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Sipunga, Elias

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Optimization of the flotation of copper smelter slags from Namibia Custom Smeltersô Slag Mill Plant

Elias Sipunga

A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in partial fulfillment of the requirements for the degree of Master of Science in Engineering

Johannesburg, South Africa

Supervisor

Professor V Sibanda

August, 2015

Declaration

I declare that this research report is my own unaided work. It is being submitted for the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

_____

Nambili Elias Sipunga

3rd Day of August 2015

Synopsis

Namibia Custom Smelters treats complex copper concentrates. At the time of the research, three furnaces were in operation namely, the Top Submerged Lance Furnace, the reverberatory furnace and the converters. All these three furnaces produce fayalite slag as a byproduct. The slags contain copper with the content ranging between 0.8 to 5% copper. The slags cannot be discarded due to the high content of copper and hence they are sent to a milling and flotation plant (Slag Mill Plant) for liberation and recovery of copper. This work focuses on optimizing the recovery of copper minerals in copper smelter slags by means of froth flotation. Most of the copper minerals present in the Namibia Custom Smeltersô slags are free sulphide minerals, however a certain proportion is copper minerals that cannot be floated easily because they could either be in oxide form or locked in or occluded in the gangue matrix. This residual copper content continues to present a tough challenge in the copper mineral recovery process. It was initially postulated that these órefractoryô copper minerals were oxide minerals and an acid solubility test was performed after fine griding in an attempt to validate this hypothesis. It is known that oxides tend to dissolve in dilute sulphuric acid more readily while sulphides are refractory to acid leaching. The acid liquor obtained from the acid tests were found to contain dissolved copper which re-enforced the school of thought that the copper minerals were oxide minerals, however doubt still remained because literature has shown that copper sulfide also dissolves slightly before passivation sets in.

To further investigate the nature of the refractory copper minerals in the slag, mineralogical analysis on the slag samples were performed using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques.

Both these techniques did not reveal the presence of copper oxide minerals, most scans showed that copper sulphide minerals are locked and occluded in fayalite gangue. The slags were milled to 75 percent less than 45 microns in order to liberate the copper minerals sufficiently for the flotation tests which were performed on slag samples from three different sources (TSL furnace, copper converters, reverberatory furnace) to recover the copper minerals. A range of commercial flotation reagents including xanthates, dithiophosphates, mercaptobenzothiazole, thionocarbamates, fatty acids, sulphides and sulphates were tested in the flotation tests. The highest recovery obtained in the first mill-float stage was about 75.8%. Flotation tailings were milled and floated again in a Mill-Float-Mill-Float (MF2) configuration. After re-grinding and floating again, the highest recovery (cumulative) obtained was 92.2% which represented a significant improvement in the copper recovery. The best flotation performance was obtained with the reagent FC 4146 which contains thionocarbcarbamate and methyl isobutyl carbinol as a froth enhancer.

Dedication

To the African Continent and all its Living beings

By

Elias Sipunga

Acknowledgements

Firstly I would like to thank God for bringing me to this stage of my life. I have seen so many obstacles in my life, yet he carried me through them. I will forever remain indebted to him.

Secondly, I would like to thank my supervisor and Lecturer, Prof. V Sibanda. His advice and guidance was key in making this work a success. I highly appreciated it.

Thirdly, I would like to thank the University of the Witwatersrand, School of Chemical and Metallurgical Engineering, together with my class mates. I have been with the most gifted and highly intellectual people I have ever met, in such a short space of time.

Lastly, I would like to thank everyone at Dundee Precious Metals who contributed to this work. I will never stop giving my best, for as long as I am in the companyôs employ.

Thank you,

Elias Sipunga.

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List of nomenclature and symbols

Complex concentrate	A concentrate that contains multiple minerals, suitable for economic recovery, though different processing paths.
Copper oxide or oxide copper:	A copper mineral that contains at least one oxygen atom.
Copper sulfide or sulfide copper:	Copper minerals containing sulfide ($S^{2\bar{}}$) as the major anion.
Enrichment ratio:	The ratio of the concentrate grade over the feed grade.
Flux:	A metallurgical flux is a chemical that is added to combine with gangue during ore and concentrate smelting, to form a slag that can be separated from the metal.
Gangue:	The unwanted portion of an ore, that is usually closely associated with the wanted mineral or element.
MF2:	Mill-float-mill-float process configuration.
PAX:	Potassium Amyl Xanthate
PGMs:	Platinum Group Metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum).
SEM:	Scanning Electron Microscope.
Sulfidizer/Sulphidizer:	Chemical reagents used to alter oxide mineral surfaces, by giving it a pseudo sulfide layer.
UG2:	The Upper Group 2 Reef, known to contain most of the world's reserves of platinum group metals.
XRD:	X-ray Diffraction.
□	Breakage rate parameter characteristic of the material.

bi,j	Mass fraction arriving in size interval i from breakage of size interval j.
Bi,j	Cumulative breakage function of particles of size j into size i.
µ	is the particle size at which the denominator in the selection function equation is 0.5
Ø	Fraction of the fines produced.
Ŭ	Parameter characteristic of the material.
	Particle size (micrometers).
	Flotation rate constant (per minute).
	Mass of solids in the flotation cell (kilograms).
∈	Parameter dependent on hydrodynamic conditions in the flotation cell.
ɓ	Breakage parameter characteristic of the material used.
ɔ	Breakage parameter characteristic of the material whose values typically are found to be between 0.5 and 1.5.
ş	Positive number representing an index of how rapidly the rate of breakage falls as size increases in the abnormal region.
	Rate of disappearance of material of size i or specific rate of breakage of particles of size i, also known as selection function

1. Introduction

1.1 General Introduction

Namibia Custom Smelters treats complex concentrates. At the time of the research, three furnaces were in operation namely, the Top Submerged Lance furnace, the reverberatory Furnace and the converters. All these three furnaces produce fayalite (Fe_2SiO_4) slag as a byproduct. The slags contain a copper content ranging between 0.8 to 5% copper. The slags cannot be discarded due to the high content of copper and hence they are sent to a milling and flotation plant (Slag Mill Plant) for liberation and recovery of copper. The slag from the furnaces are rapidly cooled by means of granulation with water, therefore copper minerals tend to be trapped in solid gangue phases. The Slag Mill Plant achieves on average copper recovery of 75% and a tailings grade of 0.65% copper.

Copper minerals in slags are made up of elements in the mother ore, however, fluxing to aid the smelting process also contributes to the mineralogical composition of the slags. The use of silica and lime rock as fluxes during smelting processes, produces a new ócoreô which bears free sulphide copper and locked/or refractory copper minerals. The presence of locked or occluded and/or refractory copper minerals hampers efficient recovery of copper from the slags. Sulphide bearing ores such as those smelted at Namibia Custom Smelters, produce slags that can be treated by froth flotation while the locked copper and/or refractory copper minerals present are often lost to tailings. It is therefore crucial to follow a reliable mineral processing route that can recover the majority of these locked minerals.

The optimization of copper recovery from copper slag was studied by means of froth flotation experiments. It has generally been assumed at Namibia Custom Smelters, that copper sulfide minerals coexist in the slag with copper oxide minerals and that copper sulfide minerals float with relative ease whilst poor recoveries are attributable to the presence of copper oxide minerals that do not float easily. An attempt to validate the existence of both sulfide and oxide copper minerals in the slags was done through a laboratory assay method, which involved the acid leaching of copper from slags and detecting the atomized ions by means of atomic absorption spectrophotometry. This diagnostic route is based on the fact that copper sulfides are refractory to acid leaching while copper oxide readily leaches, therefore any copper ions found in solution would be originating from copper oxide minerals. For many years it was accepted that the presence of copper oxide minerals hamper the flotation process. Most of the work done on improving copper recoveries at the Namibia Custom Smeltersô Plant was aimed at improving the floatability of copper oxide minerals. In the past, sulphidizing agents have been deployed in the flotation circuit in an attempt to convert the oxides to sulphides and mixed results have been obtained, often with no correlation at all.

Figure 1.1 shows a process flow diagram of the slag recovery plant that is in operation at Namibia Custom Smelters.

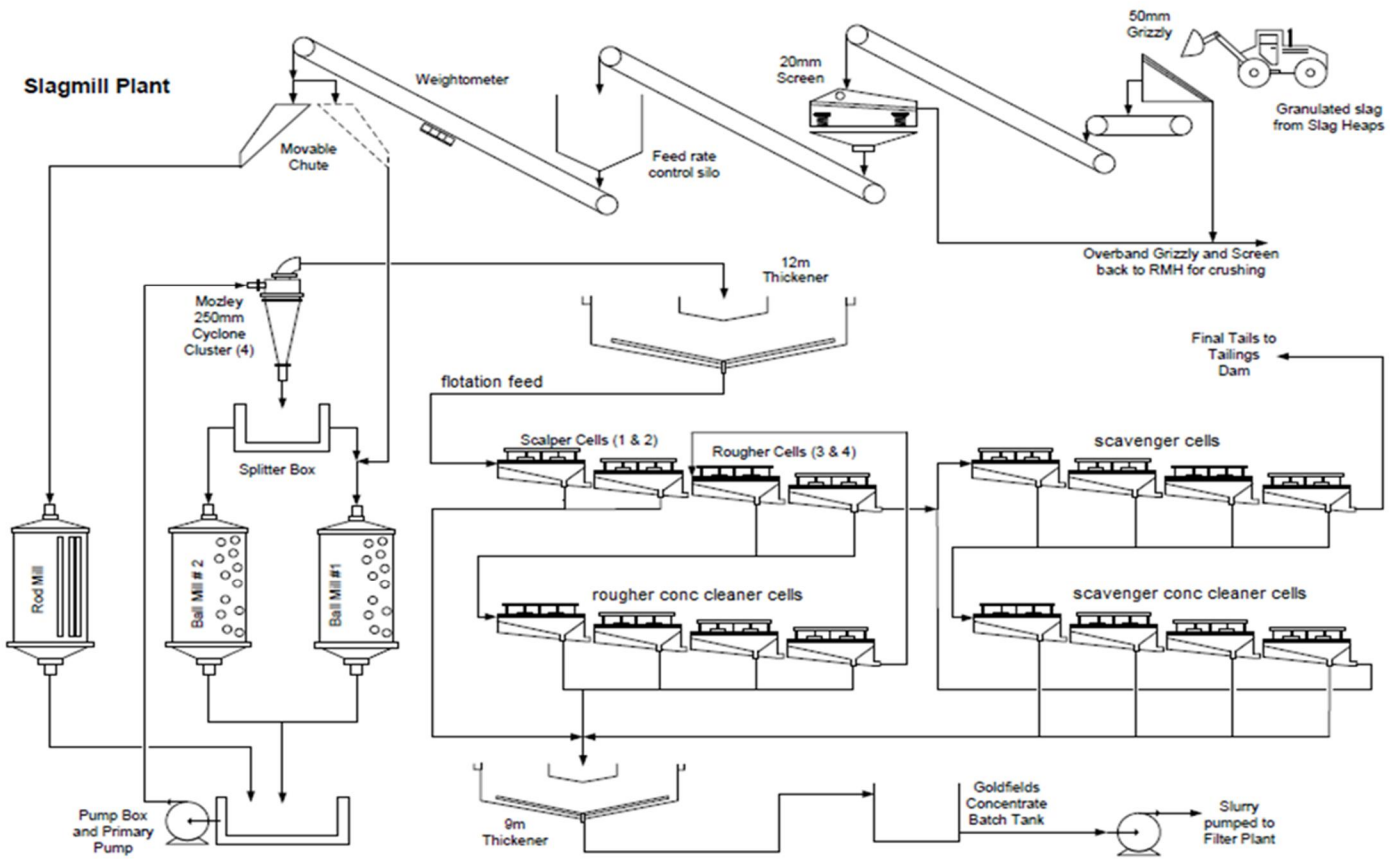


Figure 1.1 A detailed plant overview.

The circuit has a crushing plant up-stream of the mill and a flotation plant. The crushed and screened slag is fed into a rod mill and the rod mill product is classified through hydrocyclone classifiers where the cyclone over-flow forms the mill plant product and the cyclone under-flow is milled further in parallel ball mills. The mill plant product is dewatered in a thickener before being floated. The flotation plant has 2 scalper cells which feed the rougher cells. The tailings from the rougher cells are treated further in a scavenger cell bank which produces the final plant tailings. The concentrate from the rougher cells is cleaned through a cleaner cell bank to form final concentrates. The cleaner tailings are fed back to the rougher bank. The scavenger concentrates are cleaned in a scavenger concentrate cleaner cells to form concentrate that is combined with the rougher concentrate cleaner product to form final concentrate. The scavenger concentrate cleaner tailings are fed back into the scavenger cell bank.

1.2 Problem Statement

The Slag Mill plant consists of a milling circuit, which produces a fine circuit product (75% passing 45 microns) at 25 tonnes per hour. The milling circuit product is thickened to 30% solids by mass and is fed to a flotation circuit. The flotation circuit consists of a scalper section, followed by a rougher section. The rougher concentrate is fed to cleaner cells and the cleaner tailings are returned to the rougher cells. The rougher tails are fed to a series of scavenger cells before exiting the plant as final tailings. Potassium amyl xanthate (~300 g/t) is the primary flotation reagent used, followed by Sodium Dialkylditiophosphate (200 g/t). The main concern with this process is that tailings grades in the excess of 0.9% Cu are generally produced and this copper content is too high to be lost in the final waste stream.

Therefore, the scope of the present work involves an investigation into how the flotation recoveries of the copper minerals can be enhanced by studying the mineralogy of the slags, the milling and liberation profile of the slags and the flotation reagent suite that can be used to optimally recover the copper minerals from the respective slags.

1.3 Aims and Objectives

- To study the mineralogical composition of the different slags which form the feed to the slag milling and flotation plant. The slags are (i) Top Submerged Lance Furnace slag (ii) reverberatory furnace slag (iii) copper converter slag (iv) final flotation plant tailings.
- To determine the grind that gives best liberation of the copper minerals in the slag.
- To study the influence of selected flotation reagents on the recovery of the copper minerals in the milled slags.
- To recommend a liberation and flotation procedure that will optimize recoveries and grade of concentrate.

2. Literature Review

2.1 Utilization of secondary resources

Mining and extractive metallurgy is largely viewed as environmentally unfriendly thus over the years, strict laws relating to the mining industry have been passed by governments. Mining activities make up a large chunk of the worldôs economy and the challenges that the mining industry faces therefore become global challenges. Mining and minerals extraction play a critical role in the transition to a sustainable society. Extractive metallurgy is at the back-end of the mining process and a variety of waste streams emanate from the processing of mined ores. These process by-products can be in the form of tailings (dumps), ashes, dilute process streams and furnace slags. The world is now of the view that economic and ecological considerations have to be integrated into the extraction processes, hence the emergence of the concept of sustainable metallurgy (Zander *et al.,* 2013).

Sustainability in extractive metallurgy is not only achieved by treating metallurgical process wastes and byproducts but also by treating other secondary resources such as municipal solid waste. According to Grosso *et al.* (2010) metals recovery from ashes generated by municipal solid waste incineration is a major sustainable metallurgy drive in Italy. Up to 21 000 tonnes of aluminum were predicted to have been recovered in Italy in 2015. Wastes like ash have found extensive use in the construction industry i.e. in the cement and concrete manufacture. Recent studies have shown that removal of metals from the ashes before application in the construction industry is beneficial.

Metal removal from ashes have been found to increase mechanical strength of the concrete, the presence of aluminum in concrete, when raw ash is used, is associated with swelling and expansion of the concrete which weakens the concrete (Pecquer *et al.*, 2001). Gold dumps have long posed a serious health and environmental risk to the estimated 1.5 million people who live near them in Johannesburg. In 2013, DRD Gold reprocessed some Johannesburg gold dumps and recovered 33,600 ounces of gold, worth nearly $40 million (Tilsley, 2014). The gold dumps are reclaimed and mixed with water and the slurry is pumped to a processing plant, 3km to the south of Johannesburgôs CBD. The slurry is milled and gold is leached using carbon in pulp (CIP) technology.

Other process waste stream that have generated interests are those coming out of PGM plants. Ferriera (2004) studied the electrochemical removal of metals from a PGM industrial waste stream containing palladium (146 g/t), copper (211 g/t) and a small concentration of platinum (6.8 g/t). The spent electrolyte from this process contained values of the metal that fall within the specified metal discharge limit set for the respective metal, which is approximately 0.1 ppm for all three metals. Metal recoveries of above 99.9% were achieved. The work done clearly indicate that trace metals in industrial effluents, once regarded as waste, now have the potential to be recovered as valuable byproducts.

Slags which are produced from smelting of ferrous and non-ferrous metal ores and concentrates are also often a subject of great environmental and health debate. Slags are formed by the fluxing agents used to aid high temperature liquid-liquid separation.

