively. By assuming that chalcopyrite is the main copper mineral present and pyrite is the main sulphide gangue mineral (Zheng and Manton, 2010), the flotation rate constant k of copper mineral, pyrite and Au was calculated from the first-order flotation model. In this study, the flotation rate constant k is 0.17 min^{-1} for Au, 0.32 min^{-1} for copper mineral and 0.96 min^{-1} for pyrite. These results are similar to those achieved in the Telfer plant. Copper and gold recovery and rate constant were quite low, while pyrite (indicated by sulphur) recovery and rate constant were relatively high compared to those in normal flotation where pyrite is rejected. The poor copper and gold flotation and poor pyrite rejection should be related to the reducing regrinding condition. Javadi Nooshabadi et al. (2013) proposed that hydrogen peroxide formed on fresh pyrite surfaces even in the absence of oxygen, and oxidized the pyrite surfaces. However, in this study, the oxidation of pyrite surfaces may be limited due to the large amount of fresh surfaces produced after regrinding and the reducing regrinding condition.

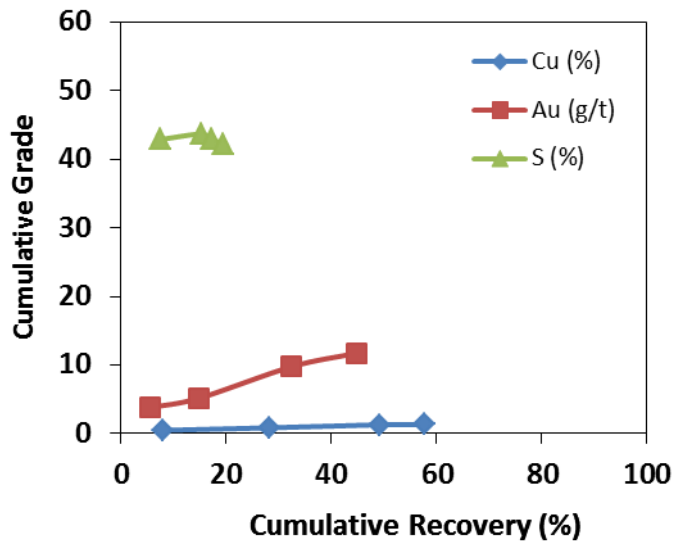


Figure 6.3 The cumulative grade as a function of cumulative recovery after regrinding with N₂ purging.

The difficulty in depressing pyrite at high pH can be caused by copper activation which forms CuS species on the pyrite surface. The copper-activated pyrite has a strong floatability at alkaline conditions (Finkelstein 1997, Chandra and Gerson 2009). In the rougher flotation stage before regrinding, pyrite was recovered to concentrate, therefore, the surfaces had already been activated. It is possible that these activation species were carried to the final regrinding products, as discussed in Chapter 4. Meanwhile, as more copper minerals were liberated during regrinding, fresh pyrite surfaces were further activated by copper ions released from the copper minerals depending on the chemical condition during regrinding. As previously studied by Peng et al. (2012), more copper activation occurred in a reducing condition than an oxidizing condition. In this current study, a strong reducing condition was produced during regrinding, which may promote the copper activation of pyrite. The copper-activated pyrite competed for collector with the copper and gold minerals, resulting in a poor pyrite rejection and a lower copper and gold flotation recovery and concentrate grade (Grano 2010).

It has been reported that oxygen is necessary for copper and gold flotation with xanthate as the collector, because xanthate adsorption cannot proceed without oxidation (Kuopanportti et al. 2000, Allan and Woodcock 2001, Srdjan 2010). Although the effect of oxygen on the adsorption of thionocarbamate collector used in this study has not been extensively studied, oxidation should also be essential for its adsorption on copper and gold minerals (Leppinen et al. 1988).

To depress pyrite flotation while increasing copper and gold flotation after regrinding, oxidising the flotation slurry is the key. In the following section, a range of oxidation schemes were tested.

6.2.3 Application of oxidizing methods during regrinding and cleaner flotation

6.2.3.1 Pre-aeration before cleaner flotation

Aeration was firstly applied before cleaner flotation to increase the DO and Eh of the regrinding product. After applying aeration at 5 L/min for 10 min, the DO increased to about 2 ppm but dropped to a low level near zero after switching off the air. This could be caused by the large amount of fresh pyrite surfaces produced. Unlike DO, the Eh increased to 110 mV (SHE). The flotation results after aeration are shown in Figure 6.4. Copper and gold flotation was greatly improved compared to the baseline test without aeration. Copper mineral recovery increased from 58% to 65% with the rate constant increasing from 0.32 min^{-1} to 0.98 min^{-1} , while gold recovery increased from 45% to 71% with the rate constant increasing from 0.17 min^{-1} to 1.06 min^{-1} . Pyrite flotation was strongly depressed as indicated by sulphur recovery which decreased from 20% to 8% with the rate constant of pyrite decreasing from 0.96 min^{-1} to 0.43 min^{-1} . Final gold grade increased significantly from 11.7 g/t to 32.6 g/t, while, the final copper also increased from 1.31% to 3.33%. This test suggests that oxidation plays an important role in the flotation by increasing copper and gold flotation and depressing pyrite flotation.

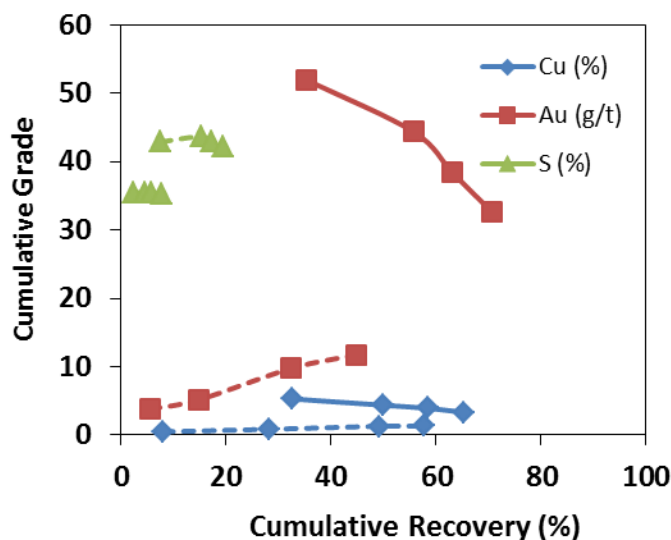


Figure 6.4 The cumulative grade as a function of cumulative recovery in the flotation with pre-aeration (solid line) and without pre-aeration (dashed line).

The depression of pyrite by pre-aeration is normally attributed to the formation of hydrophilic surface oxidation species, such as iron oxide and sulphate. As well as the presence of oxygen in the

slurry, hydrogen peroxide may form during regrinding on pyrite surfaces and play a role in the oxidation of pyrite surfaces (Javadi Nooshabadi et al. 2013). XPS was used in this study to investigate surface oxidation species. Figure 6.5 (a) shows the XPS S 2p and Fe 2p spectra of the particle surfaces before and after applying aeration to the regrinding product of pyrite concentrate. The S 2p spectra were fitted using the 2p_{1/2} and 2p_{3/2} doublet with a fixed 1:2 intensity ratio and 1.18 eV energy separation. The doublet with the S 2p_{3/2} binding energy at 162.3 eV is attributed to disulphide S₂²⁻ from pyrite (Nesbitt, 1998; Schaufuß et al., 1998; Smart et al. 1999). An energy loss (EL) feature has been fitted at approximately 164.6 eV, which is associated with S 3p to Fe e_g excitation (Schaufuß et al., 1998; Peng et al. 2012). The broad peak at 168.9 eV represents the sulphate SO₄²⁻. The quantification of these sulphur species is summarized in Table 6.1. The concentration ratio of SO₄²⁻ species was increased from 4.7% to 10.3% after aeration, indicating the further oxidation of pyrite surfaces by aeration. Another important oxidation product of pyrite is iron hydroxide. Therefore, the iron surface species were also analysed by XPS. The Fe 2p XPS spectra are shown in Figure 6.5 (b). Fe²⁺ in the pyrite bulk is represented by a narrow single peak with a binding energy of 707.0 eV, and Fe²⁺ on the surface appears as a tail with about 0.5 eV higher binding energy (Buckley and Woods 1987, Nesbitt 1998, Schaufuß et al. 1998). The broad peak centred at 711.1 eV is attributed to Fe³⁺-O/OH species (Buckley and Woods 1987, Schaufuß et al. 1998). As shown in Table 6.2, the percentage of Fe in the form of Fe³⁺-O/OH was increased from 41.2% to 50.5% after applying aeration, which further confirmed the oxidation of pyrite surfaces by aeration.

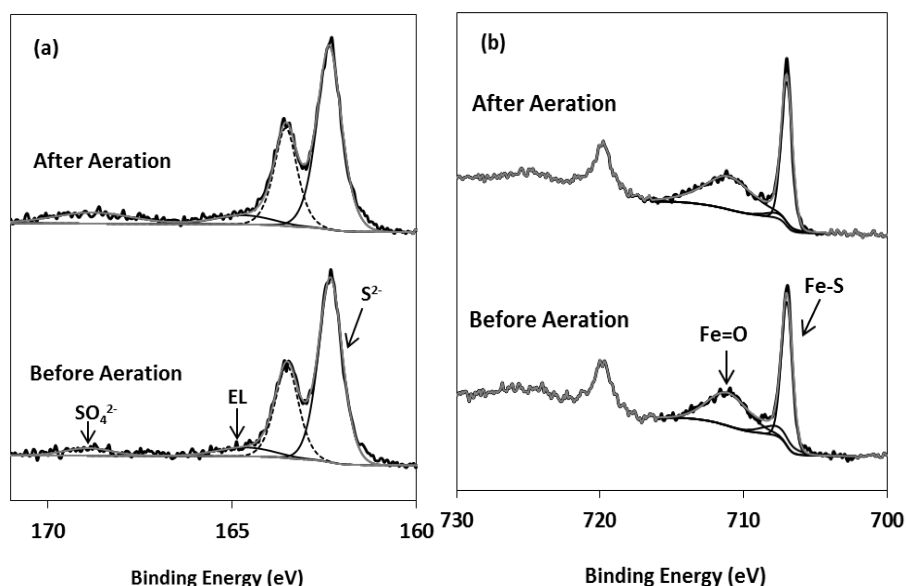


Figure 6.5 S 2p (a) and Fe 2p (b) XPS spectra of particle surfaces before and after applying aeration to the regrinding product of pyrite concentrate.

Table 6.1 S 2p quantification for the particle surfaces before and after aeration.

Sample	Species	2p _{3/2} position	Area contribution (%)
Before Aeration	S ²⁻	162.3	88.6
	Energy loss	164.6	6.7
	SO ₄ ²⁻	168.9	4.7
After Aeration	S ²⁻	162.4	83.5
	Energy loss	162.7	6.2
	SO ₄ ²⁻	164.1	10.3

Table 6.2 Fe 2p quantification for the particle surfaces before and after aeration.

Sample	Species	2p _{3/2} position	Area contribution (%)
Before Aeration	Bulk Fe-S	707.0	49.5
	Surface Fe-S	707.6	9.4
	Fe ³⁺ -O/OH	711.1	41.2
After Aeration	Bulk Fe-S	707.0	46.1
	Surface Fe-S	707.6	3.42
	Fe ³⁺ -O/OH	711.0	50.5

These oxidation species prevented collector adsorption on the surface. As studied by Mielczarski et al. (1998), the collector has to be in contact with a “fresh” mineral surface in order for the electrochemical reaction with the mineral surface to proceed. Smart (1991) indicated that the hydrophilic oxidation species may be removed by the addition of a large amount of xanthate collectors. However, Leppinen et al. (1988) reported that thionocarbamate collectors were not capable of removing the oxidation species from pyrite surface even with a high dosage. Therefore, pyrite depression by the oxidising condition is more pronounced when using thionocarbamate collector in this study. Since the collector adsorption on pyrite was inhibited, more collectors were adsorbed on copper and gold minerals, improving their flotation recovery.

Unlike pyrite, the oxidising condition improves copper flotation, due to the formation of hydrophobic oxidation species, such as, metal-deficient sulphide and polysulphide. Zheng and Manton (2010) studied collectorless flotation in the Telfer copper-gold operation. They found that chalcopyrite floated even without a collector due to the surface oxidation whilst pyrite did not float without a collector, and pre-aeration tended to promote the collectorless flotation of chalcopyrite but it had a negative effect on pyrite flotation.

Furthermore, as the Eh and DO govern the collector adsorption on mineral surfaces, the increase in Eh and DO by pre-aeration may also improve the collector adsorption rate, further improving the copper and gold recovery.

6.2.3.2 Addition of oxidizing agents during regrinding

It has been found by Monte et al. (1997) that the use of oxidizing agents in flotation increased gold floatability by cleaning the free gold surfaces, and depressed the pyrite flotation by the oxidation of their surfaces. In this study, the effect of oxidizing agents on the subsequent flotation was investigated. The oxidizing agents H_2O_2 , $KMnO_4$ and $K_2Cr_2O_7$ were added in the grinding mill respectively. It was expected that the addition of oxidizing agents in the mill could provide a longer reaction time with the minerals than adding them in the flotation conditioning stage.

Addition of H_2O_2

After adding 300 g/t H_2O_2 during regrinding, the Eh had a slight increase to -110 mV (vs SHE), and the DO was still zero. The cleaner flotation results are shown in Figure 6.6. Sulphur recovery was decreased from 20% to 10% at the end of flotation with the rate constant of pyrite decreased from 0.96 min^{-1} to 0.69 min^{-1} , indicating strong pyrite depression. Meanwhile, gold recovery was increased from 45% to 58% with the rate constant increased from 0.17 min^{-1} to 0.47 min^{-1} , while copper recovery was increased from 58% to 67% with the rate constant of copper mineral significantly increased from 0.32 min^{-1} to 1.36 min^{-1} . After increasing H_2O_2 dosage to 600 g/t, the Eh reached to -20 mV (vs SHE), although the DO was still low. As shown in Figure 6.6, the flotation recovery and rate constant of copper and gold were further improved. Copper recovery and gold recovery increased to 72% and 64%, respectively. While the pyrite was further depressed with the sulphur recovery decreased to 8%.

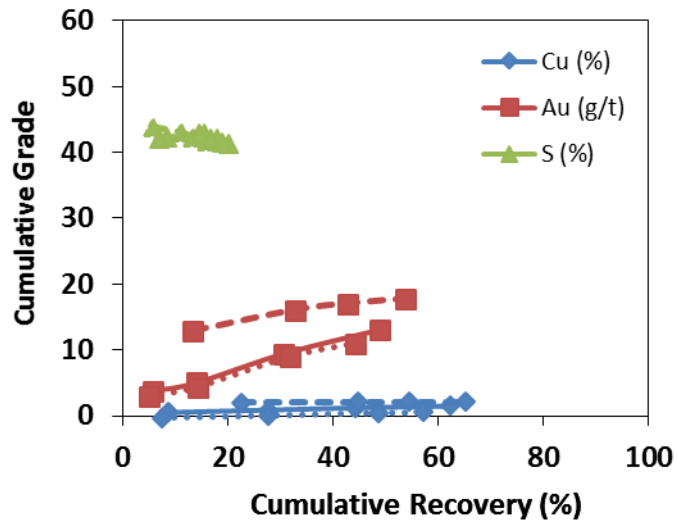


Figure 6.6 The cumulative grade as a function of cumulative recovery after regrinding without adding reagent (round dot line), with adding 300 g/t H₂O₂ (solid line) and 600 g/t H₂O₂ (dashed line).

The pyrite flotation was depressed due to oxidation by H₂O₂, which has a similar effect to the pre-aeration before flotation. The surface oxidation after adding 300 g/t H₂O₂ was analysed by XPS. The quantification of sulphur and iron species is summarized in Table 6.3. The concentration ratio of sulphate SO₄²⁻ increased from 4.7% to 9.5% after adding H₂O₂, and the concentration ratio of iron hydroxide species Fe³⁺-O/OH also increased from 41.2% to 46.4%. This indicates that the pyrite surfaces were oxidized by H₂O₂. However, compared to the flotation result with pre-aeration (section 6.2.3.1), a lower gold recovery and higher copper recovery were achieved, and the rate constant followed the same trend. The lower gold recovery may be due to the low collector adsorption rate since the addition of H₂O₂ did not significantly increase the DO of the regrinding product. The slightly higher copper recovery should be related to the surface oxidation of copper minerals which produced more hydrophobic oxidation species favouring chalcopyrite flotation (Zheng and Manton 2010).

Table 6.3 S 2p and Fe 2p quantification for the pyrite concentrate after regrinding without and with addition of 300 g/t H₂O₂.

	Species	2p _{3/2} position	Area contribution (%)	
Without addition of H₂O₂	S	S ²⁻	162.3	88.6
		Energy loss	164.6	6.7
		SO ₄ ²⁻	168.9	4.7
	Fe	Bulk Fe-S	707.0	49.5
		Surface Fe-S	707.6	9.4
		Fe ³⁺ -O/OH	711.1	41.2
With addition of 300 g/t H₂O₂	S	S ²⁻	162.2	84.9
		Energy loss	164.6	5.7
		SO ₄ ²⁻	168.9	9.5
	Fe	Bulk Fe-S	706.9	45.8
		Surface Fe-S	707.5	7.8
		Fe ³⁺ -O/OH	711.0	46.4

Addition of KMnO₄

After adding 300 g/t KMnO₄ during regrinding, the Eh increased to 40 mV (vs SHE), and the DO was still zero. However, as shown in Figure 6.7, the addition of KMnO₄ during regrinding just slightly increased copper and gold recovery, while the sulphur recovery didn't change. The rate constant was 0.15 min⁻¹ for Au, 0.24 min⁻¹ for copper mineral and 1.06 min⁻¹ for pyrite, which is also similar to the N₂ baseline test. After increasing the dosage of KMnO₄ to 600 g/t, the sulphur recovery decreased to 16.2%, which indicates that the pyrite was oxidized at a higher dosage of KMnO₄. The flotation recovery and rate constant of copper and gold were further improved, but still much lower than that after regrinding in presence of H₂O₂.

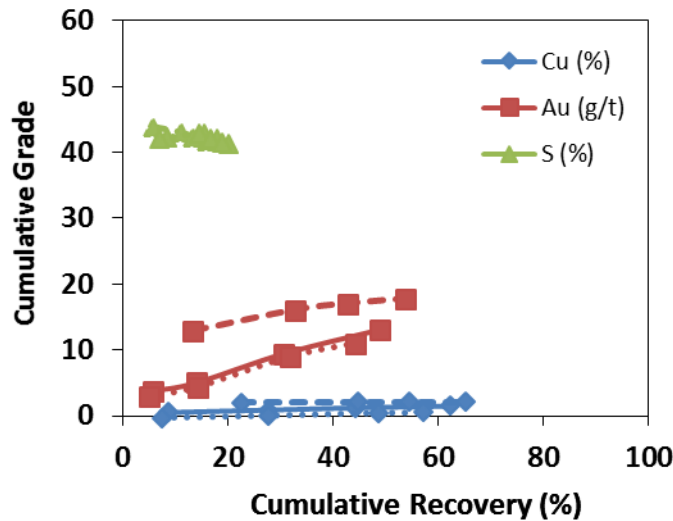


Figure 6.7 The cumulative grade as a function of cumulative recovery after regrinding without adding reagent (round dot line), with 300 g/t KMnO_4 (solid line) and with 600 g/t KMnO_4 (dashed line).

XPS was used to analyse the surface species of the pyrite concentrates after regrinding with 300 g/t KMnO_4 . The quantification of sulphur and iron surface species is shown in Table 6.4. Compared to the baseline test, the percentage of sulphate slightly increased to 6.6%, and the percentage of oxidized iron was slightly increased to 43.5%. This indicates that KMnO_4 did not effectively react with sulphide minerals compared to H_2O_2 , although a higher Eh was observed at the same addition. This may be because the oxidizing capability of KMnO_4 is weak at alkaline conditions, since the Mn(VII) can only be reduced to Mn(IV). In addition, the molecular weight of KMnO_4 (158 g/mol) is much higher than that of H_2O_2 (34 g/mol). Therefore, when the same dosage by weight was used during flotation, KMnO_4 provided a smaller amount of oxidizing groups than H_2O_2 , which may also lead to its ineffectiveness in this study.

Table 6.4 S 2p and Fe 2p quantification for the pyrite concentrate after regrinding without and with addition of 300 g/t KMnO₄.

	Species	2p _{3/2} position	Area contribution (%)	
Without addition of KMnO₄	S	S ²⁻	162.3	88.6
		Energy loss	164.6	6.7
		SO ₄ ²⁻	168.9	4.7
	Fe	Bulk Fe-S	707.0	49.5
		Surface Fe-S	707.6	9.4
		Fe ³⁺ -O/OH	711.1	41.2
With addition of 300 g/t KMnO₄	S	S ²⁻	162.3	87.5
		Energy loss	164.6	6.0
		SO ₄ ²⁻	168.9	6.6
	Fe	Bulk Fe-S	707.0	49.4
		Surface Fe-S	707.6	7.1
		Fe ³⁺ -O/OH	711.1	43.5

Addition of K₂Cr₂O₇

The effect of K₂Cr₂O₇, as a common strong oxidizing agent, was also tested in this study. After adding 300 g/t K₂Cr₂O₇ during regrinding, the Eh increased to -85 mV (vs SHE), and the DO was still zero. The flotation results are shown in Figure 6.8. Sulphur recovery was 19% and the rate constant of pyrite was 0.84 min⁻¹, similar to the results from the N₂ baseline test, indicating that the pyrite was not effectively depressed by K₂Cr₂O₇. The copper recovery and gold recovery slightly increased to 63% and 51%, respectively. The rate constant slightly increased to 0.37 min⁻¹ for copper mineral and 0.22 min⁻¹ for Au. After increasing the dosage of K₂Cr₂O₇ to 600 g/t, as shown in Figure 6.8, the sulphur recovery decreased to 17%, while the copper recovery and gold recovery increased to 67% and 56%, respectively. The results indicate that K₂Cr₂O₇ was not an effective oxidizing agent compared to H₂O₂, which can be also confirmed by the XPS analysis of the surface species. As shown in Table 6.5, the percentages of SO₄²⁻ and Fe³⁺-O/OH were slightly increased after the addition of K₂Cr₂O₇ compared to the N₂ baseline test. In addition, similar to KMnO₄, K₂Cr₂O₇ also has a high molecular weight (294 g/mol) compared to H₂O₂ (34 g/mol). Therefore, K₂Cr₂O₇ provided a smaller amount of oxidizing groups than H₂O₂ when the same dosage by weight was added in flotation, which may not sufficient to oxidize pyrite surfaces and promote copper-gold flotation.