The gangue portion of the ore is absorbed by the slag phase and the valuable portion is tapped off. Slags have a wide range of applications including civil engineering work, fertilizer production, road construction, cement production and landfill (Ziemkiewicz *et al.*, 1998).

According to Zander *et al.* (2011), fayalitic slag still contains up to 1% of copper and other valuable metals like nickel, cobalt or molybdenum. In addition to economic motive, future regulations may restrict the heavy metal contents in slags used for construction purposes.

Due to furnace bath instability, entrapment of valuable minerals in slags often take place. Slag cleaning is the process of removing wanted minerals and metals from the slag. Slag cleaning can be divided into two types; the first is pyrometallurgical reduction and settling, performed in a slag-cleaning furnace, the second is minerals processing of solidified slag, including crushing, grinding and froth flotation (Davenport *et al.*, 2002).

Pyrometallurgical cleaning of copper slags involves conditions that encourage suspended matte (Cu_2S) droplets to settle to a matte layer. The conditions are low slag viscosity, low bath turbulence, longer residence time and a thin slag layer. These conditions are often difficult to obtain in a smelting vessel, particularly the necessary residence time. As a result, copper producers have since the 1960's constructed separate furnaces specifically for cleaning smelting and converting slags (Davenport *et al.*, 2002).

2.2. Utilization of copper slags

2.2.1. Origins

Copper concentrates are mixed with lime and silica flux before entering the Top Submerged Lance (TSL) furnace. The furnace is initially ignited with fire wood, recycled slag and heavy fuel oil.

Once the desired temperature is attained (1150°C - 1200 °C) and the slag is molten, the feed is introduced from the top and oxygen enriched air is introduced through the lance. Two layers of immiscible liquids are formed, namely matte and slag. The slag layer floats above the matte phase. According to Mounsey *et al*. (1999) the following reactions take place in the two phases;

In the matte phase:

$$CuFeS_2 \rightarrow \frac{1}{2}Cu_2S + FeS + \frac{1}{4}S_2(g)$$

In the slag phase:

$$FeO + \frac{1}{2}O_2(g) \rightarrow FeO_{1.5}$$

At the phase boundary:

$$FeS\ (\text{in matte}) + 6FeO_{1.5}\ (\text{in slag}) \rightarrow 7FeO\ (\text{in slag}) + SO_2(g)$$

Nagamori (1974) and Bamett (1979) Suggested that Cu_2O becomes the dominant form of dissolved copper at matte grades above 70%, by following the reaction regime;

$$Cu_2S\ (\text{in matte}) + FeO\ (\text{in slag}) \rightleftharpoons Cu_2O\ (\text{in slag}) + FeS\ (\text{in matte})$$

slag (≥2.5% Cu) and matte (≥60% Cu) are tapped off alternately. The slag is granulated with water and transferred to the slag milling and flotation plant for copper recovery. The matte is transferred to the reverberatory furnace in ladles. The reverberatory furnace is fired continuously with pulverized coal and air is prevented from entering, in order to maintain a silent reducing environment, different from the turbulent oxidizing environment of the TSL furnace.

Secondary copper sources such as high grade slags and copper reverts, are also smelted in the reverberatory furnace. Cu_2S droplets are allowed to settle from the slag layer into a copper enriched matte layer. Any Cu_2O present in the slag layer is reduced according to the equation suggested by (Davenport *et al.*, 2004)

$$Cu_2O + C \rightarrow 2Cu + CO$$

Reverberatory furnace slag is cleaner than TSL furnace slag, as it contains approximately 0.8 % copper. Matte from the reverberatory furnace in transferred to the Pierce-Smith converters and silica flux is added. Oxygen enriched air is blown through air valves called tuyeres. Copper in matte is converted to molten copper blister (~98% Cu). The converting process yields a converter slag layer which contains up to 5% copper. Copper converters can treat matte directly from the TSL furnace, but due to their batch operations, the reverberatory furnace acts as a matte holding furnace, as well. The overall converting process can be summarized as (Davenport *et al.*, 2004);

$$Cu - Fe - S_{(l)} + O_2(g) + SiO_2 \rightarrow Cu_{(l)} + 2FeO - SiO_2 - Fe_2O_{3(s)} + SO_2(g)$$

2.2.2. Copper slag mineralogy

During the cooling of slag by means of granulation, new crystallized phases are formed. Studies have shown that fayalite slags have adsorption properties for heavy metals like copper and lead. Minerals that are adsorbed or absorbed in gangue phases pose a big challenge when liberation is attempted. Mihailova *et al.* (2010) found that flash smelting furnace slag and copper converter slag contained isomorphic impurities of Al, Mg, Zn, Cu and Ca.

The two slags tested have fayalite (Fe_2SiO_4) as the dominant crystal phase, followed by magnetite (Fe_3O_4) and copper sulphide inclusions. Votjech *et al.* (2009) studied the mineralogy and environmental stability of slags from the Tsumeb smelter. They found that slag obtained from smelting of Cu and Pb sulphide ores were composed of glassy fragments, with small inclusions of metallic and sulphide droplets. Those obtained from the smelting of Cu-Pb carbonate/oxide ores were made up of silicate phases with zoned Cu bearing oxides (Cu-Fe oxide, Cu-Cr oxide) and feldspar crystals within a Pb-arsentae matrix. Wang *et al.* (2011) studied the chemical and mineralogical compositions of fayalite based slags. It was reported that the main constituents of copper slags are FeO and SiO_2 and they further concluded that entrapment of metal droplets takes place to a considerable extent.

Jackman and Hayward (1933) studied the forms of copper found in reverberatory furnace slags obtained from five different smelters. Two methods were used;

- Specimens were polished and magnified under microscope varying from 2000 to 50 microns.
- Slag samples were ground and treated by froth flotation. The concentrate was characterized by x-ray diffraction and SEM. The concentrate was compared with

patterns made from copper matte, bornite, chalcopyrite, chalcocite, cuprite and metallic copper.

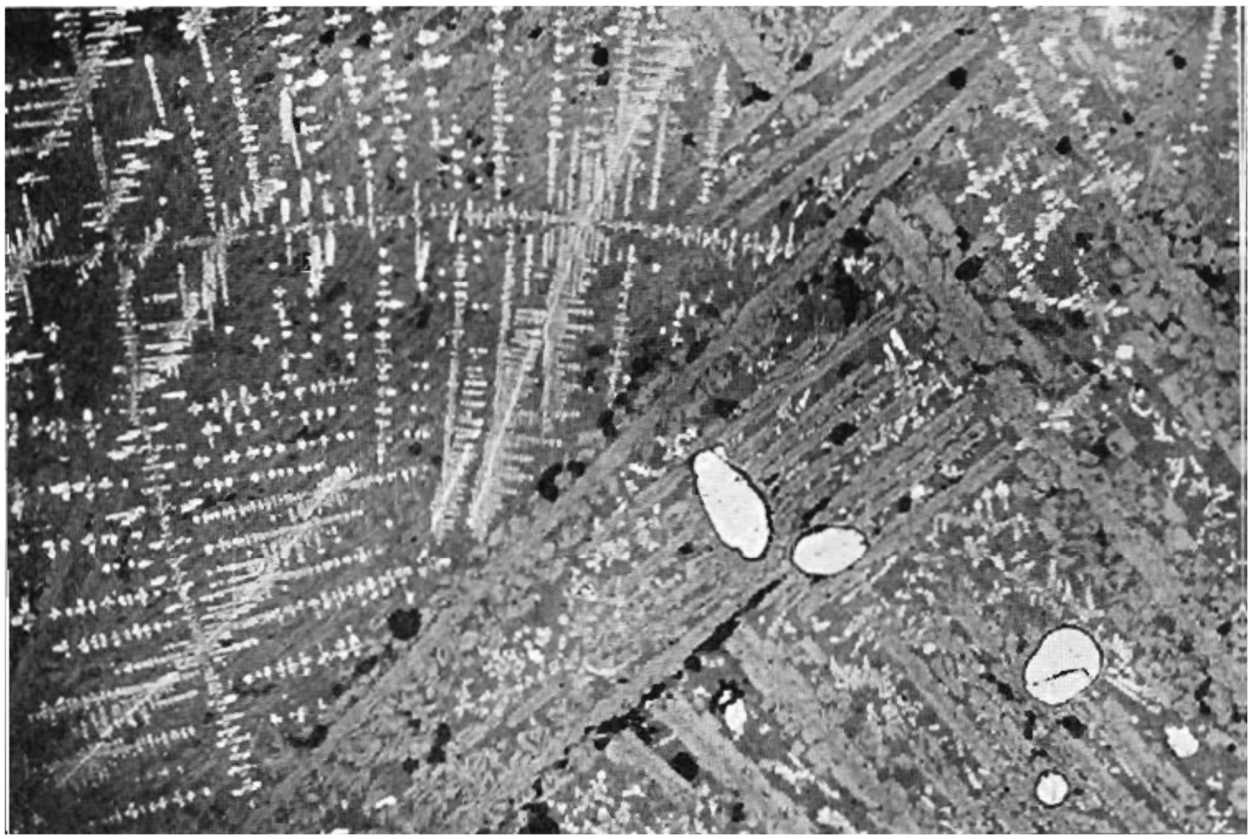


Figure 2.1 The SEM micrograph magnified to 20 microns, showing copper sulfide as white rounded areas, dendritic magnetite crystals, crystalline light gray siliceous portions and non-crystalline dark gray magnetite spots (Jackman and Hayward, 1933).

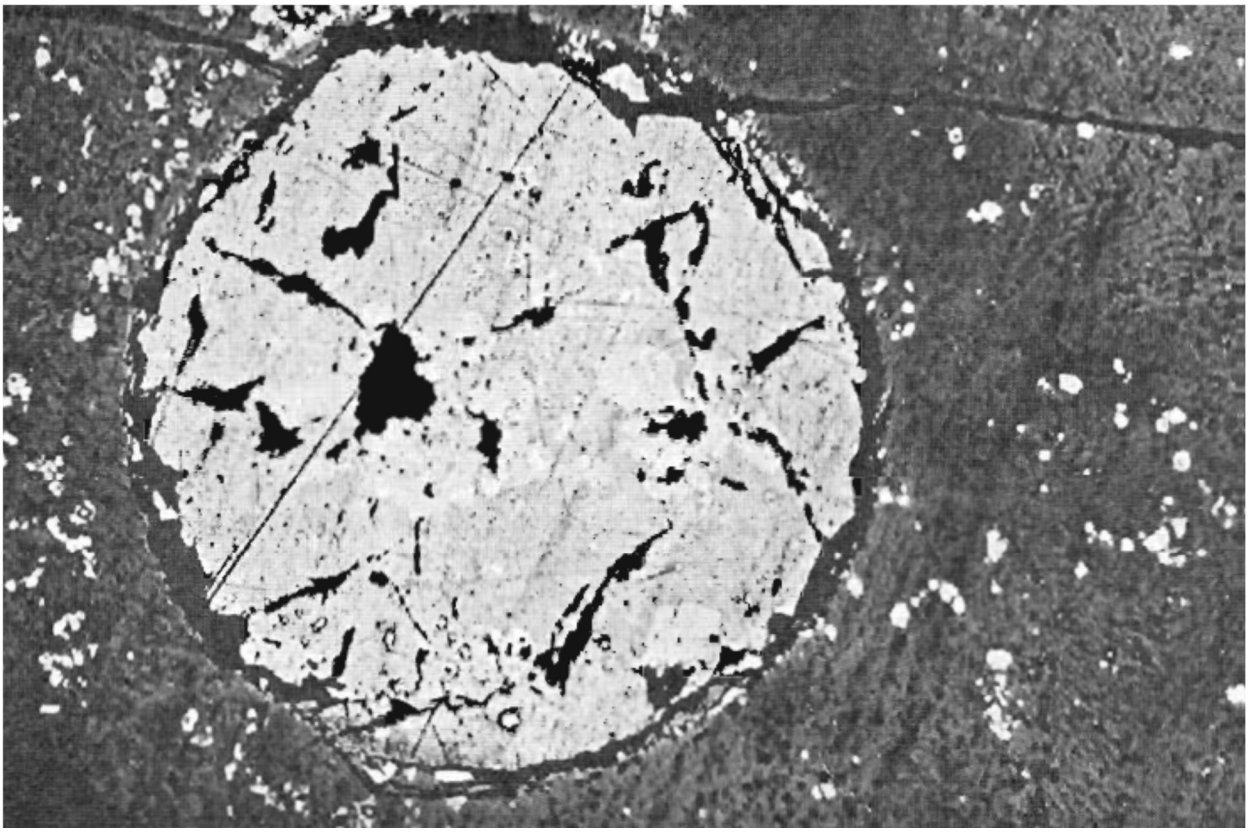


Figure 2.2 SEM image of the concentrate obtained after treating the slag by flotation. A large inclusion of bornite can be seen embedded in a magnetite crystal, (Jackman and Hayward, 1933).

Figure 2.1 shows the presence of copper sulphide in the reverberatory furnace slag. It also reveals the presence of magnetite and siliceous gangue. This is typically the mineralogical composition expected in slags that are derived from smelting copper sulphide ores. The siliceous gangue emanates from silica flux blended into the furnace charge. Silica flux aids the separation of iron from chalcopyrite and bornite (Davenport *et al.*, 2002). This explains the presence of magnetite in this particular slag. The flotation of the reverberatory furnace slag, whose mineralogy is depicted in Figure 2.1, yielded material which closely resembles copper flotation concentrate.

A large bornite particle can be seen in the SEM image in Figure 2.2. Jackman and Hayward (1993) revealed that reverberatory furnace slag from copper smelters, closely resemble copper sulphide ore.

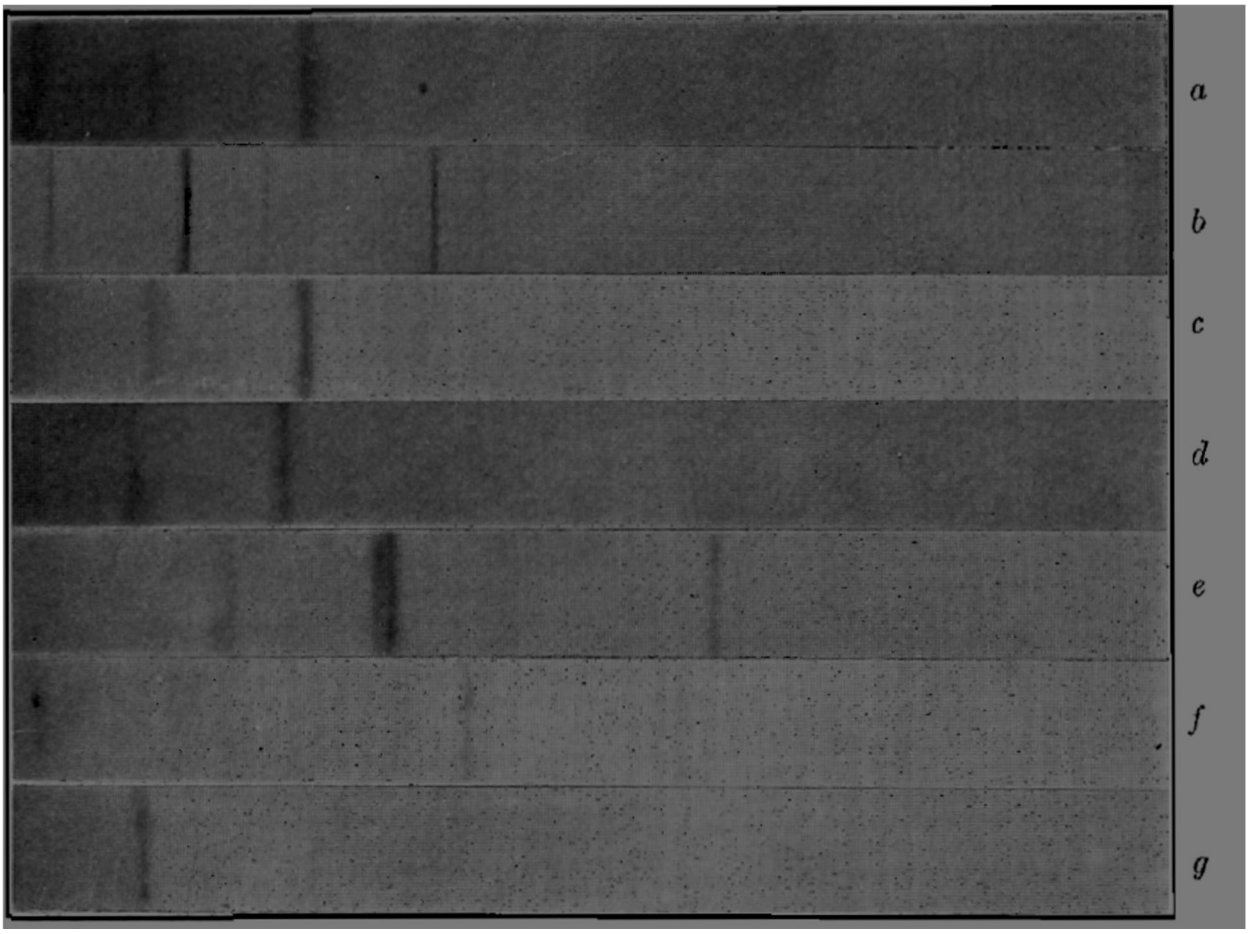


Figure 2.3 Diffraction patterns of slag concentrate and constituent minerals. (a) Slag concentrate. (b) Metallic copper. (c) Bornite. (d) Chalcocite. (e) Chalcopyrite. (f) Copper reverberatory matte. (g) Cuprite (Jackman and Hayward, 1933).