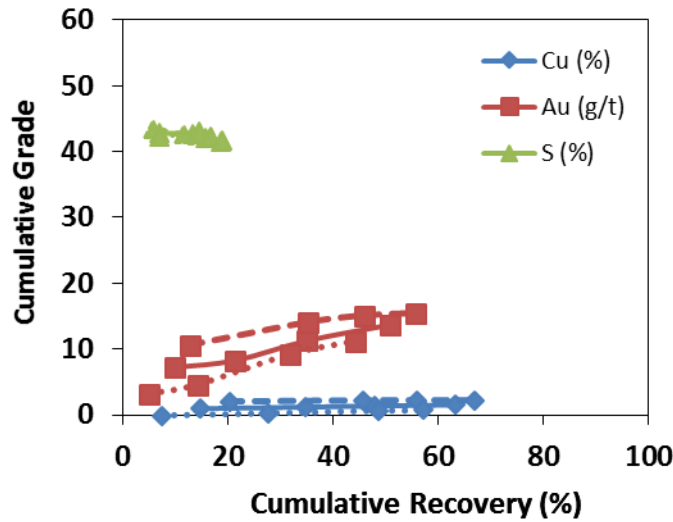


Figure 6.8 The cumulative grade as a function of cumulative recovery after regrinding without adding reagent (round dot line), with 300 g/t $K_2Cr_2O_7$ (solid line) and with 600 g/t $K_2Cr_2O_7$ (dashed line).

Table 6.5 S 2p and Fe 2p quantification for the pyrite concentrates after regrinding without and with addition of 300 g/t $K_2Cr_2O_7$.

	Species		2p _{3/2} position	Area contribution (%)
Without addition of $K_2Cr_2O_7$	S	S ²⁻	162.3	88.6
		Energy loss	164.6	6.7
		SO ₄ ²⁻	168.9	4.7
	Fe	Bulk Fe-S	707.0	49.5
		Surface Fe-S	707.6	9.4
		Fe ³⁺ -O/OH	711.1	41.2
With addition of 300 g/t $K_2Cr_2O_7$	S	S ²⁻	162.2	87.3
		Energy loss	164.6	6.0
		SO ₄ ²⁻	168.7	6.7
	Fe	Bulk Fe-S	706.8	47.9
		Surface Fe-S	707.4	8.6
		Fe ³⁺ -O/OH	711.1	43.4

6.2.3.3 *Regrinding without nitrogen purging*

The previous tests show that the oxidation of pyrite concentrate, either by aeration before flotation or by the addition of proper oxidizing agents in the mill, can improve the Cu/Au flotation

performance in the cleaner flotation. In this section, the pyrite rougher flotation concentrate was reground without nitrogen purging (with air during regrinding), and the Eh of the regrinding product was about 380 mV (SHE), much higher than that after regrinding with nitrogen purging (-150 mV, SHE). The DO also increased to about 1.5 ppm. As shown in Figure 6.9, the flotation is greatly improved after regrinding in an oxidizing atmosphere. Gold recovery increased from 45% to 77% with the rate constant increased to 2.46 min^{-1} , and copper recovery increased from 58% to 74% with the rate constant of copper mineral increased to 1.17 min^{-1} , whilst sulphur recovery decreased from 20% to 10%. The significant improvement was due to a combined effect of all the factors discussed previously: strong pyrite depression caused by the surface oxidation (Leppinen et al. 1988, Smart 1991, Mielczarski et al. 1998), an increased collector adsorption rate on copper and gold surfaces due to the higher Eh and DO (Kuopanportti et al. 2000, Allan and Woodcock 2001, Srdjan 2010), and the surface oxidation of chalcopyrite producing hydrophobic species (Zheng and Manton 2010). The surface oxidation of pyrite can be proved by the XPS analysis. As shown in the Table 6.6, the concentration ratios of SO_4^{2-} and $\text{Fe}^{3+}\text{-O/OH}$ were significantly increased after aeration. Furthermore, as studied in Chapter 4, the further activation of fresh pyrite surfaces by copper ions can be prohibited during regrinding at oxidizing conditions, which can also decrease the pyrite floatability and then improve copper and gold flotation.

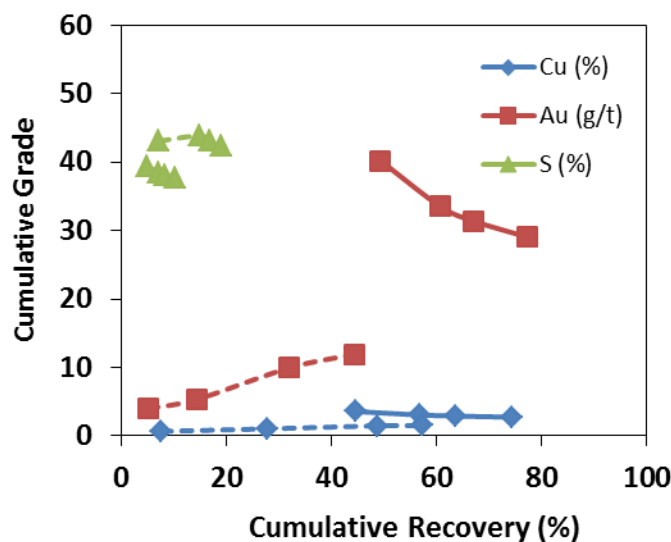


Figure 6.9 The cumulative grade as a function of cumulative recovery after regrinding with (dashed line) and without nitrogen purging (solid line).

Table 6.6 S 2p and Fe 2p quantification for the pyrite concentrate after regrinding without nitrogen purging.

Species		2p _{3/2} position	Area contribution (%)
S	S ²⁻	162.4	83.1
	Energy loss	164.7	6.2
	SO ₄ ²⁻	168.8	10.8
Fe	Bulk Fe-S	707.1	45.5
	Surface Fe-S	707.7	3.8
	Fe ³⁺ -O/OH	711.1	50.7

Following regrinding in an oxidising atmosphere, the effect of further oxidation by pre-aeration prior to flotation was also studied. As shown in Figure 6.10, gold recovery was further increased from 77% to 85%, while copper and sulphur recovery remained the same. The results indicate that the further oxidation after regrinding can still improve the gold flotation, however, this did not influence the copper and pyrite flotation. Therefore, the improvement could result from the increased floatability of free gold, which may be due to the increased collector adsorption rate in the presence of more oxygen (Srdjan 2010).

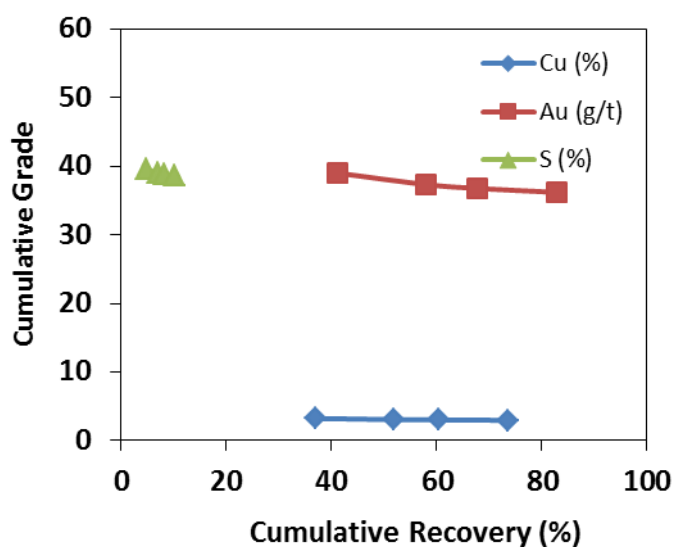


Figure 6.10 The cumulative grade as a function of cumulative recovery after regrinding without nitrogen purging and with pre-aeration before flotation.

6.2.3.4 *Regrinding under higher pH condition*

The pH is important in controlling the hydrolysis of metal ions, and the adsorption of metal hydroxides onto sulphide minerals controls their flotation properties to a great extent (Grano 2010). Grano (2010) reported that grinding at high pH increased chalcopyrite recovery and selectivity against pyrite from a high pyrite feed, because the pyrite was quickly passivated at high pH. In the baseline test, the pH in the regrinding product was 9.0. To investigate whether increasing pH in the regrind mill can influence the flotation behaviour in this study, more lime was added before regrinding to achieve pH of 10.5 in the final regrinding product. The Eh of the regrinding product significantly increased to 140 mV (vs SHE), although the DO was still almost zero. The flotation results are shown in Figure 6.11. Regrinding in a higher pH significantly improved the flotation. Gold recovery increased from 45% to 68% with the rate constant increased from 0.17 min⁻¹ to 0.43 min⁻¹, Copper recovery increased from 58% to 70%, and the rate constant of copper mineral significantly increased to 1.17 min⁻¹, whilst sulphur recovery decreased from 20% to 13% with rate constant of pyrite decreased from 0.92 min⁻¹ to 0.77 min⁻¹.

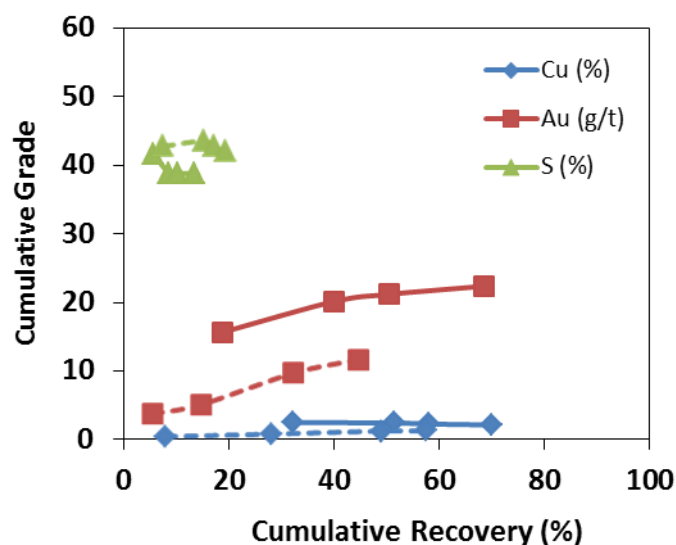


Figure 6.11 The cumulative grade as a function of cumulative recovery after regrinding at higher pH (solid line) and at normal pH (dashed line).