Figure 2.3 illustrates that the x-ray diffraction lines for bornite correspond closely to certain lines present in the slag concentrate pattern. The chalcocite pattern is very similar to the bornite pattern, the only difference being that the lines do not exactly correspond.

This is due to the fact that bornite is a copper sulfide containing some iron in solid solution, while chalcocite is pure copper sulfide. The presence of the iron changes the position of the lines with respect to the origin, but otherwise does not affect the pattern. This observation indicates that the copper in the slag concentrate is in a form similar to bornite, which is a copper sulfide containing varying amounts of iron or iron sulfide in solid solution. Several lines for the copper reverberatory matte appear to correspond to some of those in the slag concentrate pattern, and it is assumed that some substance similar to matte is also present in the slag concentrate. Since no similarity can be detected between the pattern for the slag concentrate and those for chalcopyrite, cuprite and metallic copper, these substances are considered as being absent in the concentrate and hence in reverberatory furnace slag.

2.3. Grinding in flotation processes

Milling in mineral processing serves the purpose of reducing ore particle sizes to a suitable size that would enable optimum recovery during mineral beneficiation stages. Coarse feed enters the mill and undergoes breakage actions, exiting the mill with a finer size distribution. The energy input is converted into mechanical breakage to form the broken finer size particles (Simba, 2010).

Austin *et al.* (1984) developed the population balance model for grinding mills. The model postulates that grinding is assumed to be guided by two functions, namely the selection function, giving the probability of breakage of particles and the breakage distribution function,
giving the distribution of feed following a breakage event. Batch grinding according to the model is defined by first order breakage as;

$$\ln \frac{P_{i(t)}}{P_{i(0)}} = -S_1 t \qquad (2.1)$$

Where $P_{i(t)}$ is the mass fraction of the mill discharge at time, t in the first class. A plot of $\ln\left(\frac{P_{i(t)}}{P_{i(0)}}\right)$ against time determines S_1 which is defined as the first order rate constant for grinding.

In order to obtain S_i for any arbitrary class, the following equation is used:

$$S_i = a(l_i / l_0)^{\alpha}\left[\frac{1}{1+(\frac{l_i}{\mu})^{\Lambda}}\right] \qquad (2.2)$$

Where α and Ŭare given as constants for the ore. l_i is the size class, while l_0 is a reference class (usually 1mm). μ is the particle size at which the denominator is 0.5 and α is an index of how rapidly the rate of breakage falls away. The breakage distribution function is mathematically defined as:

$$B_{ij} = \frac{\text{[illegible]}}{\text{[illegible]}}$$

The cumulative breakage distribution function B_{ij} is modeled by the equation:

$$B_{ij}(\ell_i, \ell_j) = \phi\left(\frac{\ell_i}{\ell_{j+1}}\right)^{\gamma} + (1-\phi_j)\left(\frac{\ell_i}{\ell_{j+1}}\right)^{\beta} \qquad (2.3)$$

Where ϕ characterizes the size distribution of fines produced from breakage of top size material, γ characterizes the size distribution of coarse progeny and β indicates the fraction of fines produced. Equation 2.3 is used to calculate B_{ij} as follows:

$$\text{[illegible]} - B_{ij} = B_{ij} \qquad (2.4)$$

The Discrete Element Method (DEM) is used to determine the parameters in equations 2.3 and 2.4. Computer software is programed to perform the numerical method approach which applies Newtonôs and contact laws to calculate motion of interacting particles. For calculations of such, the input data is particle size distribution obtained from a laboratory milling experiments.

The mineral processing simulator, MODSIM which is widely used by many engineers to design, construct and optimize grinding mills using Austinôs mill model (King, 2001) can be applied to predict milling product once the model parameters are established.

King (2001) established that flotation rate of particles is largely dependent on three factors, namely particle size, the mineral composition of the particle, and the surface activity. If the feed to a flotation circuit is too coarse, low recoveries will be attained due to gangue being attached to poorly liberated minerals. If the feed is too fine, gangue particles float with ease by entrainment mechanisms, thereby reducing concentrate grade. Across industry a feed size of 75% less than 45 microns is typically adequate for effective flotation.

During literature review it was found that regrinding after flotation (MF2) is quite common in the flotation of PGM ores, particularly in the case of the UG2 ore, in the North West province of South Africa. Lonmin had two major problems in the beneficiation of PGMs from UG2 ores, firstly, the PGMs are locked up in the silicate phases and further grinding was required, secondly, one stage fine grinding increased the amount of fine chromite recirculating in the milling circuit. The means to remove the fast floating PGM fraction and the chromite was needed before the locked PGMs can be liberated and floated.

This called for the installation of an MF2 milling circuit, (SGS Mineral services, 2002). The upgrade of the Lonmin plant can be seen in the Figure 2.4 and 2.5 below.

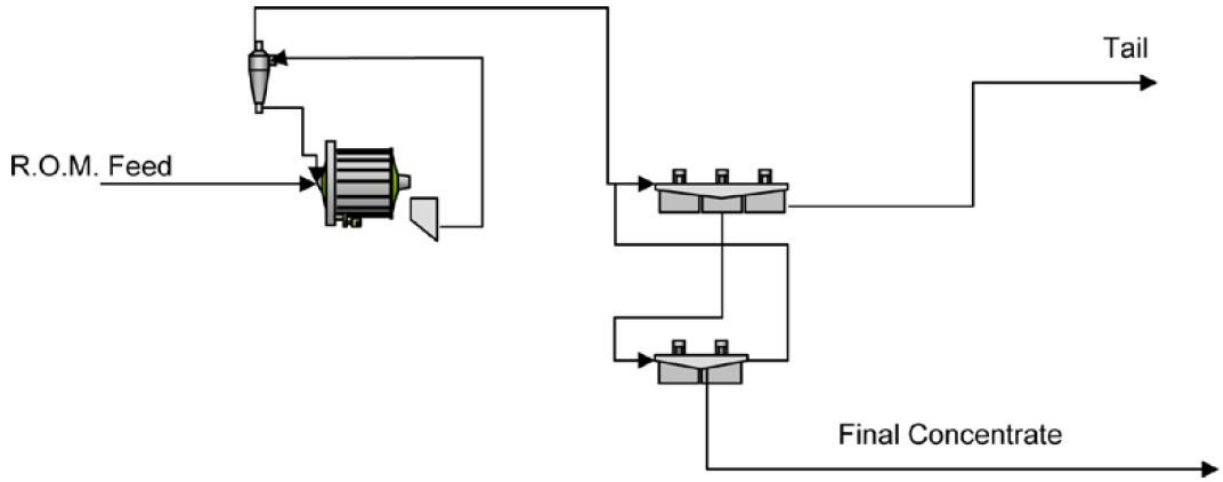


Figure 2.4 UG2 beneficiation circuit setup 1991-1994, (SGS Mineral services, 2002).

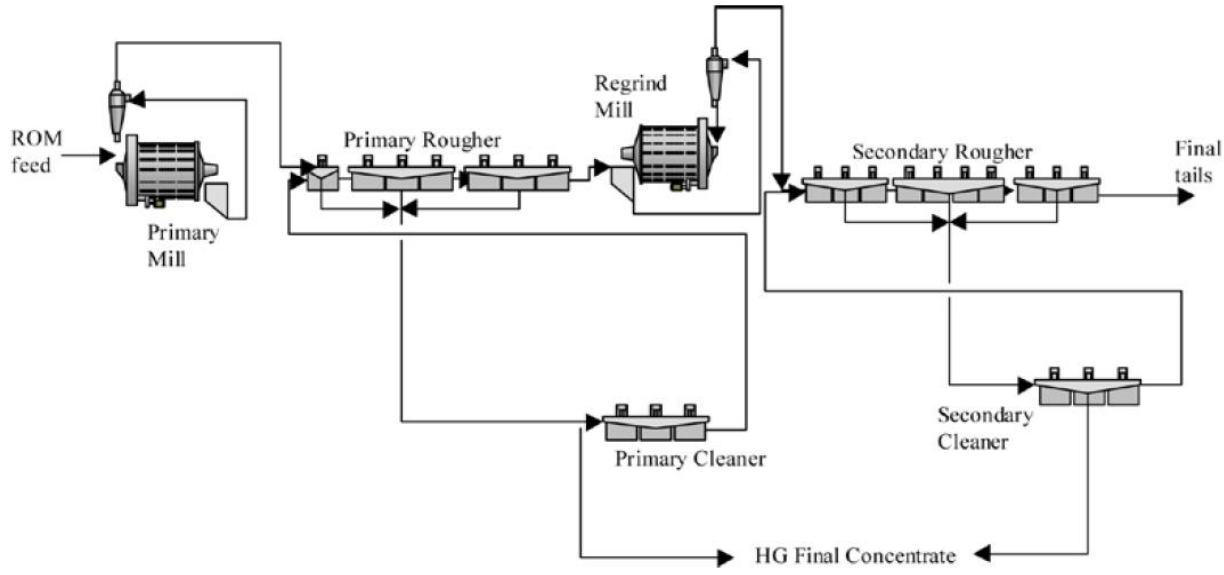


Figure 2.5 UG2 beneficiation circuit 1994-2001, (SGS Mineral services, 2002).

In 2010, Anglo American commissioned Unki platinum mines in Zimbabwe, opting for a similar setup as that of Lonmin UG2 mines i.e. the installation of an MF2 milling circuit (Nyakudarika *et al.*, 2012). Granulated copper slags are formed by rapid cooling, thus it possible that the copper minerals are locked in gangue phases. The MF2 set up could be ideal for copper recovery from granulated slags.

2.4. Copper flotation

2.4.1. Principles

Flotation is a physical and chemical separation process that utilizes the difference in surface properties of the valuable minerals and the unwanted gangue minerals. The process was originally patented in 1906, subsequently allowing for the mining of low-grade and complex ores which used to be ruled out as uneconomic (Wills, 2006). Recovery of materials during flotation can be explained by the following three mechanisms:

a) Selective attachment to air bubbles (ñtrue flotationò).
b) Entrainment in water passing through froth.
c) Physical entrapment between particles in the froth attached to air bubbles (ñaggregationò).

The majority of the recovery takes place via true flotation, as it is a highly chemically selective process. The separation efficiency between gangue and valuable mineral is also dependent on the degree of entrainment and physical entrapment. The two are not chemically selective processes, hence gangue and valuable minerals are both recovered by entrainment and entrapment.

True flotation uses the differences in physical and chemical surface properties of particles of various minerals. After treatment with reagents, such differences in surface properties between the minerals within the flotation pulp become apparent and for flotation to take place, an air bubble must be able to attach itself to a particle and lift it to the water surface. The agitator provides turbulence in the pulp phase to promote collision of particles and bubbles, resulting in attachment of valuable particles to bubbles and their transport into the froth phase for recovery. It is important that the particles should be fine enough not to be dropped off by the bubbles. The particle should also be hydrophobic, if they are to attach to air bubbles. Once the bubbles reach the surface, they should be able to form a stable froth, otherwise they will burst and drop the mineral particles into the pulp. Most minerals are not hydrophobic by nature and flotation reagents must be added to the pulp. The most important reagents are;

- Collectors: organic chemicals which renders the surface hydrophobic and hence the mineral is capable of being collected in the process.
- Frothers: organic chemicals which reduce the surface tension of the water, in order to stabilize the bubbles into a froth layer at the top of the flotation, cell to make concentrate removal easier.
- Modifiers: organic or inorganic chemicals used to modify the slurry conditions to enhance the difference in surface chemistry between the valuable and gangue minerals. They also regulate the pH of the system.

2.4.2. Flotation Mechanisms

King (1976) developed a model for the design and control of flotation plants. For design purposes it predicts plant performance from laboratory and pilot scale data. For an already existing plant it can be used to determine optimum operating conditions. The model assesses the effects of reagent addition rate, aeration rate and pulp level on plant performance.

The model provides for a distribution in the values for flotation rate constants, particle size and mineral fraction, and due to its complexity the method requires computer programming software such as Matlab or preprogramed software such as MODSIM.

King (1976) assumed that the flotation cell consists of a perfectly mixed pulp phase through which the bubbles rise. Particles that are floated are transported at the bubble-pulp interface into the layer of froth that is removed from the top of the cell. Properties of particle that influence flotation rate significantly are particle size, D, the mineral composition of the particle, g, and the surface activity, *k*. The assignment of numerical values to *k* is difficult, and it should properly be regarded as an empirical rate constant that carries quantitative information about the rates of many sub-processes contributing to the overall rate of flotation. To accommodate the distribution of particle values in a mathematical structure King (1976) developed a function of the form $F\hat{o}(k,g,D)$ which is defined as the fraction of particles in the system that are smaller than or equal to *D* in size and have a mineral-composition less than or equal to *k.* The particle population is necessarily finite, and consequently, $F\hat{o}(k,g,D)$ is not a continuous function. However, for even moderately small populations, the size of discontinuities will be small populations and some small continuous function $F(k,g,D)$ is substituted for $F\hat{o}(k,g,D)$ and approximates it very closely.

The derivative of the function becomes;

$$\frac{dR}{dt} = \frac{R^{\infty}}{t_{1/2}} f(E, A, W) \quad (2.5)$$

Another hypothesis added is that the flotation rate is also proportional to the amount of free bubble surface area. This hypothesis covers the heavy loading experienced by bubbles at high production rates and also for the effect of aeration rate in the cell. The rate is accordingly written as;

$$R, E, A = \text{Øø ø øøø øøø } f(E, A, W) \text{ in kg/s} \quad (2.6)$$

In this expression, *k* is a rate constant and should allow for all small-scale effects that influence the rate of flotation. Function ∧ (D) accounts for all the influences of particle size, A is the total bubble surface area per unit of pulp volume, S is the fraction of the surface area of a single bubble that is not covered by adhering solids, and W is the mass of solids in the cell. Colborn (1969) has analyzed the microscopic factors influencing the collision, adhesion and levitation processes that are important and derived a function of the form;

$$\text{Ø}(D) = \frac{\text{øøøøø}}{D} (1 - (D/\Delta))^{2.5} D^{\left(\frac{\epsilon}{D}\right)} \quad (2.7)$$

The parameter ∈ is a function that depends on the hydrodynamic conditions in the cell and φp is the largest particle that can be attached to a bubble. Tomlinson *et al*. (1965) found that at large D, ∧ (D) has a single maximum before decaying to zero. Thus;

$$\text{Ø}(D) = \frac{2.\text{øøø}^{2/3}}{D} D^{2\epsilon/3} \quad (2.8)$$

The value of D that maximizes ʌ (D) is related to ⌊ by;

$$D_{max} = 2 \in^{2/3} \quad (2.9)$$

It is noted that D_{max} is the particle size of the feed at which flotation rate is maximum. To illustrate the type of result that can be obtained from the model, King (1976) tested a set of hypothetical data in a typical four-stage scavenger-rougher-cleaner-recleaner set up. The numerical results were presented as a series of grade recovery curves that were generated by varying individually the fineness of grind, the volume of the scavenger, the volume of the cleaner and the feed rate to the plant.

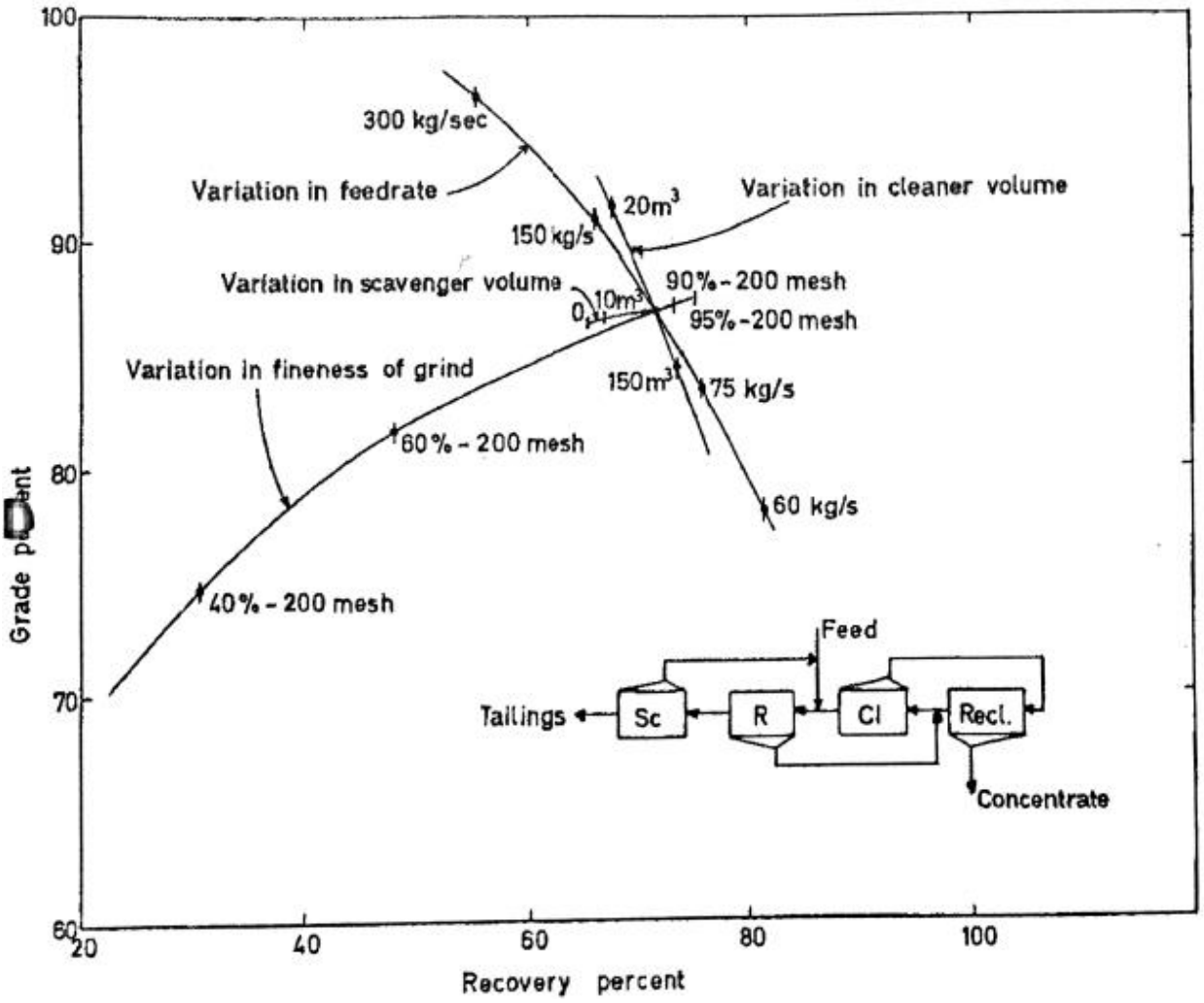


Figure 2.6 Grade recovery curves showing variation with design variables (King, 1976).

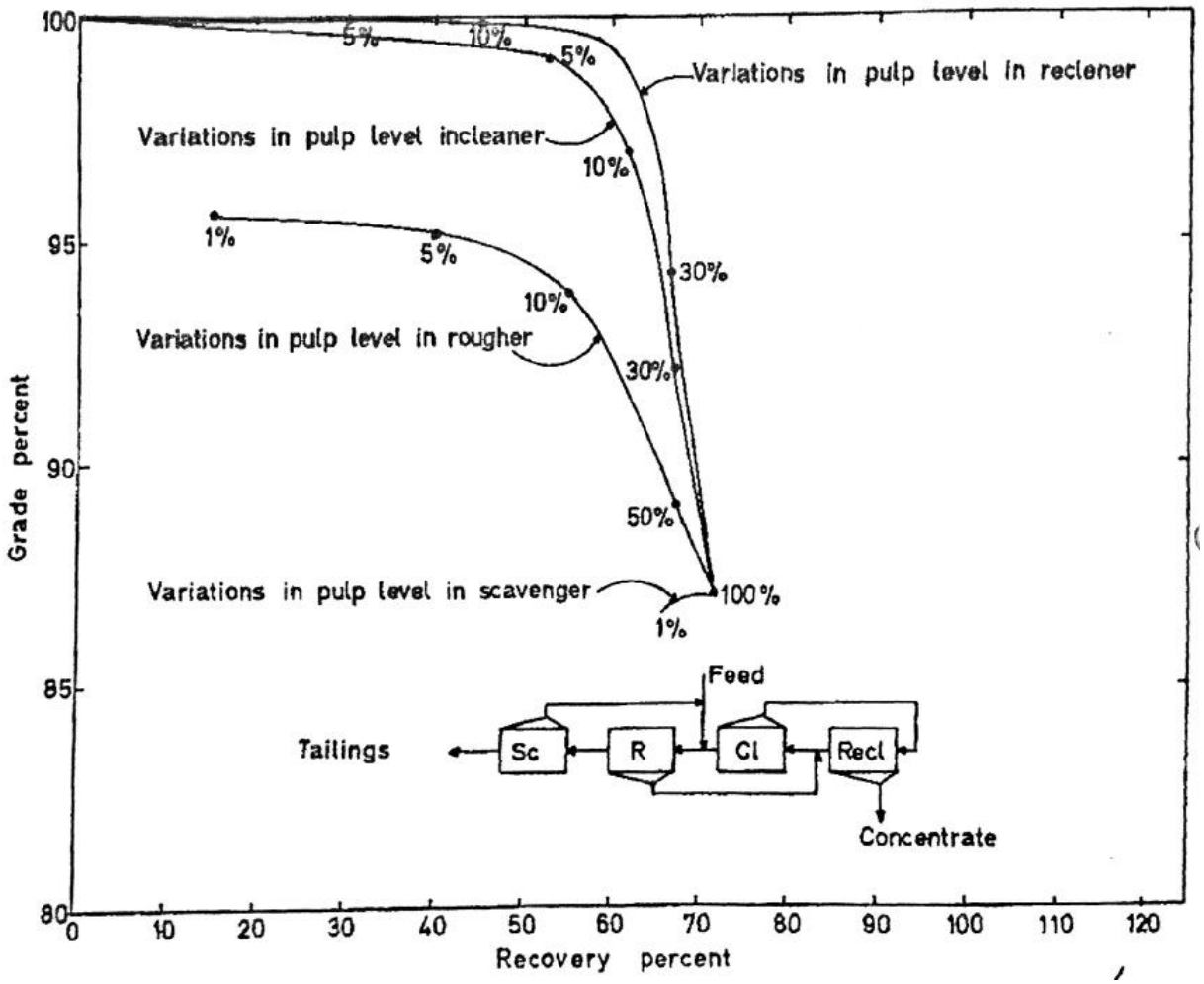


Figure 2.7 Grade-recovery curves showing variation with control variables (King, 1976).

The grade recovery curves in Figure 2.6 and 2.7 illustrate how plant control and design can be done using the model. King (1976) developed an efficient computational scheme which permits the calculation of plant performance over a wide range of possible design and control variables.

2.4.3. Copper flotation - Practice

According to Wills, (2006) copper sulfide minerals have good flotation response to anionic collectors such as amyl, iso-propyl and butyl xanthates, concentrations of collectors added usually vary between 3 to 300 g per tonne. Rougher concentrates and middlings are usually reground and floated for maximum recovery.

Arakatsu *et al*. (1977) patented a method for the flotation of copper ores and copper smelter slags. Reagents used were collectors, containing xanthates, dithiophosphates, thiocarbamate esters, dithiocarbamates, mercapatans and dixanthogens. A challenge faced, was the presence of elemental copper and oxidized copper in slags. Sulphidizing agents such as sodium sulphides, sodium hydrosulphide and phosphorus pentasulphide were added to convert these copper minerals to sulfides. According to Zhang *et al.* (1991), the addition of sulphidizers must be carefully administered as over dosage results in a phenomenon called over sulphidization. This often leads to the depression of copper sulphide minerals and even the sulphidized oxides. Shergold (2006) suggested that oxygen is required in the pulp for the adsorption of sulphydryl collectors on sulphide surfaces. Excess sodium sulphide removes oxygen as follows, thus reducing flotation efficiency;

$Na_2S + 2O_2$ Ÿ Na_2SO_4

Zhang *et al.* (1991) further suggested that the detrimental effect of residual hydrosulphide can be eliminated by the addition of ammonium sulphate with hydrosulphide.

They found that the consumption of the relatively expensive hydrosulphide was reduced and its activating effect also increased. Zhou and Chandler (2006) further suggested the supremacy of sodium tetrasulphide over sodium sulphide as a sulphidizing agent. Fuerstenau *et al.* (1984) suggested a mechanism for the flotation of copper ores with mercaptan collectors. It was suggested that molecular mercaptans react on copper sites, this results in the formation of copper mercaptide at the surface and splitting off of a molecule of water. The mercaptide is relatively insoluble and hydrophobic.

Bruckard *et al*. (2004) conducted a series of laboratory batch flotation tests on a suite of calcium-ferrite-based slags made in laboratory smelting trials. The objective of the flotation work was to maximize copper recovery and iron rejection from slags made in the smelting processes. The slags treated included a reduced low copper slag, an oxidized high copper slag composite, and a much reduced low copper self-pulverizing slag. The copper content of the slags varied from 2.9% to 14% Cu. The copper was present as metallic copper, oxide copper and copper-calcium ferrite phases with the phase mix related to smelting conditions. The slags were crushed, ground, wet-screened at 210 µm to remove coarse metallic particles of copper, and floated at natural pH (about pH 11) using sodium isobutyl xanthate (SIBX) as a collector and methyl isobutyl carbinol (MIBC) as a frother. In rougher/scavenger tests on the reduced low copper and self-pulverizing slags, copper recoveries above 92% were obtained with copper enrichment ratios varying between 2.3 and 2.9. For the oxidized high copper slag, copper recoveries were poor as only 47% of the copper was recovered with an enrichment ratio of 3.3. The presence of the slow floating copper-ferrite phases in the slags limited further copper recovery.

Bruckard *et al*. (2004) found that ageing of copper slag (a significant delay between grinding and flotation), results in a deterioration of the copper flotation response.

In 1965, Fuerstenau, *et al.* undertook a test to study the flotation response of chrysocolla (20.8% Cu) to selected copper chelating compounds. Ethylenediamine, hexamethylenetetramine, potassium octyl hydroxamate, dimethylglycoxime and alpha benzoin oxide were the compounds used. Good recoveries were obtained considering that the ore is very difficult to float with conventional techniques. The greatest result obtained was with octyl hydroxamate at pH 6.5 and 55 °C, as illustrated in Table 2.1. Concentrate and tailings grades of 31.6 and 0.38 % Cu were achieved, respectively.

Table 2.1 Experimental results obtained with 181 mg/L octyl hydroxamate at pH 6.5 and 55°C Celsius (Fuerstenau *et al.*, 1965).

Product	Weight (g)	%Cu	Mass Cu (g)	Recovery (%)
Concentrate	12.4	31.6	3.92	76
Tailing	337	0.38	1.28	

Lee *et al.* (2008) investigated the use of n-octyl hydroxamate (AM28 made by Ausmelt Limited) on pure sulphide ore, oxide ore and a blend of 70% sulphide ore and 30% oxide ore. Direct collection with AM28 was tested against sulphidizing with sodium hydrosulphide followed by collecting with potassium amyl xanthate. MIBC was used as a frothing agent. The feed analysis is shown in Table 2.2.

Table 2.2 Feed assay for sulphide, oxide and blend ores (Lee *et al.*, 2008).

Ore type	Total Cu (%)	Oxide Cu (%)
Sulphide	3.7	0.2
Oxide	3.5	3.5
Blend	3.6	1.4

Mineralogical analysis on the ores revealed that the sulphide ore consisted of bornite and chalcopyrite containing magnetite inclusions. The oxide ore consisted of malachite and azurite, dominated by composite particles of quartz and feldspar. It also contained a small amount of biotite. Magnetite and quartz are minerals expected to be present in smelter slags. Laboratory batch flotation tests were done on the sulphide composite with PAX as a collector and on the oxide composite using AM28 as collector. A third test was done on the ore blend using both AM28 and PAX collectors. Results are shown in Figure 2.8.

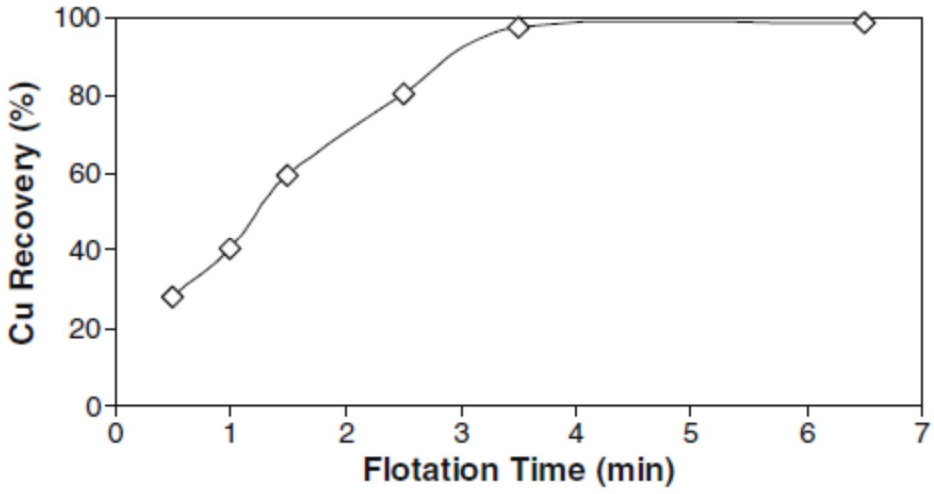


Figure 2.8 Flotation response for copper sulphide composite using PAX as the copper collector. Total PAX and MIBC doses were 14 g/t and 48 g/t, respectively (Lee *et al.*, 2008).

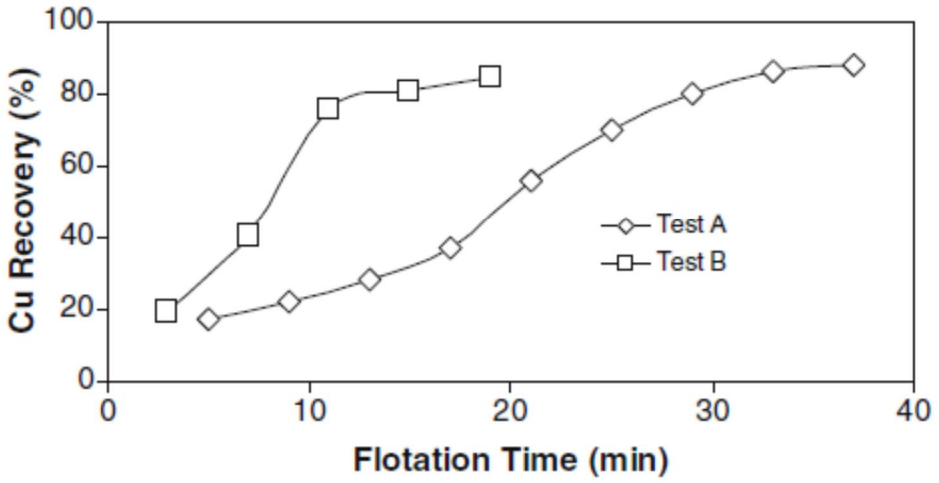


Figure 2.9 Flotation response for copper oxide composite using AM28 as the copper collector.

Figure 2.9 illustrates the results obtained by using AM28 and MIBC as a frother. Total AM28 and MIBC doses for both Tests A and B were 1200 g/t and 50 g/t, respectively. Test A was performed at an initial hydroxamate collector dose of 400 g/t followed by successive 100 g/t additions, with a total flotation time of 37 min (Lee *et al.*, 2008).

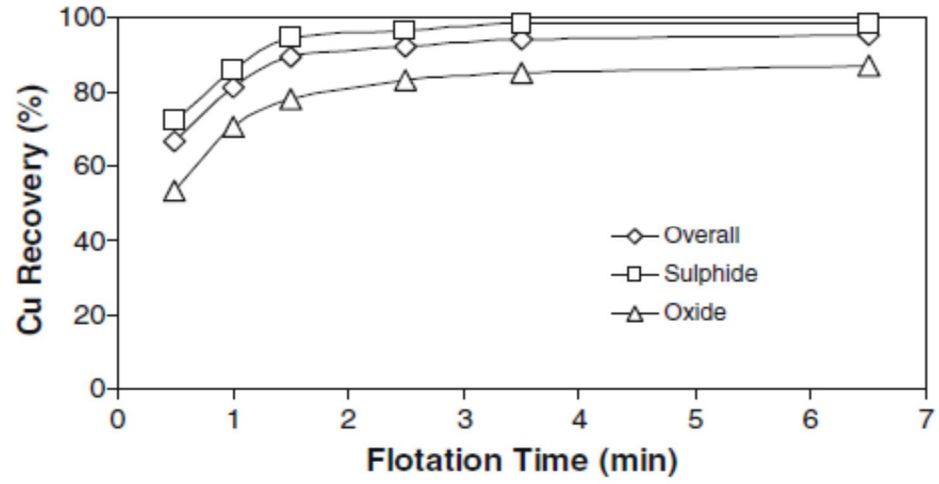


Figure 2.10 Flotation responses on the blend composite using PAX and AM28 as the copper collector.