The decreased sulphur recovery indicates that pyrite was strongly depressed after increasing the regrinding pH. Lime was used in this study as the pH regulator, which was also an effective depressant for pyrite flotation. Although there are still some debates on the depression mechanism, it is generally agreed that the depression is related to the formation of a mixed film of Fe(OH)₃, FeO(OH), CaSO₄ or CaSO₃ on pyrite surfaces, which can prevent collector adsorption (Bulatovic 2007). Since the collector adsorption on pyrite is reduced, more collector molecules are available to

adsorb on copper and gold minerals, increasing the copper and gold recovery. The results in this study indicated that the addition of lime during regrinding to passivate pyrite surfaces was effective. When pyrite surfaces are passivated, oxygen may not be consumed completely during regrinding, resulting in the improved copper and gold flotation. Furthermore, the pH may also influence the production of hydrogen peroxide on fresh pyrite surfaces during regrinding as reported by Javadi Nooshabadi et al. (2013), which may contribute to different flotation performance as well.

6.3 Conclusions

This study indicates the critical importance of pulp chemistry during regrinding rougher flotation concentrates on subsequent copper-gold flotation and pyrite depression. The results show that the flotation performance can be improved by applying pre-aeration, an oxidizing regrinding atmosphere or the addition of an appropriate oxidizing agent to oxidize the regrinding product.

Pyrite flotation was strongly depressed when using all these methods except the addition of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$. The depression is mainly through the oxidation or passivation of pyrite surfaces, inhibiting the collector adsorption on pyrite. As a result, more collector was available to adsorb on copper and gold minerals, improving their recovery. Also, pyrite activation by copper ions may be lessened in an oxidizing condition, further depressing pyrite flotation.

The addition of H_2O_2 gave a similar sulphur recovery when compared to aeration oxidizing methods, however, the gold recovery was lower. The increase of DO by the addition of H_2O_2 was not as significant as the aeration methods. This indicates that the improved gold flotation recovery not only results from pyrite depression but also from other factors, such as the DO of the regrinding product, controlling the collector adsorption rate.

The gold recovery was significantly improved by regrinding without nitrogen purging and/or applying aeration prior to flotation. This provides further evidence that the increase of dissolved oxygen in the slurry plays an important role, which increases the collector adsorption rate on gold and copper mineral surfaces. The improvement of copper flotation by the oxidizing methods may also result from the surface oxidation of chalcopyrite, producing hydrophobic sulphur rich species.

Furthermore, regrinding in a higher pH environment also depressed pyrite flotation and improved the copper-gold flotation due to the pyrite surface passivation during regrinding. The passivation of pyrite can also increase the Eh and residual oxygen to allow greater collector oxidation and adsorption on copper and gold mineral surfaces.

Chapter 7 The Effect of Particle Breakage Mechanisms during Re grinding on the Subsequent Cleaner Flotation

7.1 Introduction

The objective of this study is to investigate the effect of particle breakage mechanisms during re grinding on subsequent cleaner flotation. Stirred mills have been widely used for re grinding and are acknowledged to be more energy efficient than traditional tumbling mills in the generation of fine particles (Jankovic 2003). Besides the different energy efficiency, these two types of mills break particles through different mechanisms. Whether different particle breakage mechanisms can influence mineral floatability in the subsequent cleaner flotation should be considered in the plant operation and is also the research question of this study.

As discussed in Chapter 2, the different breakage mechanisms have been proved to influence the particle size distribution (Kelly and Spottiswood 1982, Gao and Forssberg 1995, Hogg 1999, Vizcarra 2010), particle shape (Andreatidis 1995, Roufail and Klein 2010, Vizcarra 2010) and mineral liberation (Andreatidis 1995, Roufail and Klein 2010). All of these factors play an important role in the subsequent cleaner flotation. In addition, there are two types of surfaces after re grinding: the remaining surfaces carried over from the re grinding feed, and the fresh surfaces generated during re grinding. As shown in Figure 2.11, the different breakage mechanisms can affect the distribution of the surface species on particles at different size fractions and hence influence the mineral floatability. Moreover, the different types of grinding mills may affect mineral flotation through different oxidizing conditions, which needs to be considered when studying the effect of different breakage mechanisms.

In this study, the effect of particle breakage mechanisms on flotation was investigated by considering and isolating all the possible contributing factors. Single chalcocite mineral was used as the mineral example, thus the liberation does not need to be considered. In addition, compared to chalcopyrite and pyrite, the floatability of chalcocite is not sensitive to the redox environment in

different grinding mills and does not have strong natural floatability. Therefore, the change of mineral surfaces during regrinding can be more accurately analysed and correlated with flotation behaviour. Two types of grinding mills, a tumbling mill and a stirred mill, were used to produce ground chalcocite via different breakage mechanisms. The same type of grinding media, stainless steel, was used in the two mills in order to eliminate the potential influence of the type of grinding media on flotation. Furthermore, as ceramic media is widely used in stirred mills commercially, it was also used in this study to compare results obtained with stainless steel media.

7.2 Results and discussion

Figure 7.1 shows chalcocite recovery in the rougher flotation stage as a function of flotation time. After primary grinding with stainless steel media, 92 wt% chalcocite recovery was achieved after 8 min flotation time. The rougher flotation concentrates were reground in different mills, as described earlier, and chalcocite flotation in the cleaner stage was then examined.

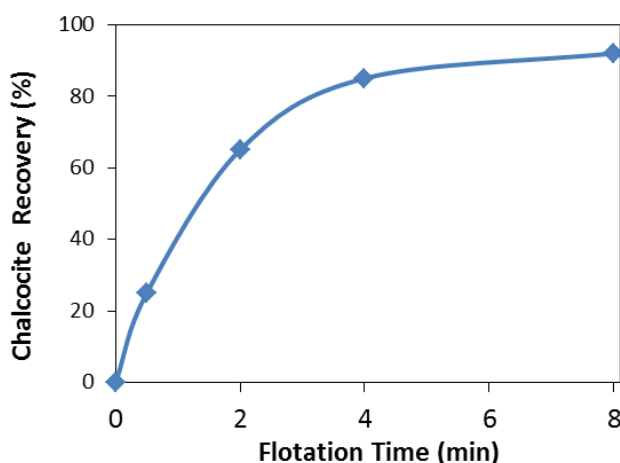


Figure 7.1 Chalcocite recovery as a function of flotation time in rougher flotation.

The rougher flotation concentrates (about 90 g chalcocite) were reground by two different grinding mills: a rod mill and a stirred mill. In the rod mill, stainless steel rods were used as grinding media, while in the stirred mill, stainless steel and ceramic media were each tested. In the subsequent cleaner flotation, no additional collector was added. Flotation results are shown in Figure 7.2. Chalcocite cleaner recovery after regrinding in a rod mill was 59 wt% after 8 min of flotation. It was only 22 wt% and 30 wt% respectively after regrinding by stirred mill with stainless steel and ceramic media. Therefore, chalcocite flotation was strongly depressed after regrinding, and

regrinding conditions significantly influenced the flotation behaviour. The rod mill produced better chalcocite flotation than the stirred mill, and when the stirred mill was used, ceramic media produced better chalcocite flotation than stainless steel media.

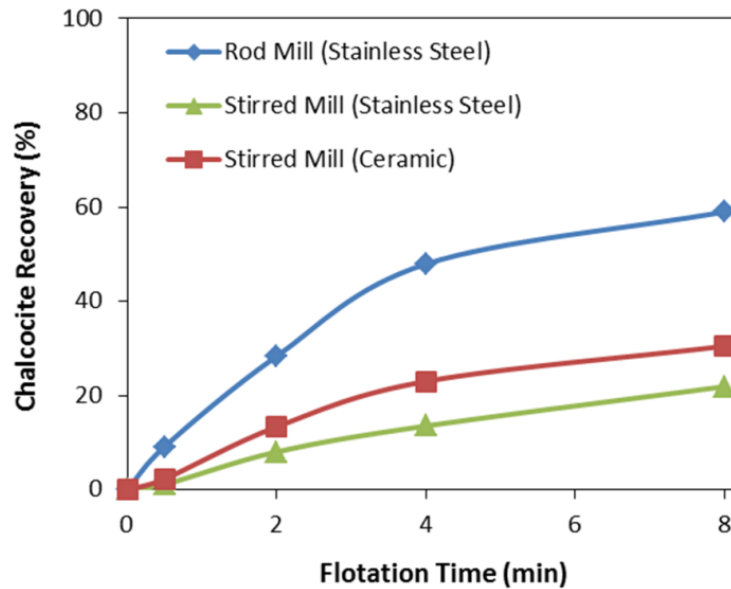


Figure 7.2 Chalcocite cleaner recovery as a function of flotation time after regrinding with different grinding mills and grinding media.

There are several factors that could affect chalcocite flotation after regrinding in this study:

- 1) Particle size. The particle size was reduced from $P_{80} 75 \mu\text{m}$ to $20 \mu\text{m}$ during regrinding, and different grinding conditions may generate different size distributions.
- 2) Particle shape. Different particle shape may be produced after regrinding in rod and stirred mills. However, as reported by Vizcarra et al. (2011), particle shape only influences the flotation of minerals with slow flotation kinetics (e.g., with no collector addition, for gangue minerals). Therefore, this factor was not considered in this study.
- 3) Fresh surfaces. After regrinding, a large amount of fresh surfaces are produced, which may change particle floatability.
- 4) Surface oxidation. The oxidation of mineral surfaces during regrinding in different mills may be different and then influence particle floatability.
- 5) The distribution of collectors. The collectors carried through from rougher flotation may have a different distribution on particle surfaces after regrinding by rod and stirred mills and with different media. This may influence the subsequent flotation.

The effects of these four factors are discussed in the following sections.

7.2.1 Particle size

The particle size was reduced from $P_{80} = 75 \mu\text{m}$ to $P_{80} = 20 \mu\text{m}$ after regrinding. It is known that fine particles show low floatability due to low bubble-particle collision efficiency (Trahar 1981). However, a great number of studies indicate that particles at $20 \mu\text{m}$ still show maximum flotation recovery given sufficient surface hydrophobicity (Grano 2009, Pease et al. 2010). Therefore, the low chalcocite flotation after regrinding in this study may be more to do with the altered surface properties resulting from the particle size reduction process rather than with the reduced particle size itself.

The particle size distributions after regrinding were measured using a Malvern sizer and the results are shown in Figure 7.3. Although the rod mill and the stirred mill present different breakage mechanisms, the final size distributions were similar with the same target $P_{80} = 20 \mu\text{m}$. Unlike the size distribution presented in Figure 2.11 which is a single particle breakage under a pure abrasion or impact, the actual breakage mechanisms during the grinding of a batch sample are a mixture of three different breakage mechanisms. In the rod mill, abrasion breakage also exists. While, in the stirred mill, the massive fracture caused by the impact breakage may dominate at the beginning of grinding and the abrasion breakage plays a more important role at the finer stage. Therefore, the final size distribution may be the same in the different mills. In this study, the stirred mill, especially with stainless steel media, produced slightly more fine particles ($-10 \mu\text{m}$) than the rod mill, which may be due to a greater degree of attrition breakage in the stirred mill (Hogg 1999, Yue and Klein 2005). However, it is unlikely that the slight difference in size distribution produced by the two types of mills is the major contributing factor to the significant difference in chalcocite flotation displayed in Figure 7.2.