The results in Figure 2.10 were obtained after AM28 was added in the beginning of the flotation test. Total PAX, AM28 and MIBC doses were 14 g/t, 420 g/t and 48 g/t, respectively (Lee *et al.*, 2008). The assays for this test are displayed in Table 2.3.

Table 2.3 Assays after flotation of the ore blend with AM28 and PAX.

Product	Total Cu (%)	Oxide Cu (%)
Feed	3.6	1.4
Concentrate	19.3	N/A
Tails	0.19	0.16

After cleaning the concentrate grade was 35.1% Cu (Lee *et al.*, 2008). A control test was then done with sulphidizer and PAX in order to compare the newly proposed flotation procedure to the conventional one.

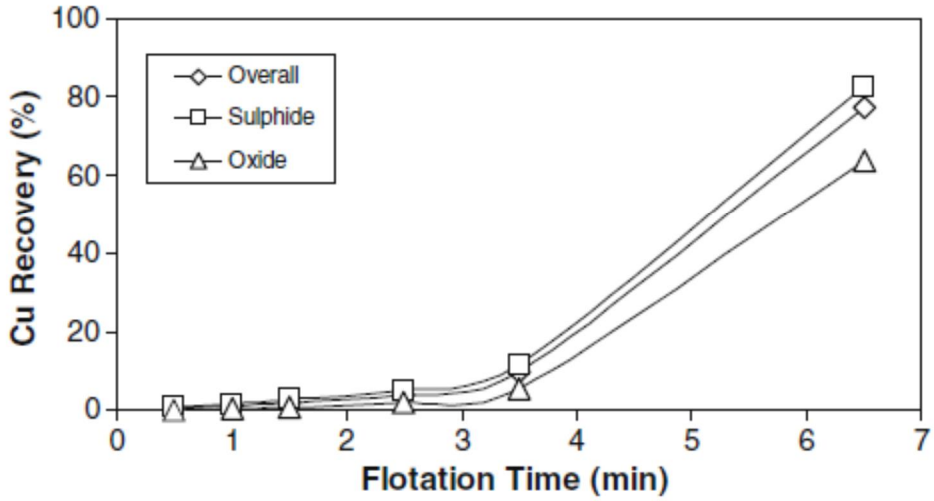


Figure 2.11 Flotation responses on the blend composite using CPS. Total NaHS, PAX and MIBC doses were 1575 g/t, 80 g/t and 48 g/t, respectively (Lee *et al.*, 2008).

It is seen from the results in Figure 2.10 that, a major advantage of using AM28 is that it does not interfere with the collection of sulphides. From Figure 2.11 it is seen that copper sulphide flotation was depressed due to the presence NaHS. This implies that the oxide and sulphide flotation banks in the conventional flotation set up can function as oxide and sulphide flotation banks, thereby allowing more retention time. From Figure 2.11 it is seen that copper sulphide flotation was depressed due to the presence NaHS. This is a major drawback with conventional

Mount Isa Mines produces concentrate from chalcopyrite ore by froth flotation (Davenport *et al*., 2002). The concentrate is smelted in a rotary holding furnace to produce matte, which is subsequently converted to blister copper in copper converters. Rotary holding furnace slag and copper converter slag is transferred to the same concentrator that treats chalcopyrite ore. In both campaigns methyl isobutyl carbinol (MIBC) and sodium isobutyl xanthate (SIBX) make up the reagent suite.

The slags and chalcopyrite ore were treated in separate campaigns as an inclusion of 2% slag by weight caused collapse in froth layer and decreased recovery. This is due to the high reagent consumption associated with slag flotation (Carr *et al.*, 2003). In order to treat the slags and ore together, a Jameson cell was introduced to clean slag rougher concentrate before the two streams are joined. This reduced reagent consumption and allowed for parallel treatment of slag and chalcopyrite ore. The major advantage of the Jameson cell is its ability to produce clean concentrates in one stage of operation (Wills, 2006).

2.5 Summary

The reserves of high grade ores are diminishing worldwide and therefore there is a need for exploration of other sources of high valuables minerals. There is a range of wastes from a variety of industrial processes that contain metals that could potentially be recovered and these include; slag dumps, low grade ore dumps, fines dumps and fly ash etc. (Jadhav *et al*., 2002). These waste dumps and slags possess risks which can include water pollution, contamination of land due to some heavy and hazardous metals in the waste and use of productive land. These wastes can however, be processed to recover valuable minerals present (Jadhav *et al*., 2002). Recovery of minerals from waste has become important as waste is considered a secondary resource with the added advantage of also conserving natural resources (Raghupathy *et al*., 2013). The recovery of value minerals from waste can be done if the method of recovery is cost effective. To recover these valuable metals, mineral processing techniques like milling, gravity separation and floatation have been applied. Slags which are produced from smelting of non-ferrous metal ores like copper ores are formed by the fluxing agents used to aid high temperature liquid-liquid separation.

The gangue portion of the ore is absorbed by the slag phase and the valuable portion is tapped off. According to Zander *et al.* (2011), fayalitic slag still contains up to 1 % of copper and other valuable metals like nickel, cobalt or molybdenum, these metals can be recovered profitably if cost and environmentally friendly methods of processing the slag material are used.

3. Experimental Methods

Test work was done with the aim of recovering the non-floating and slow floating copper, in which ever form it is represented. This necessitated an in depth mineralogy study of the copper slag as well as flotation response to a variety of reagents. Flotation test work was done in the Namibia Custom Smeltersô research and development laboratory, in Tsumeb. Mineralogical analysis was performed by SGS South Africa.

3.1. Flotation test work

The different slags (reverberatory furnace slag, TSL slag and converter slag) were milled in a laboratory scale ball mill (400 mm X 300 mm) with dual rotary shafts. Each slag type was milled for a duration of 2 hours and after every 30 minutes of milling, particle size distribution of the mill discharge was determined using a nest of test sieves mounted on a vibratory sieve shaker. The size distribution was plotted and optimum milling time was determined.

3.1.1. Milling Equipment

The following is the list of equipment that was used during the milling test work of the slag samples. Laboratory scale ball mill (400 mm X 300 mm) and dual rotary shafts for milling, Laarmann laboratory slurry press (size 13) for slurry filtration, 1L measuring cylinder for measuring and adding water, drying oven for slurry drying, steel grinding balls for milling, process water for milling and flotation, analytical balance for sample weighing, test sieves (2800 µm, 1400 µm, 600µm, 300µm, 250µm, 150µm, 125µm, 106µm, 75µm, 45µm) for size distribution determination, vibratory sieve shaker to aid screening, 20 L bucket to collect mill discharge, water bottles for washing the mill, filter paper for slurry filtration.

3.1.2. Milling experimental procedure

1 kg of slag sample was weighed and placed in the mill with 12 kg grinding steel balls. 600ml plant process water was added to the charge to achieve 62% solids by mass. Grinding time was set to 2 hours, to achieve 75% less than 45 microns. After milling, the mill discharge was removed and washed out into the bucket. Grinding media was removed from the bucket and the slurry was dewatered by filter press (Note: in order to develop milling curves, a milled slag samples were dried in the oven at 105°C and size distribution was determined. Samples used for flotation were not oven dried, in order to avoid changing the surface properties).

3.1.3. Flotation

A WEMCO FAGERGREN MINERAL MASTER (Model LA 500) Flotation machine was used. The milled slag was dewatered and placed into the flotation cell. Water was added to dilute the slurry up to approximately 30% solids by mass. Reagents specific to each test were added and a conditioning time of 3 minutes was allowed. Air was bubbled through the agitated slurry at a rate of 2-3 l/min and agitation was set at 1380 rpm. Concentrates were collected manually by scraping the froth using scraper blades. Each of the three slags was first floated separately in order to study their individual flotation responses. The second phase of the research involved regrinding and floating plant tailings, by that time the reverberatory furnace had been decommissioned and only TSL slag and converter slags were evaluated. For the second series of tests, only reagents which delivered favorable results in the first phase were used and these were FC 7245, FC 4146 and 10% Na_2S.

3.1.4. Reagents

Various reagents that are commonly used for copper flotation were selected. The reagents are tabulated in Table 3.1.

Table 3.1 Flotation reagents used.

Collectors	Frothers	Activators
Potassium amyl xanthate (PAX)	Flotanol CO7	Sodium hydrosulphide (NaHS)
Sodium alkyl dothiophosphate, mercaptobenzothiazole (FC 7245)		Sodium sulphide (Na_2S)
Isopropyl ethyl thionocarbamate (FC 4132)		Ammonium sulphate $(NH_4)_2SO_4$
Sodium diisobutyl dithiophosphate, sodium dibutyl dithiocarbamate, sodium hydrosulfide (FC 5473)		Ammonium sulphide $(NH_4)_2S$
Allyl amyl xanthate ester, sodium diisoamyl dithiophosphate, sodium mercaptobenzothiozole, methyl isobutyl carbinol (FC 7412)		
Modified thionocarbocarbamate, methyl isobutyl carbinol (FC 4146)		
Thionocarbamate (Hostaflot E 703)		
Mercaptobenzothiazole (Hostaflot M 91)		
Flotinor Fatty acids (FS-2)		
Flotinor Fatty acids (FS-100)		

Table 3.2 illustrates the range of flotation tests performed and the flotation reagents, dosage and conditioning time used. The main variables in the flotation tests were the type of secondary collector and the sulphidizing agents

Table 3.2 Flotation tests.

Test	Reagents			Time	
	PAX (300 g/t)	Flotanol CO 7	Secondary collector (200g/t)		
Test 1	10% PAX (3ml)	Frother (4 drops)	FC 7245 (0.179ml)	15 min	Secondary collector comparison
Test 2	10% PAX (3ml)	Frother (4 drops)	FC 4132 (0.2)	15 min	
Test 3	10% PAX (3ml)	Frother (4 drops)	FC 5473 (0.19)	8min PAX, 7 min FC 5473	
Test 4	10% PAX (3ml)		FC 4146 (0.18ml)	15 min	
Test 5	10% PAX (3ml)		FC 7412 (0.208ml)	15 min	
Test 6	10% PAX (3ml)	Frother (4 drops)	E 703 (0.2ml)	15 min	
Test 7	10% PAX (3ml)	Frother (4 drops)	M91 (0.2ml)	15 min	
Test 8	10% PAX (3ml)	Frother (4 drops)	FS-2 (0.2ml)	15 min	
Test 9	10% PAX (3ml)	Frother (4 drops)	FS-100 (0.2ml)	15 min	
Test 10	10% PAX (3ml)	Frother (4 drops)	(NH4)2S (0.2ml)	8 min PAX, 7 min $(NH_4)_2S$	Sulphidizing agent comparison
Test 11	10% PAX (3ml)	Frother (4 drops)	10% NaHS (5ml)	8 min PAX, 7 min NaHS	
Test 12	10% PAX (3ml)	Frother (4 drops)	10% Na2S (5ml)	8min PAX, 7 min FC Na_2S	
Test 12	10% PAX (3ml)	Frother (4 drops)	10% Na2S (5ml)	8min PAX, 7 min Na_2S	
Test 13	10% PAX (3ml)	Frother (4 drops)	10% NaHS, (NH4)2SO4	8 min PAX, 7 min NaHS; $(NH4)_2SO_4$	

3.2. Mineralogical Tests

Four slag samples (converter slag, TSL slag, reverb slag, final tailings) were submitted to an external laboratory, SGS (South Africa). Mineralogical analyses on the slags were performed, particularly for the copper and zinc phases. The samples were prepared into polished sections, sub-samples were milled for XRD analysis. Bulk mineralogy was determined by means of XRD analysis. SEM analyses were also conducted to identify and verify the minerals detected by XRD, as well as to establish how the minerals of interest occur.

4. Results and Discussions

4.1 Milling test work

The different slags were milled and chemical analysis was performed on each size class to determine the copper distribution across the spectrum of the size classes. Figure 4.1, 4.2 and 4.3 shows size by assay analysis for the converter slag, TSL slag and reverb slag respectively. It can be observed from the graphs that as the particle size decreases from largest size fraction of 250 ï 350 ε m to the finest size fraction of - 45 ε m the % content of copper generally increases. Particles less than 45 microns contain the most copper and therefore object of milling would be to maximize on this class size of -45 microns that shows the greatest liberation.