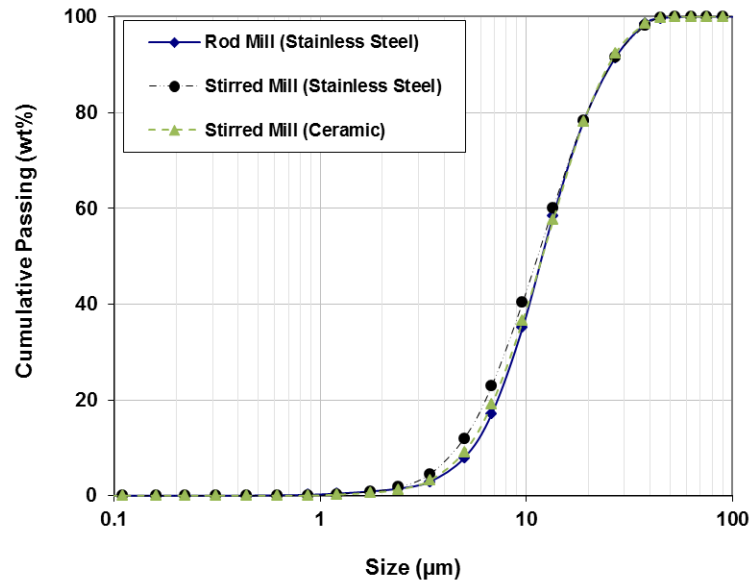


Figure 7.3 Particle size distribution after regrinding in rod mill and stirred mill.

7.2.2 Fresh surfaces

Two different types of particle surfaces are present after regrinding: the surfaces carried over from the grinding feed, and the surfaces freshly produced after regrinding. To determine the amount of new surfaces created during regrinding, the surface area of the feed and products was measured using the BET method. As shown in Table 7.1, the surface area of the regrinding feed was $0.2 \text{ m}^2/\text{g}$, and increased to $1.3 \text{ m}^2/\text{g}$ after the regrinding by the rod mill, and $1.6 \text{ m}^2/\text{g}$ and $1.4 \text{ m}^2/\text{g}$ after regrinding by the stirred mill with stainless steel media and ceramic media, respectively. The percentage of fresh surfaces produced after regrinding was calculated and is also shown in Table 7.1. The results indicate that more than 80% of the surfaces of the regrinding product are fresh. Since the fresh surfaces are presumably not covered by collector, the surface hydrophobicity was significantly diluted after regrinding, resulting in the decreased flotation recovery in general. Ye et al. (2010a) reported that the increase in surface area after regrinding strongly depressed pyrrhotite flotation. While the slightly larger percentage of fresh surfaces after stirred milling may result in a lower flotation recovery, this does not explain the different chalcocite flotation after regrinding by rod and stirred mills since the differences in amount of fresh surfaces generated are small.

Table 7.1 Surface area of the regrinding feed and product, and percentage of fresh surfaces.

	Regrinding Feed	Rod Mill Product (Stainless Steel)	Stirred Mill Product (Stainless Steel)	Stirred Mill Product (Ceramic)
Size (μm)	75	20	20	20
Surface Area (m^2/g)	0.2	1.3	1.6	1.4
Percentage of Fresh Surfaces (%)		85%	88%	86%

7.2.3 Oxidation of mineral surfaces

The oxidation species of chalcocite at alkaline conditions include $\text{Cu}(\text{OH})_2$, metal-deficient sulphide or polysulphide, elemental sulphur, and sulphur species of higher oxidation state, such as sulphate (Walker et al. 1984). Metal-deficient sulphide, elemental sulphide and polysulphide are hydrophobic, and improve chalcocite floatability. Other oxidation species such as $\text{Cu}(\text{OH})_2$ and sulphate are hydrophilic, reducing chalcocite flotation. To detect which species were present on the chalcocite surface, selected regrinding feed and products were examined by XPS. The S 2p XPS spectra are shown in Figure 7.4. These spectra were fitted using the $2p_{1/2}$ and $2p_{3/2}$ doublet with a fixed 1:2 intensity ratio and 1.18 eV energy separation. The doublet at 161.8 eV is assigned to S^{2-} from Cu_2S (Smart et al. 1999). The doublet at 162.8 eV can be attributed to the formation of polysulphide. The broad peak observed at 167.7 eV is attributed to the sulphate SO_4^{2-} . An energy loss (EL) peak was also fitted at 164.0 eV. The quantification of the regrinding feed and product is summarized in Table 7.2. A significant amount of polysulphide and sulphate species were detected in both the regrinding feed and regrinding product from the rod mill, which indicates the oxidation on the surfaces. However, after regrinding by the stirred mill, less oxidation species were detected. This indicates that the rod mill produced a more oxidizing condition than the stirred mill.

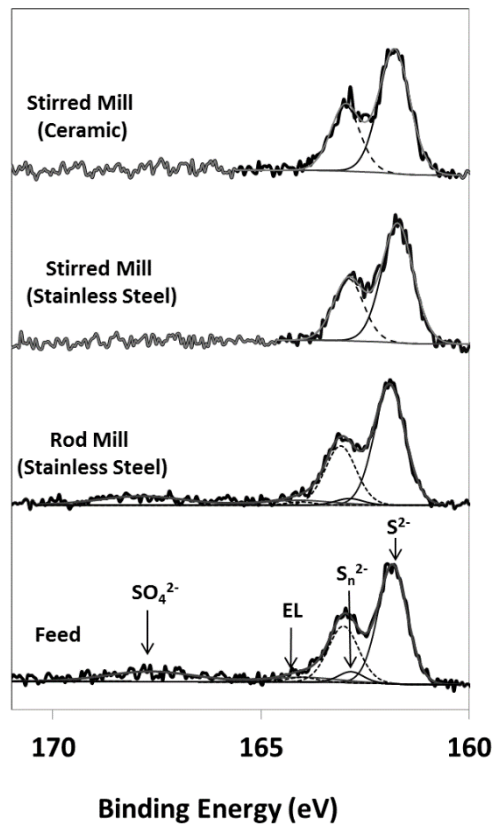


Figure 7.4 S 2p XPS spectra of mineral surfaces of regrinding feed and product.

Table 7.2 S 2p quantification for the regrinding feed and product.

	Area contribution (%)			
	Regrinding Feed	Rod Mill Product (Stainless Steel)	Stirred Mill Product (Stainless Steel)	Stirred Mill Product (Ceramic)
S ²⁻	75.8	79.5	100	100
S _n ²⁻	6.0	4.1	—	—
SO ₄ ²⁻	13.2	11.4	—	—

The surface copper species of the regrinding feed and product were also examined by XPS. The Cu 2p XPS spectra are shown in Figure 7.5. The Cu⁺ Cu 2p_{3/2} component was identified at about 932.6 eV (McIntyre and Cook 1975, Deroubaix and Marcus 1992). A second component in the Cu 2p_{3/2} at about 934.2 eV is attributable to Cu²⁺-hydroxyl species (Weisener and Gerson 2000). Quantification of the regrinding feed and product surface species is summarized in Table 7.3. As the results show, the compositions of copper species after regrinding by different mills with

different media vary only slightly. A certain amount of Cu^{2+} -hydroxyl species was detected in all the samples, which indicates copper oxidation under all regrinding conditions.

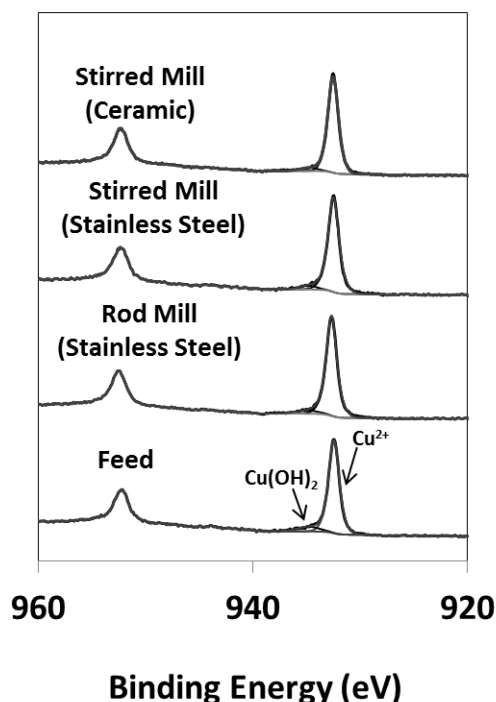


Figure 7.5 Cu 2p XPS spectra of mineral surfaces of regrinding feed and product.

Table 7.3 Cu 2p quantification for the regrinding feed and product.

	Area contribution (%)			
	Regrinding feed	Rod Mill Product (Stainless Steel)	Stirred Mill Product (Stainless Steel)	Stirred Mill Product (Ceramic)
Cu-S	89.3	91.1	92.0	91.4
Cu-OOH	10.7	8.9	8.0	8.6

To investigate further the effect of oxidation on chalcocite flotation, nitrogen purging was applied during regrinding in both mills to provide a reducing regrinding condition. The concentration of dissolved oxygen of the regrinding product dropped to zero after applying the nitrogen purging, as shown in Table 7.4. In addition, the surface change with nitrogen purging was examined by XPS analysis. Figure 7.6 shows the S 2p spectra after applying nitrogen purging. It is obvious that oxidation was significantly reduced during regrinding in the rod mill.

Table 7.4 Dissolved oxygen (DO) concentration of the regrinding product after regrinding in air and in nitrogen.

	Rod Mill Product (Stainless Steel)	Stirred Mill Product (Stainless Steel)	Stirred Mill Product (Ceramic)
Air	5.1 ppm	2.6 ppm	2.9 ppm
Nitrogen	0 ppm	0 ppm	0 ppm

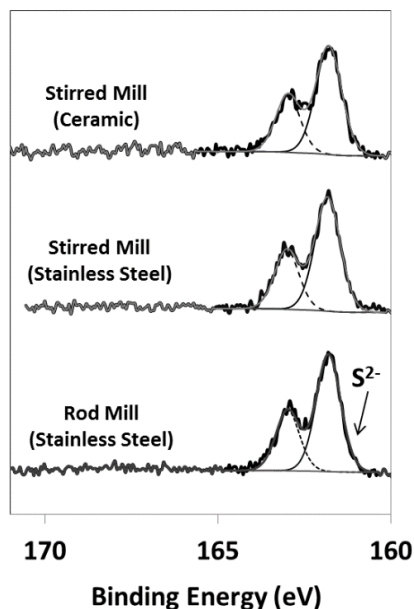


Figure 7.6 S 2p XPS spectra of mineral surfaces of regrinding product with nitrogen purging during regrinding.

Cleaner flotation was conducted on the reground product to investigate the effect of nitrogen purging during regrinding on chalcocite flotation. As shown in Figure 7.7, the flotation recovery was similar with or without nitrogen purging during regrinding. This suggests that the different flotation behaviour after regrinding in different mills was not primarily caused by oxidizing conditions.