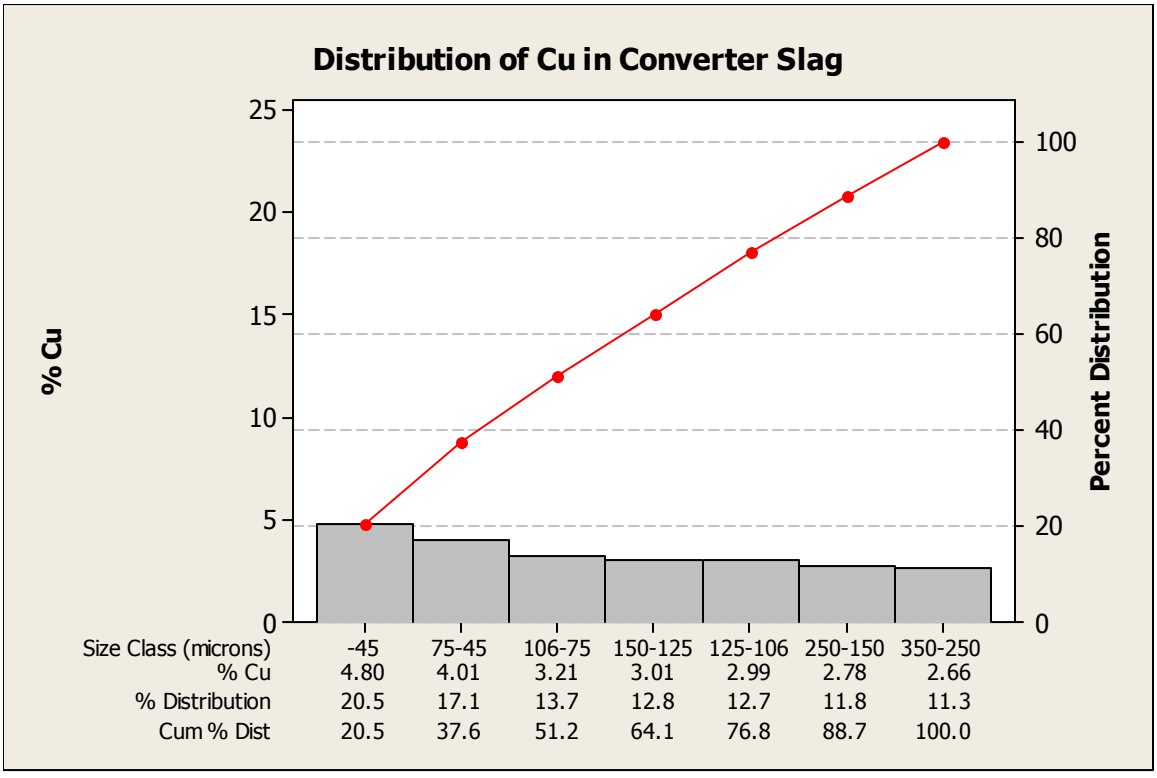


Figure 4.1

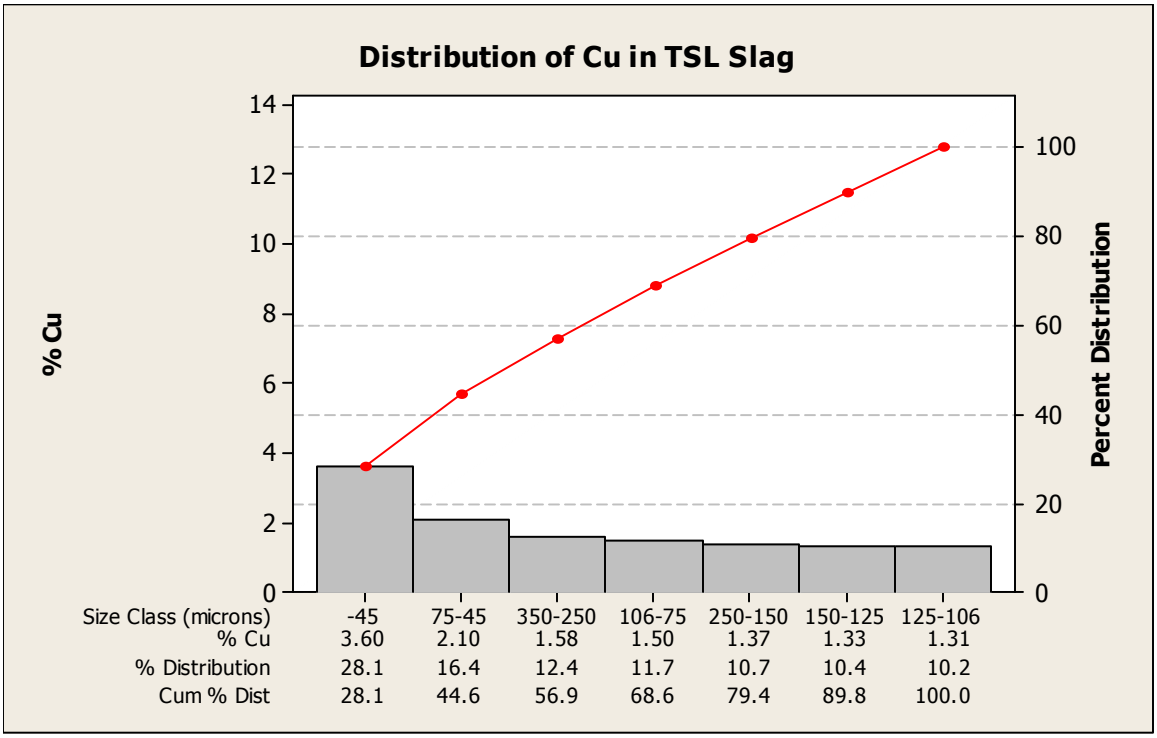


Figure 4.2

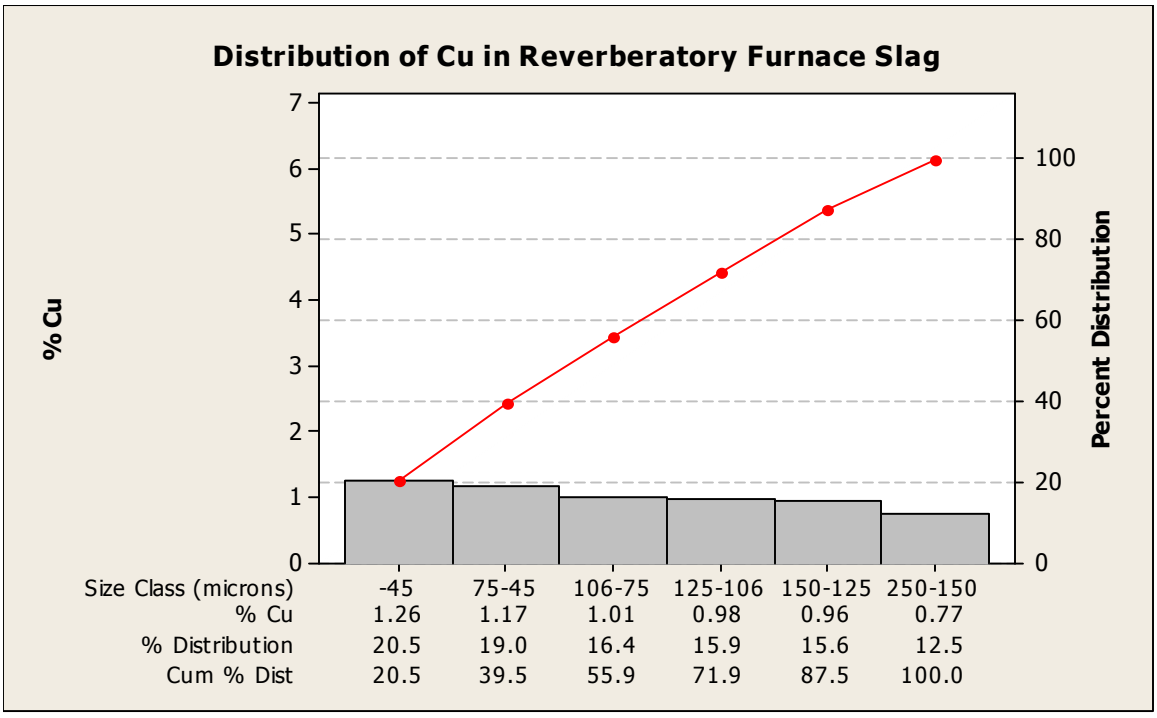


Figure 4.3

The results in Figure 4.1 to 4.3 also shows that the converter slag contains the largest amount of copper minerals compared to the other two slags with the reverberatory slag having the least amount of copper minerals. Figure 4.4 is the cumulative particle size distribution of the 3 slags as received into the milling plant from the crushing and screening circuit. It can be observed that reverberatory slag particles crush much more finer than the TSL slag and the converter slag with the TSL slag having the coarsest particles.

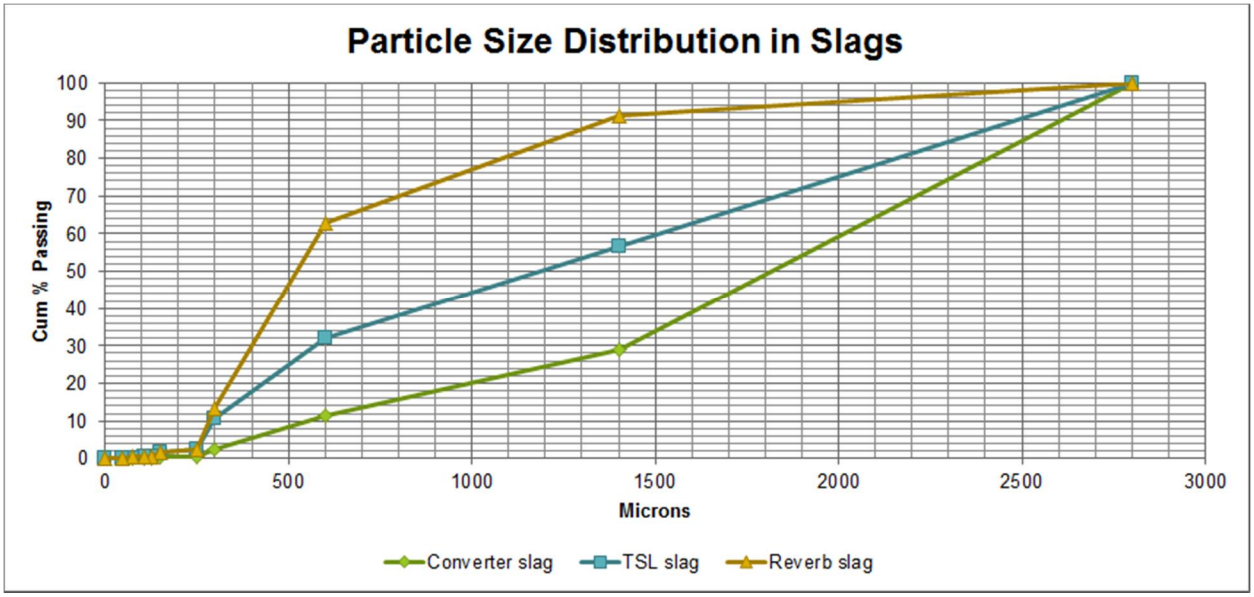


Figure 4.4

Figure 4.5 shows the milling response of the 3 slags with milling time under identical milling conditions. % passing 45ε m was measured as a function of milling time at hourly intervals up to 3 hours. The aim was to determine how long it would take to achieve the target of 75% passing 45ε m, which is the size distribution required for the flotation tests.

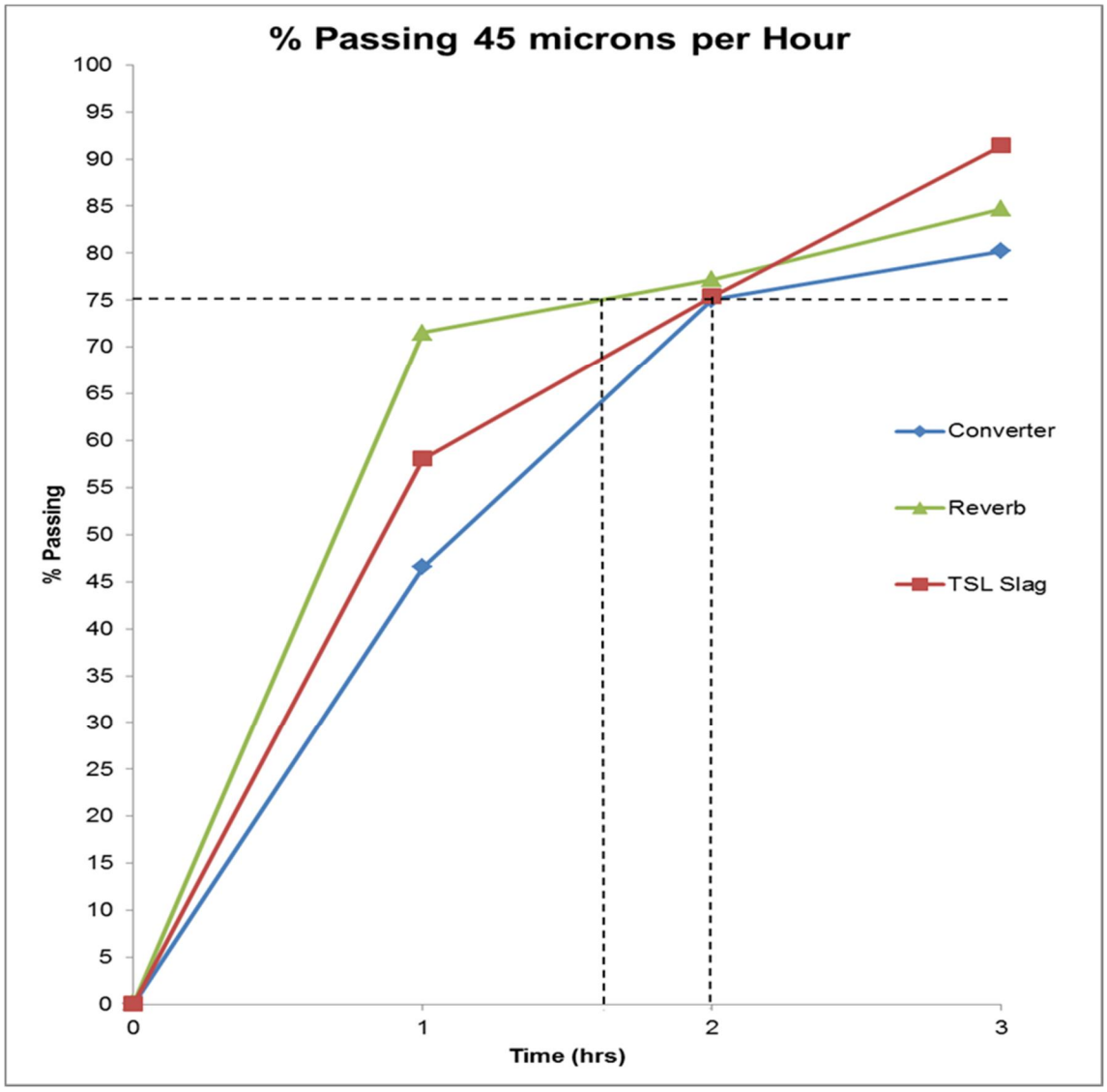


Figure 4.5

The results show that the TSL and converter slag require the same milling time (2 hours) to achieve particle size of 75% less than 45 microns. Reverb slag requires milling time of 1 hour and 40 minutes to achieve the same reduction in size. This is due to the relative ease of milling the reverb slag as also observed in Figure 4.4, showing the fineness of size distribution in reverb slag.

4.2. Flotation test work, Phase 1

Phase 1 involved the flotation of the original three slags and a composite mixture, of all the slags at a ratio of 1:1:1, after grinding to 75% passing 45 microns. The graphs below indicate the recoveries obtained from the flotation of the different slags. The raw data for the test work is in in the appendices.

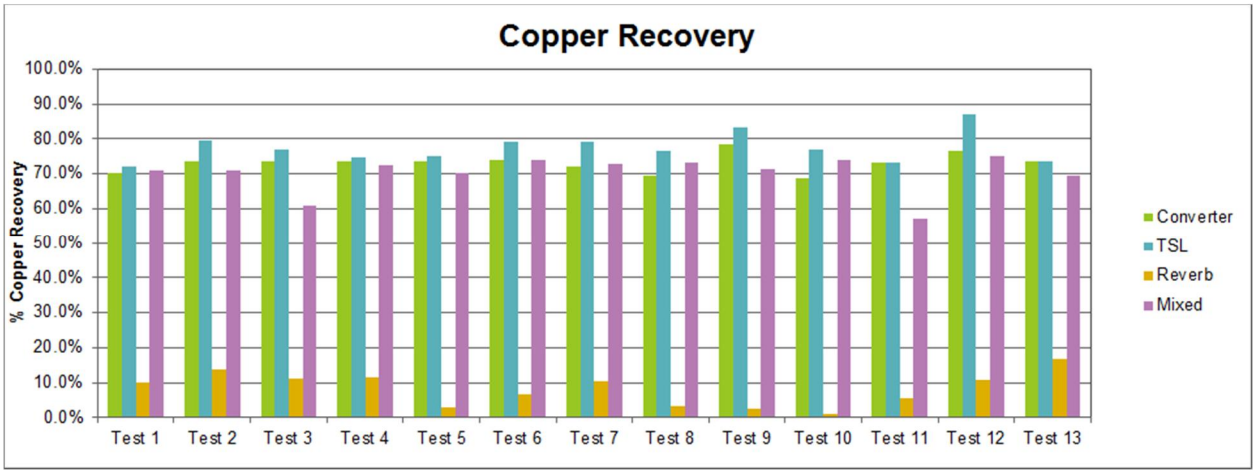


Figure 4.6

From Figure 4.6 it can be observed that reverb slag yielded the lowest recoveries, typically less than 15% for all the tests conducted. The poor recoveries from the reverb slag are due its low copper content, which is less than 1%. The recoveries from the converter slag and TSL slag are high, they were found to be consistently above 70% whilst the recoveries from the mixed slag sample was also high but lower than those of TSL and converter slags. Secondary collectors, FC 4146, FS 100 and sulphidizing agent, 10% Na_2S yielded the highest recoveries.

Milling the slags to 75% passing 45 microns shows that liberation of the locked copper minerals is generally achieved, this is proved by fairly good grades of copper recoveries during the flotation tests of the first phase.

Experiment 12 recorded the highest recoveries of almost 90% for the TSL slag and a 1:1:1 mixture of the three slags showed a recovery of 75.1%. This test also resulted in the lowest tailings grade of 0.64% Cu. The observations with Na_2S, which is a sulphidizing agent, is not what was expected, considering the fact that mineralogical analysis showed no evidence of copper oxide minerals in the slag. A possible explanation could be that gangue oxides like fayalite, with inclusions of copper minerals are sulphidized and picked up during flotation. Experiments with other sulfidizing agents used (NaHS, $(NH_4)_2S$ and $(NH_4)_2SO_4$) showed relatively low recoveries.

Enrichment ratio is an important indicator in mineral beneficiation, as it demonstrates the step up in economic value of the treated slag. Enrichment ratio is defined as the ratio of the concentrate grade over the feed grade.

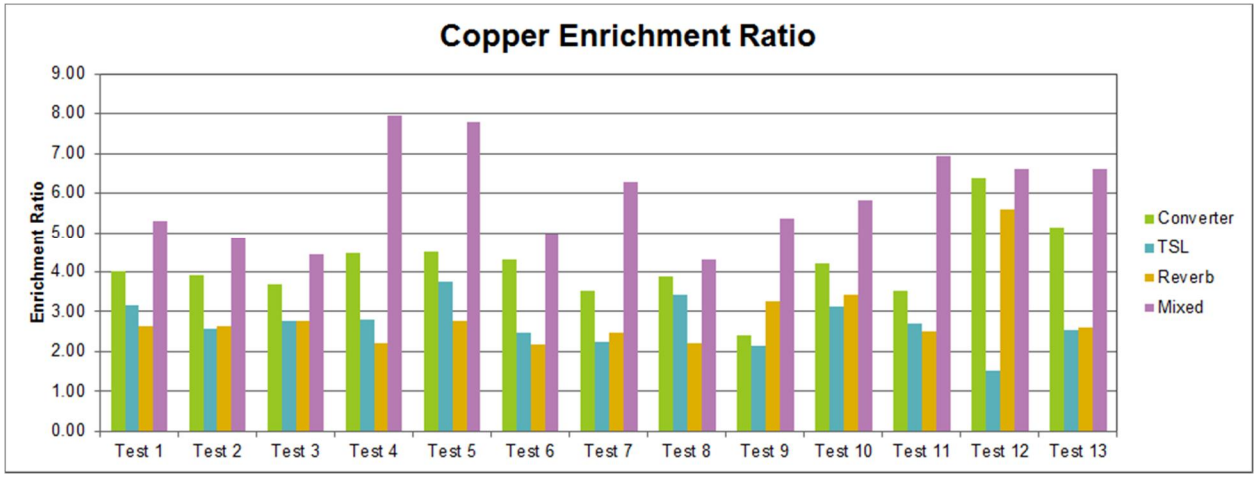


Figure 4.7

From Figure 4.7 it can be observed that the greatest enrichment was obtained with mixed slag. Feed grades for TSL, converter, reverb and mixed slags were 2.27, 2.39, 1.09 and 2.35% Cu, respectively. Lower feed grades tend to produce dilute concentrates, as gangue minerals float with relative ease.

4.3 Flotation test work, Phase 2 (regrinding of tailings).

Phase 2 of the flotation test work involved regrinding the tailings from phase 1 experiments and floating them in the hope that additional liberation will result in improved recoveries. The tailings were milled to 90% passing 45 microns. When the tests on flotation of the milled tailings were undertaken, the reverb furnace had been de-commissioned so the reverb slag was not tested in phase 2. It should be noted as well that the reverb slag had performed poorly in the first phase recovery tests as shown in Figure 4.6. Reagents for phase two tests were narrowed down to include; Na_2S, FC 7245 and FC 4146, which were the reagents that gave the best results in the phase 1 studies. Table 4.1, 4.2 and 4.3 shows the results after regrinding and flotation of plant tailings.

Table 4.1 Results obtained with reagent FC 7245.

FC 7245						
	1:1 Mix		TSL		Conv	
	% Cu	% Mass Recovery	% Cu	% Mass Recovery	% Cu	% Mass Recovery
Feed	2.65	1	1.88	1	3.33	1
Conc	24.16	0.08	24.35	0.06	30.70	0.08
Tails	0.87	0.92	0.46	0.94	0.99	0.92
Rec 1	72.9%		77.8%		73.7%	
Feed 2	0.87	0.92	0.47	0.94	0.99	0.92
Conc 2	4.13	0.074	2.44	0.092	4.63	0.068
Final Tails	0.59	0.846	0.25	0.848	0.47	0.852
Rec2	38.2%		50.8%		34.6%	
Final Conc	14.5%	0.154	11.1%	0.152	18.7%	0.148
Tot Rec	83.7%		89.2%		88.8%	

Table 4.2 Results obtained with reagent FC 4146.

FC 4146						
	1:1 Mix		TSL		Conv	
	% Cu	% Mass Recovery	% Cu	% Mass Recovery	% Cu	% Mass Recovery
Feed	2.65	1	1.88	1	3.33	1
Conc	24.16	0.08	24.35	0.06	30.70	0.08
Tails	0.87	0.92	0.46	0.94	0.99	0.92
Rec 1	72.9%		77.8%		73.7%	
Feed 2	0.87	0.92	0.47	0.94	0.99	0.92
Conc 2	3.48	0.103	3.14	0.053	5.21	0.074
Final Tails	0.54	0.817	0.30	0.887	0.33	0.846
Rec2	44.8%		37.7%		42.3%	
Final Conc	12.5%	0.183	14.4%	0.113	18.4%	0.154
Tot Rec	85.5%		86.2%		92.2%	

Table 4.3 Results obtained with reagent 10% Na_2S.

10% Na_2S						
	1:1 Mix		TSL		Conv	
	% Cu	% Mass Recovery	% Cu	% Mass Recovery	% Cu	% Mass Recovery
Feed	2.65	1	1.88	1	3.33	1
Conc	24.16	0.08	24.35	0.06	30.70	0.08
Tails	0.87	0.92	0.46	0.94	0.99	0.92
Rec 1	72.9%		77.8%		73.7%	
Feed 2	0.87	0.92	0.47	0.94	0.99	0.92
Conc 2	2.33	0.088	2.81	0.016	3.00	0.187
Final Tails	0.72	0.832	0.42	0.924	0.48	0.733
Rec2	25.6%		10.2%		61.6%	
Final Conc	12.7%	0.168	19.8%	0.076	11.3%	0.267
Tot Rec	80.8%		80.0%		88.9%	

The results in Table 4.1, 4.2 and 4.3 shows that plant tailings (tailings from Phase 1) contain an appreciable amount of copper minerals in them that could be recovered, but are being currently disposed. By regrinding and flotation, copper recovery increases by more than 10% and up to 15% for the converter slag with all the three reagents. This indicates that significant additional liberation occurs.

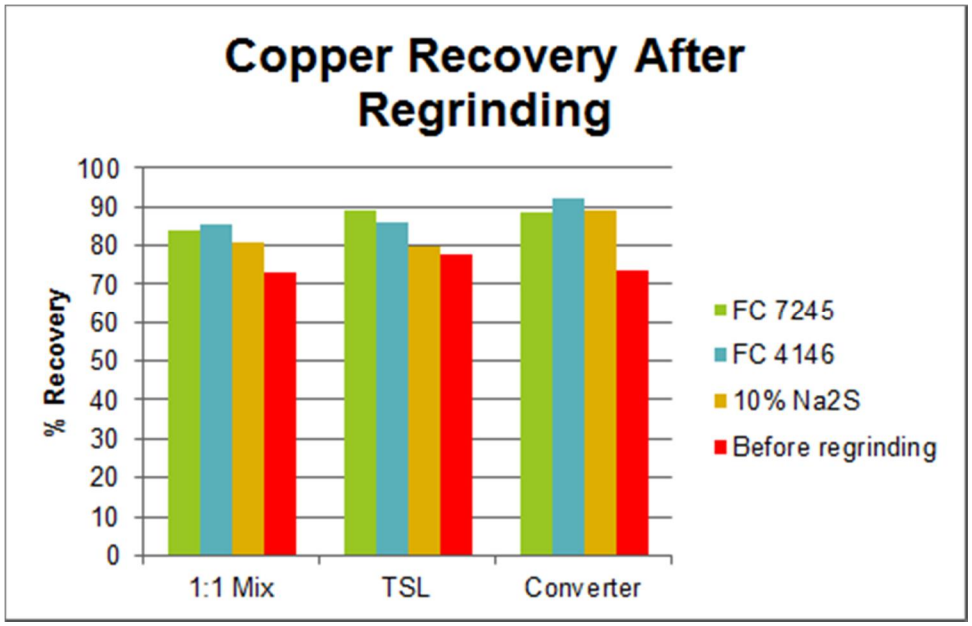


Figure 4.8

Figure 4.8 depicts increased copper recovery after regrinding, with converter slag showing the biggest leap, converter slag and mixed slag yielded greatest recovery increase with Reagent FC 4146, while TSL slag yielded greatest recovery with FC 7245.

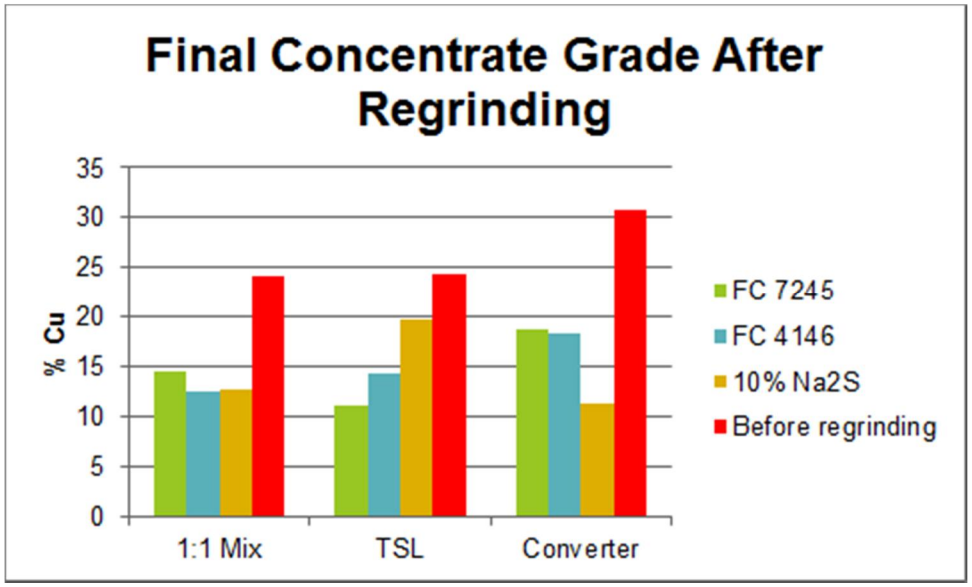


Figure 4.9

Treating TSL slag with Na_2S yielded better grade than FC 4146, however recovery is higher with FC 4146. The concentrate grades decreased after regrinding due to the extensive liberation of gangue, however commercial smelters treat concentrate grades at 14% and above, meaning it is more economical to have a lower grade and a higher recovery for TSL slag. Treating converter slag with FC 4146 and FC 7245 yielded roughly equal grades, but recovery is greater with FC 4146.

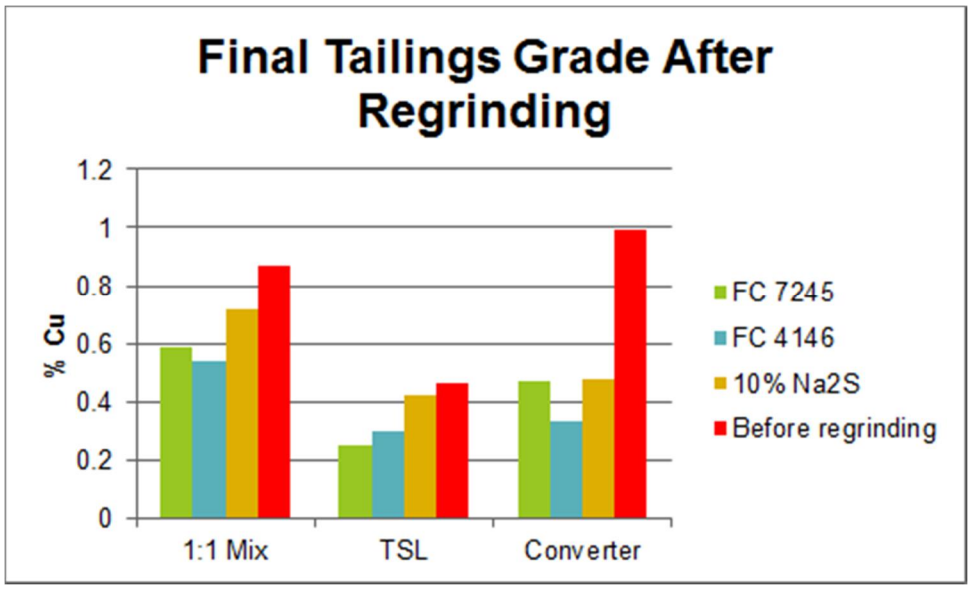


Figure 4.10

It can be seen from Figure 4.10 that regrinding and flotation reduces copper losses to tailings. It also is more economical to treat the slags apart, as losses to tailings stream are minimized. Losses to tailings are highest when treating the slags with Na_2S.

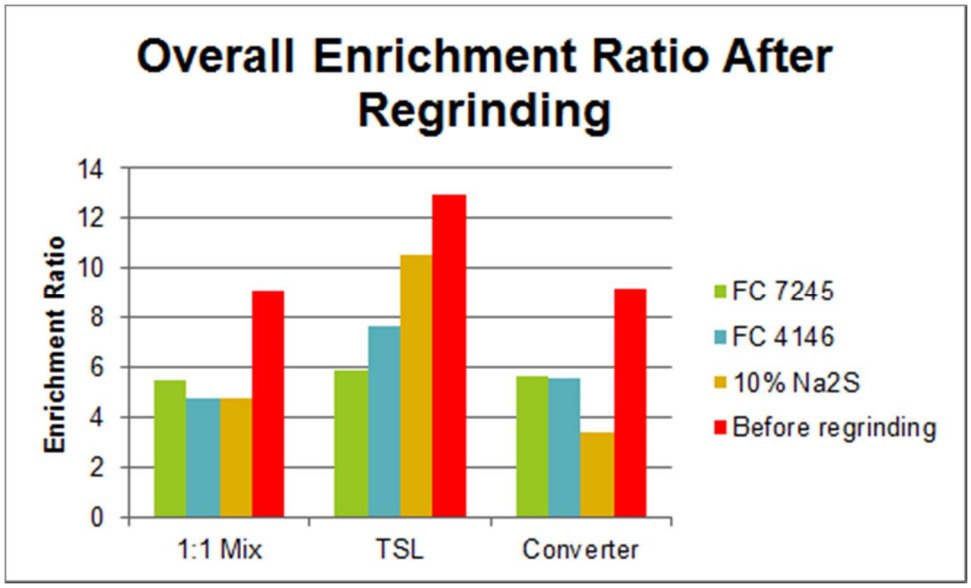


Figure 4.11

Figure 4.11 shows an overall decrease in enrichment after regrinding. This is due to the lower concentrate grades that were produced. Amongst the slags, enrichment is highest in TSL slag with Na_2S and in converter slag with FC 7245. This is due to the relatively higher concentrate grades produced using these reagents.

4.4 Mineralogical analysis

Analysis of the mineralogical composition of the three slag types i.e. converter slag, TSL slag, reverb slag and that of the final tailings was done. X-ray diffraction (XRD) and scanning electron microscopy (SEM) tests were done at SGS laboratories in South Africa and the results are discussed below.

4.4.1 X-Ray Diffraction (XRD) Analysis

The results of the XRD analyses are given in Table 4.4 It includes final plant tailings after processing the three slags in equal ratios.

Table 4.4 Crystalline phases as determined by x-ray diffraction.

Converter Slag		
Mineral Name	**Mineral Formula**	**Approximate Abundance**
Fayalite	Fe_2SiO_4	20 – 50 %
Magnetite	Fe_3O_4	20 – 50 %
Diopside	$CaMgSi_2O_6$	10 – 20 %
Quartz	SiO_2	3 – 10 %
Sphene	$CaTiSiO_5$	3 – 10 %
Chalcocite	Cu_2S	3 – 10 %
TSL Slag		
Mineral Name	**Mineral Formula**	**Approximate Abundance**
Diopside	$CaMgSi_2O_6$	20 – 50 %
Magnetite	Fe_3O_4	20 – 50 %
Chalcocite/digenite	Cu_2S/Cu_9S_5	3 – 10 %
Bornite	Cu_5FeS_4	3 – 10 %
Reverb Slag		
Mineral Name	**Mineral Formula**	**Approximate Abundance**
Diopside	$CaMgSi_2O_6$	20 – 50 %
Magnetite	Fe_3O_4	20 – 50 %
Quartz	SiO_2	20 – 50 %
Plagioclase	$NaAlSi_3O_8$	10 – 20 %
Fayalite	Fe_2SiO_4	10 – 20 %
Final Tailings		
Mineral Name	**Mineral Formula**	**Approximate Abundance**
Diopside	$CaMgSi_2O_6$	20 – 50 %
Magnetite	Fe_3O_4	20 – 50 %
Fayalite	Fe_2SiO_4	10 – 20 %
Chalcopyrite	$CuFeS_2$	10 – 20 %

From the XRD analysis chalcocite was found to be the main copper bearing mineral in the converter slag. In the TSL slag, copper is in the form of chalcocite, digenite and bornite. No copper containing minerals were detected in reverb slag, as it contains less than 1% copper.

Some chalcopyrite was detected in the final tailings but not in the feed slag, this suggests that chalcopyrite was insignificant in the feed (< 3%) and that it could have been very finely disseminated in the slag matrix but become concentrated in the tailings stream.

4.4.2 Scanning Electron Microscope (SEM) Analysis

Figure 4.12 ï 4.21 are the scanning electron micrographs obtained from the SEM analysis of the converter slag, TSL slag, reverb slag and the final tailings, after processing the slags in equal ratios.