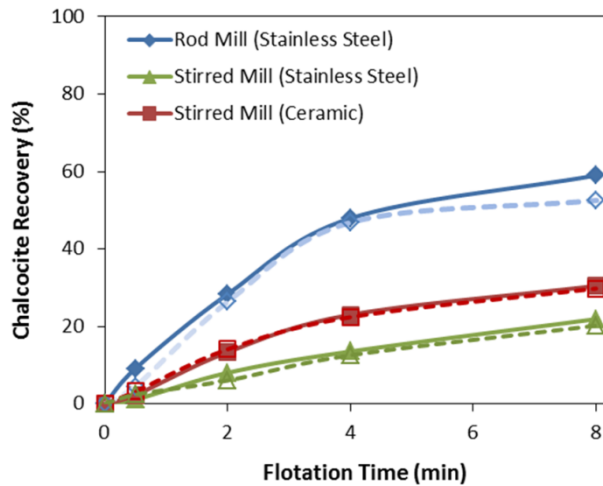


Figure 7.7 Chalcocite recovery as a function of flotation time after regrinding in air (solid line) and in nitrogen (dashed line).

7.2.4 The distribution of collectors on particle surfaces

As discussed in the sections 7.2.1 to 7.2.3, the particle size, fresh surface produced and surface oxidation only have a slight influence on the subsequent flotation. It is more likely that the significant difference in chalcocite flotation, after regrinding by rod and stirred mills with different media, can be attributed to the different distribution of collector species on the reground particles. To investigate this hypothesis, the flotation recovery of the particles with different size fractions after regrinding was evaluated. In this single mineral study, the size by size recovery was calculated by using the mass of each flotation concentrate and tailings and the size distribution of each flotation concentrate and tailings measured by Malvern Sizer. The detailed calculation procedure was described in section 3.3.2.

As shown in Figure 7.8, the recovery of the particles at different size fractions is similar after regrinding by the rod mill, but much higher than the recovery after regrinding by the stirred mill. In addition, after regrinding by the stirred mill, the floatability of particles decreased with an increase in particle size. The fine and ultra-fine particles displayed better flotation than the intermediate particles.

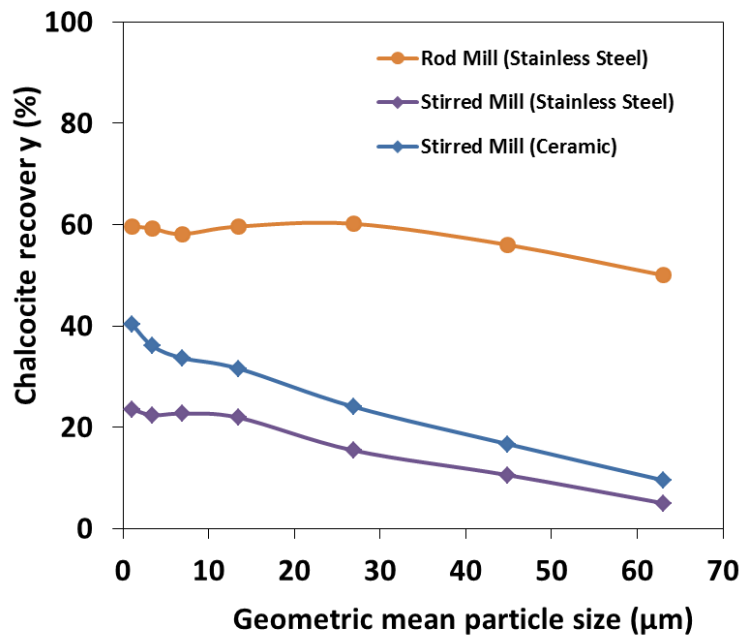


Figure 7.8 Chalcocite flotation recovery as a function of particle size after regrinding.

The size-by-size flotation data suggests that the collector was distributed evenly on the particles at different size fractions after regrinding by the rod mill. The high recovery of sub-5 µm particles may be related to the clean grinding environment. It has also been reported that ultra-fine particles can still achieve a high recovery if the surfaces are not contaminated or oxidized (Grano 2009). After regrinding by the stirred mill, more collector remained on the fine and ultra-fine particles than on the intermediate particles, leading to a higher floatability of the fine and ultra-fine particles. The collector distribution may be linked to particle breakage mechanisms. As shown in Figure 7.9, if the impact breakage and compression breakage are applied, surface collector is present on at least part of the surface of new particles. However, if the attrition breakage is applied, the collector is present on the fine and ultra-fine particles and not on the coarse particles. Impact breakage is dominant during regrinding in the rod mill, therefore, the floatability of particles is still high across all size fractions. However, the attrition breakage predominates in the stirred mill, and in subsequent flotation, reduced flotation recovery in general is observed. Fine and ultra-fine particles are produced by attrition, and these particles carry the surface collector, resulting in better flotation recovery for them compared with the intermediate particles.

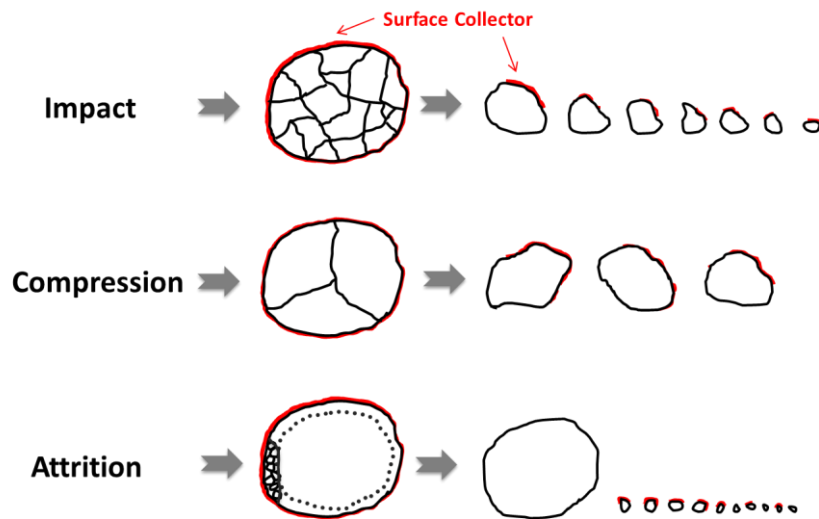


Figure 7.9 The three different proposed particle breakage mechanisms, and the resultant distribution of surface collector on broken particles (Revised based on (Kelly and Spottiswood 1982)).

ToF-SIMS was used in this study to investigate the collector distribution on chalcocite particles after regrinding. Figure 7.10(a) shows the normalised intensity of collector fragments (potassium amyl xanthate) on particles of three different size fractions after regrinding by rod mill with stainless steel media. There is no statistical difference between the intensity of collectors on particles of three size fractions, which proves the collector was evenly distributed on the particles after regrinding by rod mill. However, after regrinding by the stirred mill with stainless steel media, the collector intensity on the fine particles (<10 μm) is statistically higher than that on the coarser particles (>20 μm). This is likely due to the attrition breakage in the stirred mill, which removes the surface collectors from coarse particles through the mechanisms illustrated in Figure 7.9. These ToF-SIMS results are in accordance with the size by size flotation results as shown in Figure 7.8, further confirming that the different particle breakage imparted by rod and stirred mills influences the collector distribution.

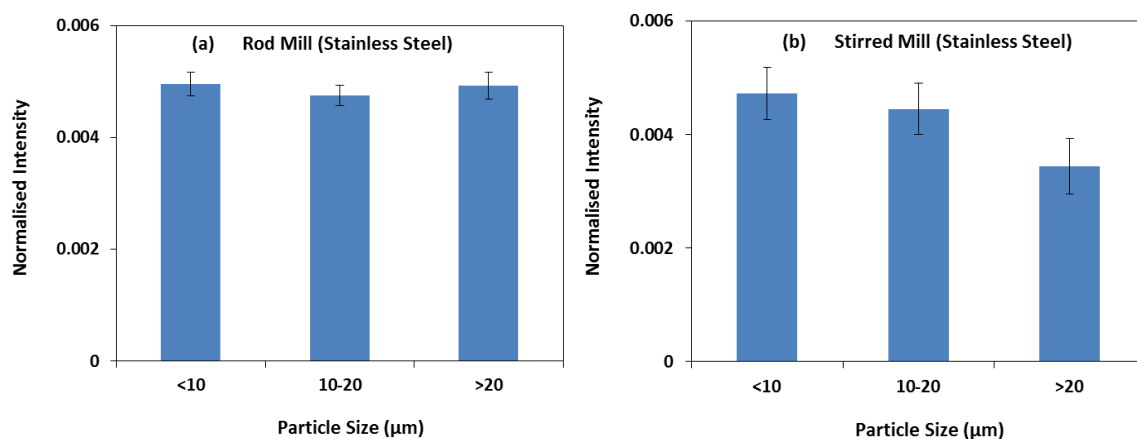


Figure 7.10 ToF-SIMS normalised intensity of collector fragments (potassium amyl xanthate) on particle surfaces of chalcocite at different size fractions after regrinding in rod mill with stainless steel media (a) and stirred mill with stainless steel media (b).

It has been reported that grinding media in a stirred mill can influence the stress intensity through media density (Jankovic 2003). In this study, the recovery after regrinding with stainless steel media was lower than that with ceramic media. It seems that more attrition breakage was created when stainless steel media was used which resulted in higher stress intensity, corresponding to a slightly larger particle surface area as shown in Table 7.1.

In summary, particle size, fresh surfaces and the surface oxidation do not play an important role in the different flotation behaviour after regrinding in different milling conditions. The main contributing factor appears to be collector distribution governed by the particle breakage mechanisms.

7.2.5 Flotation with additional collector

Since a large amount of fresh surfaces are produced after regrinding, it is reasonable to expect that additional collector in the cleaner flotation stage may improve chalcocite flotation recovery. Flotation results after adding more collector in the cleaner flotation are shown in Figure 7.11. After regrinding in both stirred and rod mills, chalcocite recovery increased with the increased collector dosage. The recovery reached the maximum at 160 g/t collector after regrinding by the rod mill. More collector was required after regrinding by the stirred mill to restore the recovery to the same level. This may be associated with the removal of collector carried over from rougher flotation concentrate by attrition breakage. The recovery after regrinding by stirred mill with stainless steel

media was always lower than that with ceramic media, which may be because more collector was removed by attrition when using high density stainless steel media.

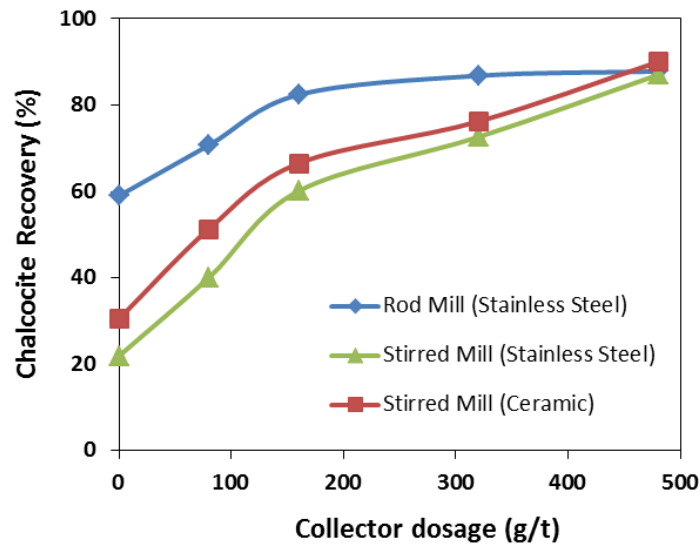


Figure 7.11 Chalcocite recovery after regrinding as a function of collector dosage.

Chalcocite recovery as a function of particle size after collector addition was further investigated. Results are shown in Figure 7.12. After regrinding by the rod mill, chalcocite recovery increased with collector addition in all size fractions, and the percentage increase was similar. After regrinding in the stirred mill, the fine and ultra-fine particles still displayed higher recovery than intermediate particles at the same collector addition. The floatability of coarser particles was more difficult to be restored, probably due to more denuded surfaces caused by attrition. The restoration of recovery was more difficult in all size fractions when using stainless steel media in the stirred mill compared with using ceramic media.

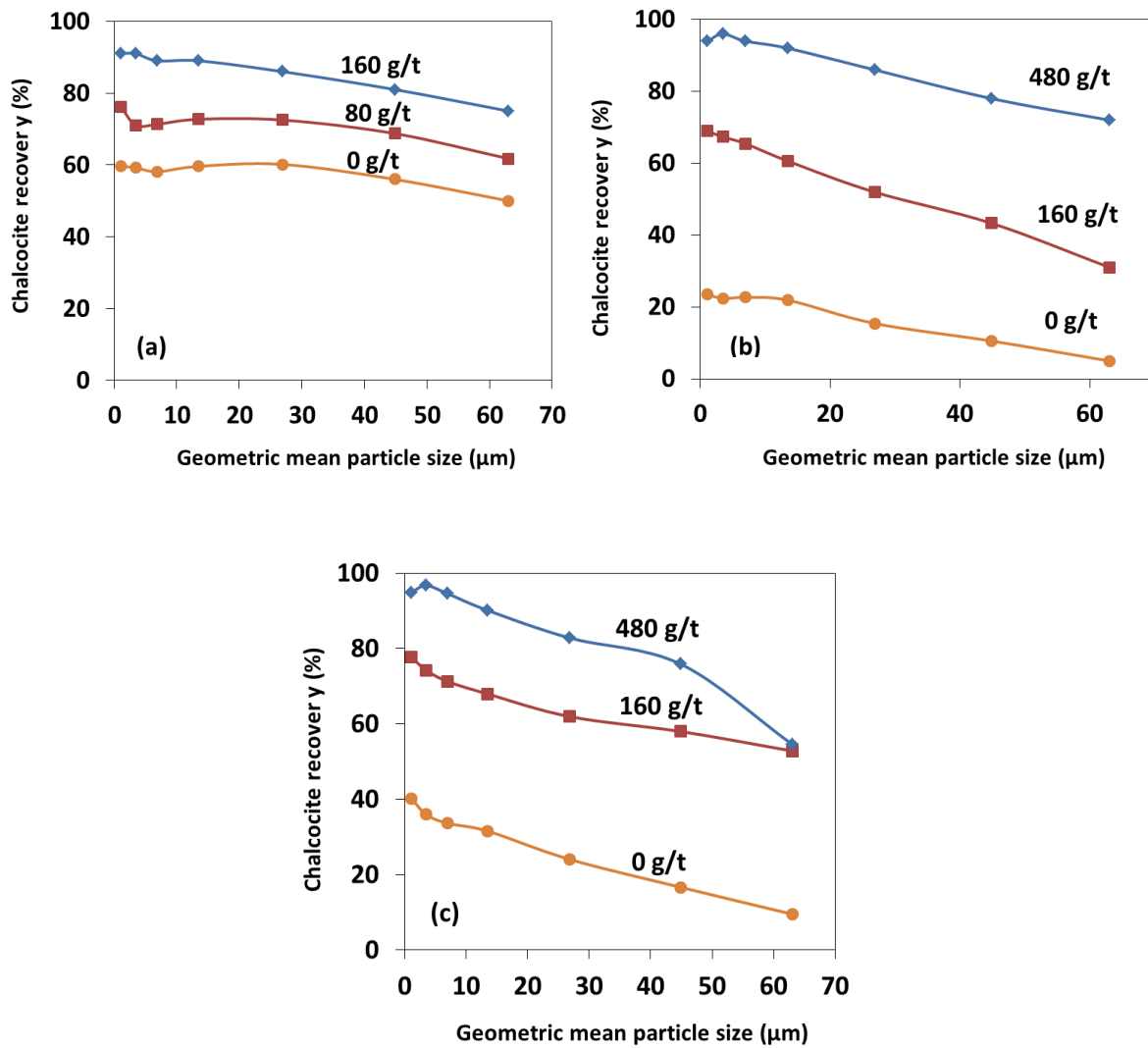


Figure 7.12 Chalcocite flotation recovery as a function of particle size in the presence of additional amount of collectors after regrinding in rod mill with stainless steel media (a), in stirred mill with stainless steel media (b), and in stirred mill with ceramic media (c).

7.3 Conclusions

A rod mill with stainless steel media and a stirred mill with stainless steel and ceramic media were used to regrind chalcocite rougher flotation concentrates so as to examine chalcocite flotation recovery in the cleaner stage. The factors which could influence the flotation response of the regrinding product were investigated, and these included: the particle size, the fresh surfaces produced, the oxidation of particle surfaces, and the distribution of collector carried over from rougher flotation.

The major contributing factor to different chalcocite flotation observed was believed to be the distribution of collector carried over from rougher flotation, which was in turn controlled by the particle breakage mechanism. In the rod mill, the main breakage mechanism is impact, and the collector can remain on surface of particles of all size. In the stirred mill, the attrition breakage predominates and tends to remove the collector from surfaces onto fine and ultra-fine particles resulting in lower flotation recovery, especially with coarser size fractions. Furthermore, stainless steel and ceramic media in the stirred mill produced different chalcocite flotation in the cleaner stage. This may be associated with a different proportion of attrition breakage mechanism as well.

The chalcocite flotation recovery can be improved by the addition of more collector in the cleaner stage. More collector addition is required after regrinding in the stirred mill than in the rod mill to restore the flotation recovery to the same level.

Chapter 8 Conclusions and Future Work

8.1 Summary

The overall objective of this thesis is to investigate the effect of regrinding chemistry and particle breakage mechanisms on subsequent cleaner flotation. The motivation underlying this work was that regrinding rougher flotation concentrates has become a common practice when processing low grade and complex ores, and the surface properties of these fine particles produced by regrinding are critical to subsequent cleaner flotation. Therefore, understanding how regrinding chemistry influences the mineral surface properties and hence floatability would potentially allow the optimization of the chemical environment during regrinding, thereby achieving better cleaner flotation performance. Furthermore, the selection of the type of regrind mill in the processing plants does not usually consider the potential influence of different particle breakage mechanisms on mineral floatability. A better understanding of the relations between them could provide an additional means by which the cleaner flotation performance can be enhanced. A comprehensive literature review was conducted to evaluate the existing knowledge related to this study. Based on the research questions and the gaps identified in the literature review, the research is conducted to address the four hypotheses described in section 2.6 and the conclusions drawn from the results are presented in the following paragraphs.

8.2 Conclusions

The first hypothesis tested is that *regrinding chemistry has a more significant influence on mineral floatability compared to primary grinding chemistry, because regrinding produces more fine and ultra-fine particles with a larger surface area for various electrochemical reactions to occur*. This was assessed by regrinding rougher flotation concentrates to fine particles ($P_{80} = 20 \mu\text{m}$) under different regrinding chemical conditions (e.g. different grinding media), and then analysing the mineral floatability and the surface species. From the results in Chapter 4, it was found that regrinding with stainless steel media and mild steel media resulted in significantly different pyrite flotation behaviour in the cleaner stage, which was mainly caused by the formation of different surface properties. Firstly, the particle surface area increased more than 6 times. It indicates that a large amount of fresh surfaces was produced as particle size reducing, which significantly diluted

the surface hydrophobic species carried from rougher flotation. In addition, strong electrochemical reactions occurred inside the grinding mill due to the large surface area. From the surface analysis, the use of stainless steel media during regrinding promoted the pyrite surface oxidation, especially the copper-activated pyrite surfaces, which decreased the pyrite floatability. After regrinding with mild steel media, a significant amount of iron oxidation species was produced, which completely covered the copper-activated surfaces. Moreover, different grinding media also affected the pyrite activation by copper ions due to the generation of different pulp chemistry condition, resulting in significantly different flotation behaviour. This hypothesis is further supported by the results in Chapter 5. These results showed that chalcopyrite and chalcocite presented different separability from pyrite in the cleaner flotation after regrinding, but the differences were not significant during primary grinding and rougher flotation due to the galvanic interaction between copper mineral and pyrite being weak at coarse sizes with small surface areas. It was also found that the use of mild steel media during primary grinding did not affect the flotation of copper minerals and pyrite in the rougher, but regrinding with mild steel media strongly depressed the flotation of all the minerals in the cleaner. Therefore, it indicates that the regrinding chemistry was more influential to the mineral floatability than the primary grinding chemistry. Overall, all the results clearly demonstrated the importance of regrinding chemistry on subsequent cleaner flotation. This study can also provide guidelines for the plant operation to optimize the regrinding chemistry.

The second hypothesis tested was that *the separability of chalcopyrite and chalcocite from pyrite will be different after regrinding, because the two copper minerals have different electrochemical properties. This may not only influence the flotation of copper minerals but also affect the pyrite floatability through the galvanic interaction and copper activation.* This hypothesis was tested by the work described in Chapter 5. It was found that, when chalcopyrite was mixed with pyrite, a high chalcopyrite recovery was achieved in the cleaner flotation stage after regrinding, whilst pyrite flotation was strongly depressed and could not be restored even at a high collector addition. This indicates that an efficient separation of chalcopyrite from pyrite can be achieved. When chalcocite was mixed with pyrite, both chalcocite and pyrite flotation were depressed after regrinding, but the recovery of both minerals could be simultaneously restored by additional collector, making it difficult to achieve the required separation of chalcocite from pyrite. Surface analysis shows that these phenomena are governed by the different electrochemical activity of chalcopyrite and chalcocite and their galvanic coupling with pyrite. The oxidation of chalcopyrite does not produce sufficient copper ions for activating pyrite but generates a hydrophobic sulphur rich surface. Chalcocite is more electrochemically active than chalcopyrite and therefore a stronger galvanic

interaction occurs between chalcocite and pyrite than between chalcopyrite and pyrite. As a result, stronger oxidation occurs on chalcocite compared with chalcopyrite, producing a significant amount of hydrophilic oxidation species to depress its flotation, while also providing a quantity of copper ions which are sufficient to activate pyrite. However, chalcopyrite and chalcocite did not affect pyrite flotation in such a way in the rougher flotation after primary grinding, due to the reduced galvanic interactions at coarse particle sizes with small surface areas. Overall, the results demonstrate that the separation of different copper minerals from pyrite is highly dependent on the minerals' electrochemical properties and the grinding chemistry and the influences are more significant during regrinding and cleaner flotation than during primary grinding and rougher flotation.

The third hypothesis tested was that *pulp chemistry can be significantly changed during regrinding rougher concentrates with a high content of sulphides because of the large amount of reactive fresh surfaces created during regrinding, and the pulp chemistry can be optimized by different methods to improve the subsequent flotation.* It was assessed in Chapter 6 by investigating the flotation performance after regrinding pyrite concentrates containing copper and gold minerals obtained from the Telfer plant. A low DO and Eh were observed in the regrind mill discharge, which was caused by the large amount of fresh pyrite surfaces produced during regrinding, quickly consuming all the oxygen in the slurry. Accordingly, copper recovery and gold recovery were quite low in subsequent cleaner flotation, while pyrite recovery was relatively high. A number of methods which provide an oxidising condition were investigated, including the pre-aeration before flotation, regrinding in an oxidizing condition, and the addition of different oxidizing agents during regrinding. It was found that all the oxidizing methods improved copper-gold flotation and depressed pyrite flotation. The improved copper-gold flotation against pyrite under oxidising conditions should be due to a combined effect of several factors: pyrite depression caused by the surface oxidation, an increased collector adsorption rate on copper and gold surfaces due to the higher Eh and DO, and the surface oxidation of chalcopyrite producing hydrophobic species. Furthermore, the further activation of fresh pyrite surfaces by copper ions can be prohibited during regrinding at an oxidizing condition. Overall, this study demonstrates the importance of suitable pulp chemistry during regrinding on subsequent copper/gold flotation and pyrite depression.

The last hypothesis tested was that *different flotation behaviour can be observed after regrinding in a tumbling mill and stirred mill, because these two mills provide different particle breakage mechanisms which can affect the mineral surface properties of the grinding product and hence*

influence the mineral floatability. This was assessed in Chapter 7 by comparing the flotation performance and surface properties after regrinding the rougher flotation concentrates using a rod mill and a stirred mill. Chalcocite was used as the model mineral. Different flotation recovery was achieved in the cleaner stage after regrinding in tumbling and stirred mills. The factors contributing to the different recovery including particle size, the amount of created fresh surfaces, surface oxidation and the redistribution of collector carried from rougher flotation were examined. It was determined that the dominant factor was the different distribution of collector resulting from different particle breakage mechanisms in the stirred and tumbling mills, as confirmed by ToF-SIMS analysis. In the tumbling mill, the impact particle breakage mechanism predominates, causing the collector to remain on the surface of newly produced particles. In the stirred mill, the attrition breakage removes collector from the surface, and decreases particle floatability. Furthermore, the type of grinding media in the stirred mill also influences the subsequent flotation, again due to the change of particle breakage mechanisms. Overall, the results of this study demonstrate that the particle breakage mechanisms provided by different types of mills play an important role in subsequent flotation, and should be considered when selecting grinding mills for regrind duty.

8.3 Recommendations for the implications in plant practice

This thesis study was conducted in the context of seeking to understand the causes of common problems in mineral processing plant operation. Therefore, the research outcomes, especially the identified mechanisms, can provide guidelines for the plant operation to optimize the regrinding conditions. Following are the recommendations for the plant operation.

1) Investigation and optimization of regrinding chemistry in the plant

This study demonstrates that the regrinding chemistry has a more significant effect on cleaner flotation compared to the effect of primary grinding chemistry on rougher flotation. It is recommended that a survey should be conducted firstly in the regrinding and cleaner flotation circuit to have a clear understanding of the metallurgical performance. If there is any significant loss of valuable minerals or difficulty in depressing sulphide gangue minerals, a further chemistry survey should be conducted, including measuring the pulp chemistry (pH, Eh, Do) and applying the surface analysis methods (e.g EDTA extraction, XPS, ToF-SIMS) to analyse particle surface change after regrinding. If the poor flotation performance was suspected to be caused by the

undesirable pulp chemistry or particle surfaces, an optimization of regrinding conditions may be considered. For example, if pyrite was difficult to be depressed in the cleaner flotation after regrinding, a change of the type of grinding media or pulp chemistry may improve the flotation separation. In addition, if diagnostic and optimization test work was conducted in the laboratory, it is important to ensure the chemical condition in the laboratory matches the conditions observed in the plant. Overall, a comprehensive investigation and optimization of regrinding chemistry can benefit the plant operation and hence is highly recommended.

2) Select different regrinding and cleaner flotation conditions when processing the minerals with different electrochemical properties.

In the processing plant, the ore composition may vary widely not only from one ore deposit to another but also within the same ore body. As studied in this thesis, chalcopyrite and chalcocite have different separability from pyrite due to their different electrochemical properties. It is therefore recommended that the plant should monitor the change of compositions of regrinding feed. The regrinding and cleaner flotation conditions should be changed according to the feed composition. For example, in a copper regrinding and cleaner flotation circuit, if the dominant copper mineral is chalcopyrite and the regrinding condition is oxidizing, a lower collector dosage may be more suitable since the chalcopyrite may present a high natural floatability due to the formation of sulphur rich surface species during regrinding, and the pyrite will also be more easily depressed due to the lower activation by copper ions. However, if a large percentage of chalcocite presents, the separation of copper minerals from pyrite may become more difficult because pyrite can be strongly activated by copper ions, and therefore additional pyrite depressant may be required in this situation.

3) Application of suitable oxidizing methods when regrinding flotation concentrates with a high content of sulphides

The sulphide content of the regrinding feed is usually high compared to the primary grinding feed because the majority of non-sulphide gangue minerals has been rejected in the rougher flotation. As studied in Chapter 6, an undesirable pulp chemistry with low DO and Eh was produced after regrinding pyrite concentrates due to the generation of a large amount of reactive pyrite surfaces which quickly consumed the oxygen in the slurry. The application of oxidizing methods during regrinding can significantly improve the copper/gold flotation and depress pyrite. It is therefore

recommended that the plant operation should closely monitor the pulp chemistry in the regrinding product and subsequent flotation if the sulphide content is high in the regrinding feed. If a low DO and Eh is observed after regrinding, appropriate oxidizing methods should be selected depending on the plant condition. Some methods have been tested in Chapter 6, including pre-aeration before flotation, regrinding in an oxidizing atmosphere, and the addition of different oxidizing agents during regrinding, which may be also applicable in the plant operation. In addition, changes to the design of grinding machine and flotation conditioning tanks may also help to introduce a more oxidizing condition during the process.

4) Considering the effect of particle breakage mechanisms on subsequent flotation when selecting regrind mills

Different types of grinding mills are available for regrinding, such as the tumbling mill and stirred mill. The selection of regrind mills in the plant usually consider the energy efficiency and operating cost. However, the results in Chapter 7 show that the flotation behaviour of chalcocite was significantly different after regrinding in a rod mill and in a stirred mill. This difference was caused by the different particle breakage mechanisms, which influence the distribution of the collectors carried from rougher flotation. Therefore, it is highly recommended that the selection of regrind mills in the plant operation should consider the potential influences of particle breakage mechanisms on properties of the surfaces produced for subsequent flotation.

8.4 Recommendations for future work

To further establish the effect of regrinding conditions on subsequent cleaner flotation and to assist the plant in designing and optimizing the regrinding-cleaner circuit, the following work is recommended:

1) Model the distribution of surface species during regrinding

As studied in this thesis, there are two types of surfaces existing after regrinding. One is the remaining surfaces carried over from the regrinding feed, which are covered with collectors and other species formed during primary grinding and rougher flotation. The other type of surface is the fresh surfaces generated during regrinding. Both of them are important for subsequent cleaner flotation. In future, based on the advanced surface analysis techniques, the distribution of these two

surfaces on the regrinding product can be modelled and can be used to predict the floatability of the minerals.

2) Investigate the effect of water quality during regrinding on mineral floatability

The use of saline water in processing plants is becoming common due to the shortage of fresh water, especially in arid regions (Drelich and Hwang 2012). The saline water usually contains a large amount of electrolytes and salt ions, which may promote the galvanic interactions and electrochemical reactions during processing, especially when dealing with fine particles. Therefore, it is important to investigate the potential influence of the quality of water used during regrinding on the subsequent cleaner flotation through the modification of mineral surface properties.

3) Study the effect of particle breakage mechanisms on mineral flotation in a mixed mineral and real ore system.

The current study in this thesis focused on understanding whether the particle breakage mechanisms provided by different mills can influence flotation through the modification of mineral surfaces (e.g. the distribution of collectors carried over from rougher flotation, the formation of oxidation species). Therefore, chalcocite single mineral is used as a simplified system in order to more accurately analyse the change of mineral surfaces during regrinding. In a mixed mineral or real ore system, the effect of breakage mechanisms on the floatability of different mineral particles may be different due to the different properties of each mineral. Firstly, the collector adsorption on different minerals in a mixed mineral system varies significantly, therefore the change of floatability of each mineral after regrinding due to redistribution of collector species may be different. For example, in a copper-gold flotation circuit, most of the collectors adsorb on copper/gold particles rather than sulphide gangue minerals (e.g. pyrite). As a result, the different breakage mechanisms may have a more significant effect on the floatability of copper/gold mineral particles than the floatability of gangue minerals. Secondly, different breakage mechanisms may also affect the formation and distribution of surface oxidation species. As studied in Chapter 5, galvanic interactions occur when different minerals come in contact with each other during grinding in a mixed mineral system and affect the surface oxidation of each mineral. Therefore, the potential influence of breakage mechanisms on galvanic interactions also needs to be considered when studying a mixed mineral or real ore system. In addition, liberation of minerals is critical to the flotation performance in a real ore system. It has been proved that different breakage mechanisms can influence mineral liberation

(Andreatidis 1995, Vizcarra 2010). Therefore, the potential influence of breakage mechanisms on flotation through different liberation also needs to be considered when studying a real ore system. In summary, further studies need to be conducted to investigate the effect of particle breakage mechanisms on flotation of a real ore system.

4) Assess the effect of different stirred mills used in regrinding on the subsequent cleaner flotation

Stirred mills are becoming more and more popular in fine regrinding due to their high energy efficiency. Generally, there are two categories of stirred mills being used in the mining industry (Ntsele and Allen 2012). One is the gravity-induced stirred mill, such as the Metso VERTIMILL™. This type of mill usually operates at a relatively low tip speed and steel balls are commonly used as the grinding media. The other type is the fluidized stirred mill, such as the Metso Stirred Media Detritor (SMD), Isamill™ and Knelson-Deswik mill. The stirred mill used in this thesis study is also a fluidized stirred mill. In contrast to the gravity-induced stirred mills, the fluidized mill type uses high rotational, and speeds of either impellers or discs to cause the suspension and complete mixing of the grinding media and slurry particles. Small ceramic beads or river sands are usually used as grinding media. The different design of stirred mills may influence the subsequent cleaner flotation through the generation of different pulp chemistry and different particle breakage mechanisms, which need to be further investigated.

5) Investigate the effect of operating conditions in stirred mill regrinding on mineral floatability.

This study reveals that the particle breakage mechanisms provided by different mills can significantly affect the mineral floatability. It has been reported the breakage mechanisms in a stirred mill can be affected by operating conditions, such as size of grinding media, the material of the grinding media, the pulp density and the stirrer speed, which may result in different flotation behaviour. Therefore, it is recommended to investigate the effect of operating conditions in the stirred mill on mineral floatability.

6) Model flotation by considering the effect from regrinding chemistry and particle breakage mechanisms.

The modelling and simulation of flotation behaviour has been of great interest during the last few decades. However, most models developed up to now did not consider the influence from regrinding chemistry and particle breakage mechanisms in regrind mills. Therefore, the knowledge in this thesis study can be used in developing models which can more accurately predict the flotation behaviour after regrinding especially that of the fine particles.

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