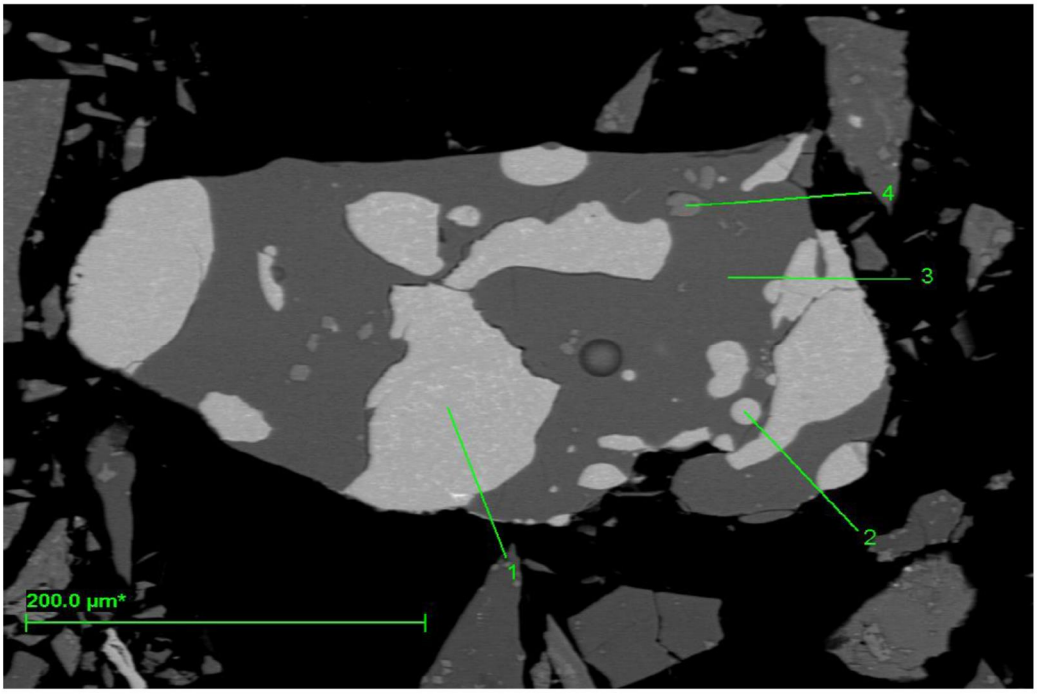


Figure 4.12 Converter slag: SEM microphotograph of fayalite grain (3) with inclusions of partially exposed bornite and locked bornite (1 and 2 respectively) and magnetite (4).

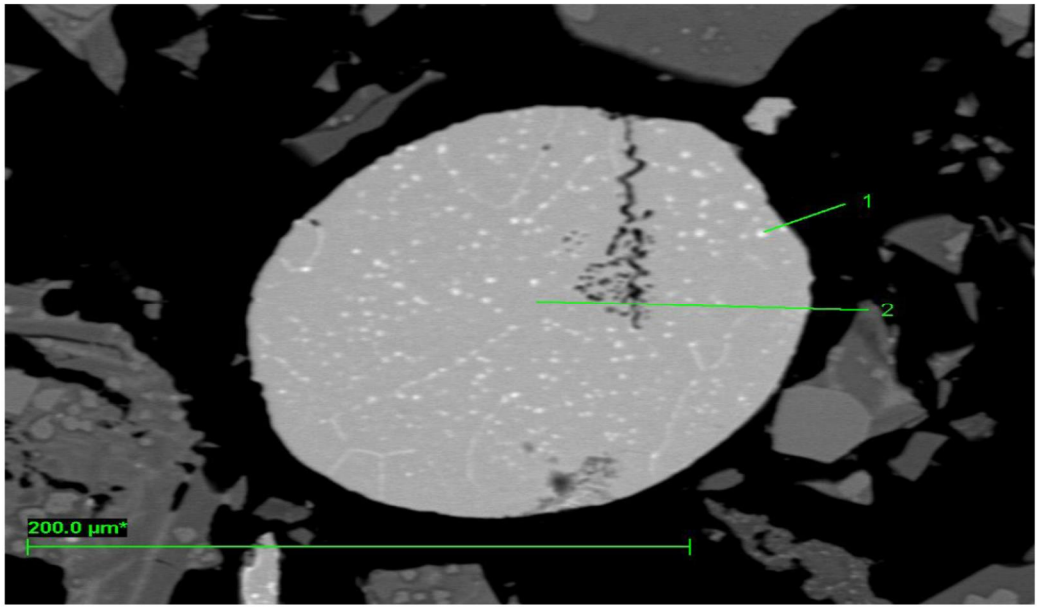


Figure 4.13 Converter slag: SEM microphotograph of a liberated chalcocite grain (2) with small inclusions of galena (1).

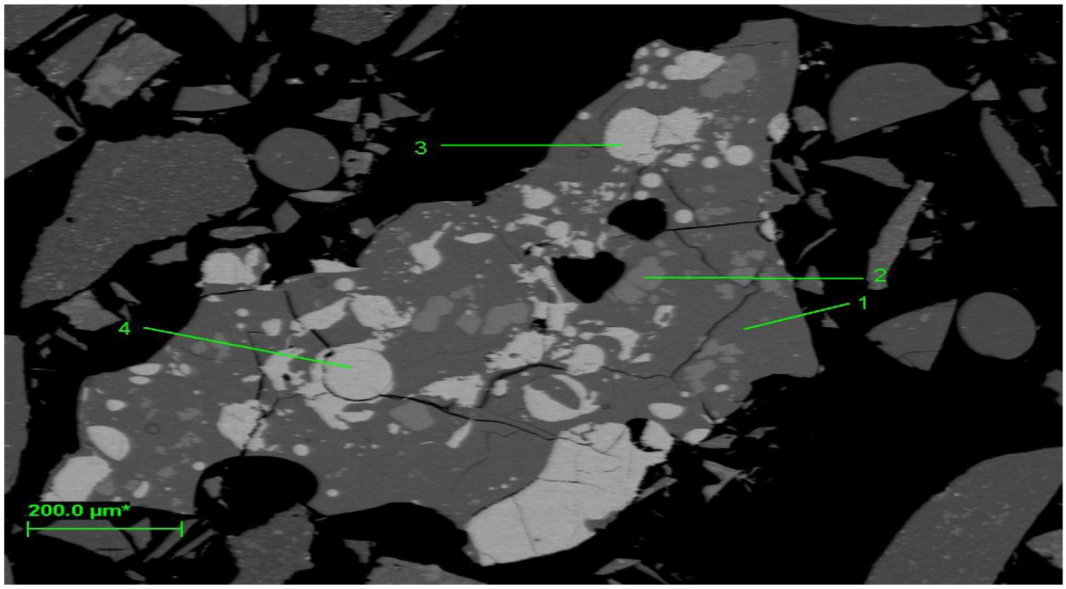


Figure 4.14 Converter slag: SEM microphotograph of fayalite grain (1) with locked and partially exposed bornite inclusions. Minerals (3) and (4) are bornite. There are also inclusions of magnetite (2).

Scanning electron micrographs shown in Figure 4.12 ï 4.14 are for converter slag. The main copper minerals in the converter slag according to the XRD scans were chalcocite and Figure 4.13 confirms the presence of a significantly liberated chalcocite grains. The other dominant phases in converter slag like fayalite and magnetite, according to the XRD were also equally dominant in the SEM micrographs. The mineral bornite was not picked up in the XRD but is present in the SEM, and finely disseminated. The reason it is absent in the XRD could be that its relative abundance is below 3%. The inclusions of galena in Figure 4.13 are attributed to rapid cooling during granulation.

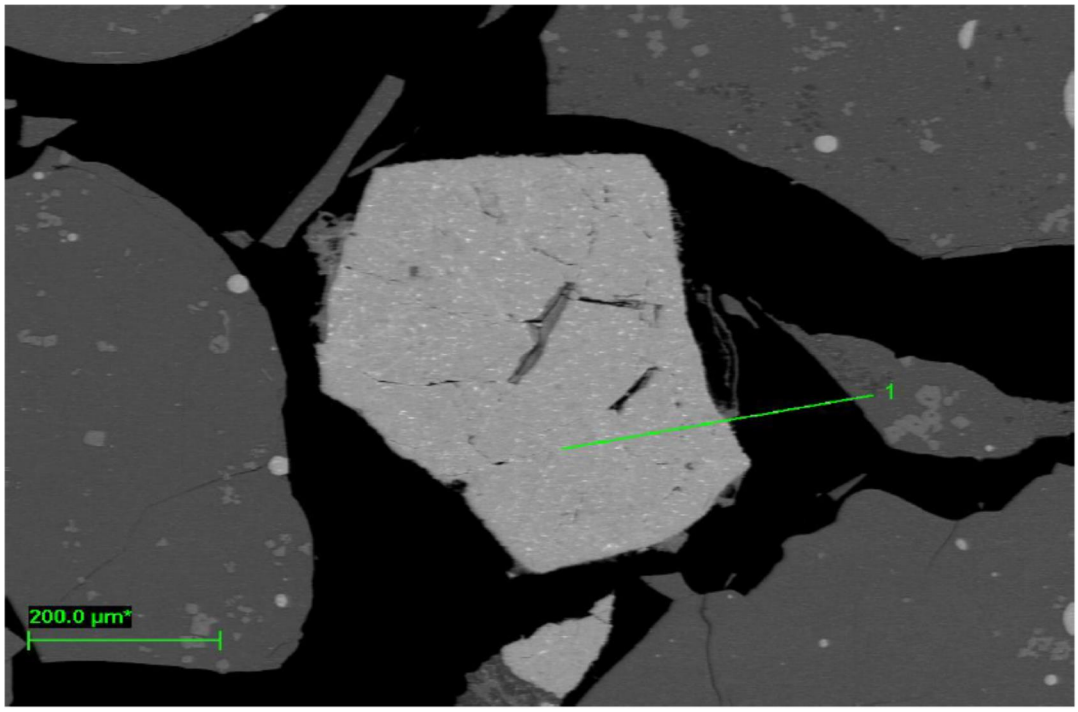


Figure 4.15 TSL Slag: SEM microphotograph of an exposed bornite (1).

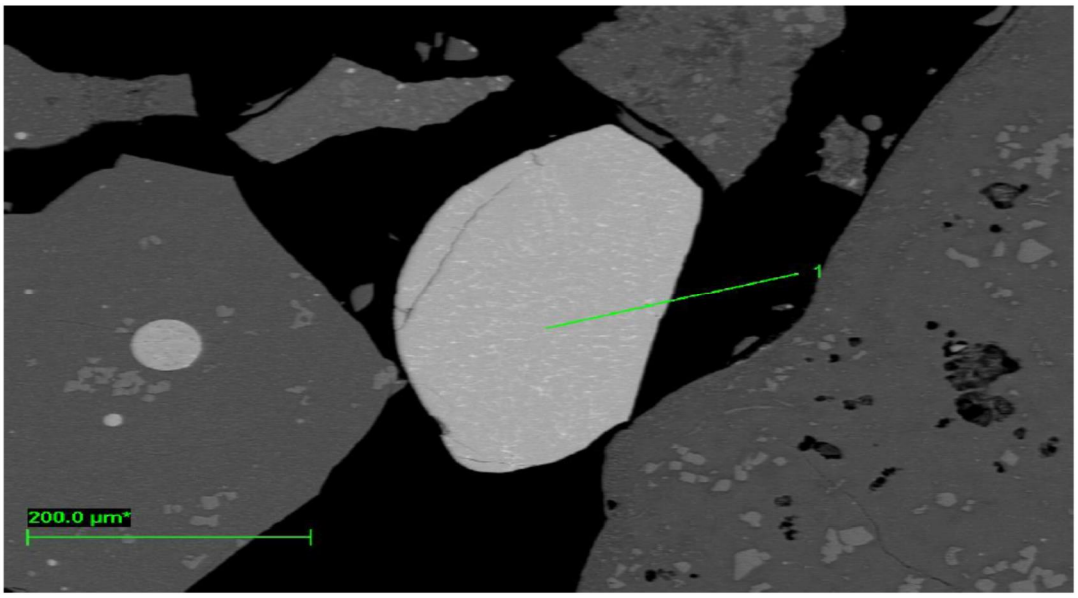


Figure 4.16 TSL Slag: SEM microphotograph of an exposed chalcocite grain (1).

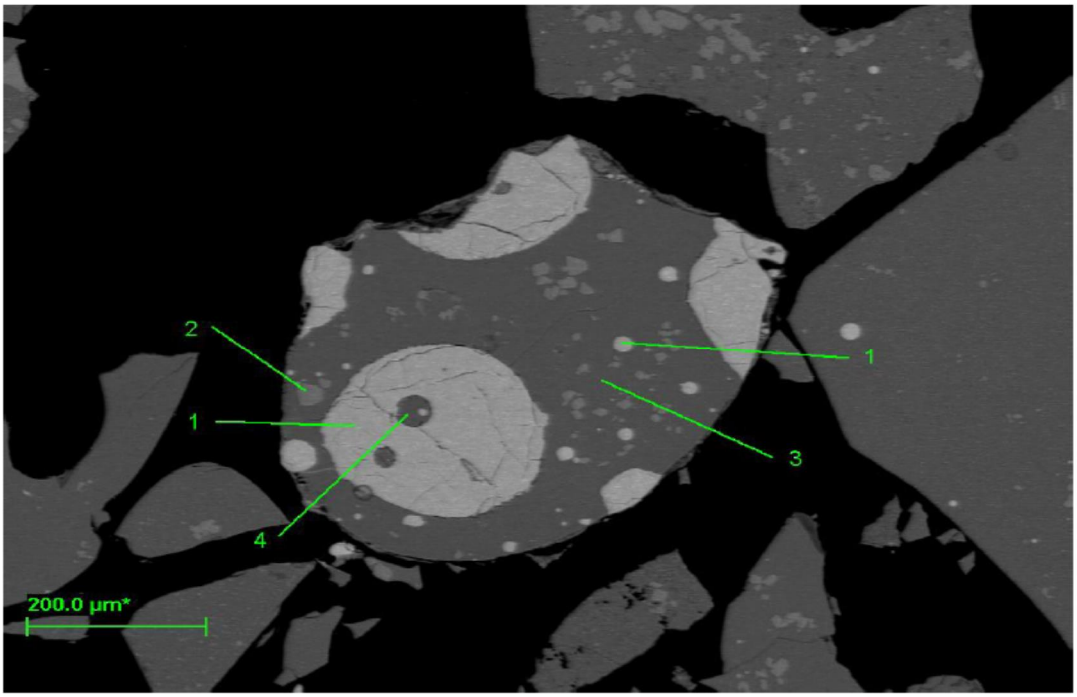


Figure 4.17 TSL Slag: SEM microphotograph of diopside grain (3) with locked chalcopyrite as well as partially exposed chalcopyrite (1).

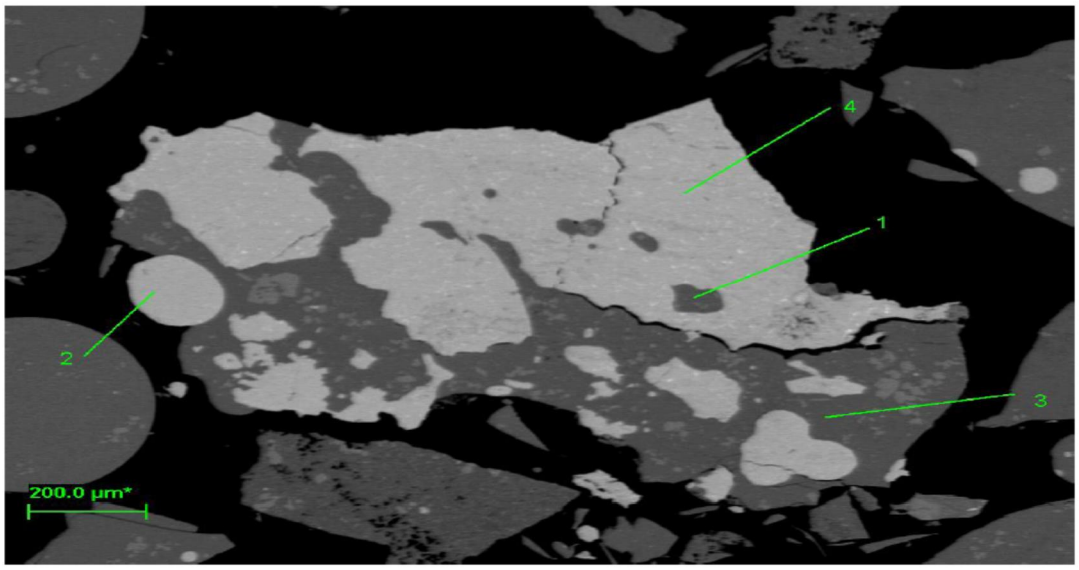


Figure 4.18 TSL Slag: SEM microphotograph of diopside grain (3) containing bornite (2 and 4) and magnetite.

Figure 4.15 ï 4.18 show the scanning electron micrographs for TSL slags. Figure 4.15 shows a well exposed and liberated bornite grain and Figure 4.16 shows a well exposed and liberated chalcocite grain. Bornite and chalcocite were also found to be the dominant copper bearing minerals according to the XRD analysis. Figure 4.17 and 4.18 show significant presence of diopside which was also found to be the main slag phase in the XRD analysis. Some chalcopyrite was picked up by the SEM as shown in Figure 4.17, though the XRD could not detect the presence of this mineral in the TSL slag. There are also magnetite inclusions (2). From this image, it can be observed that chalcopyrite is finely disseminated in diopside and thus not picked up by XRD scans. This is also why it was detected in the tailings sample, as it is known that disseminated minerals are difficult to liberate (Srdjan, 2010).

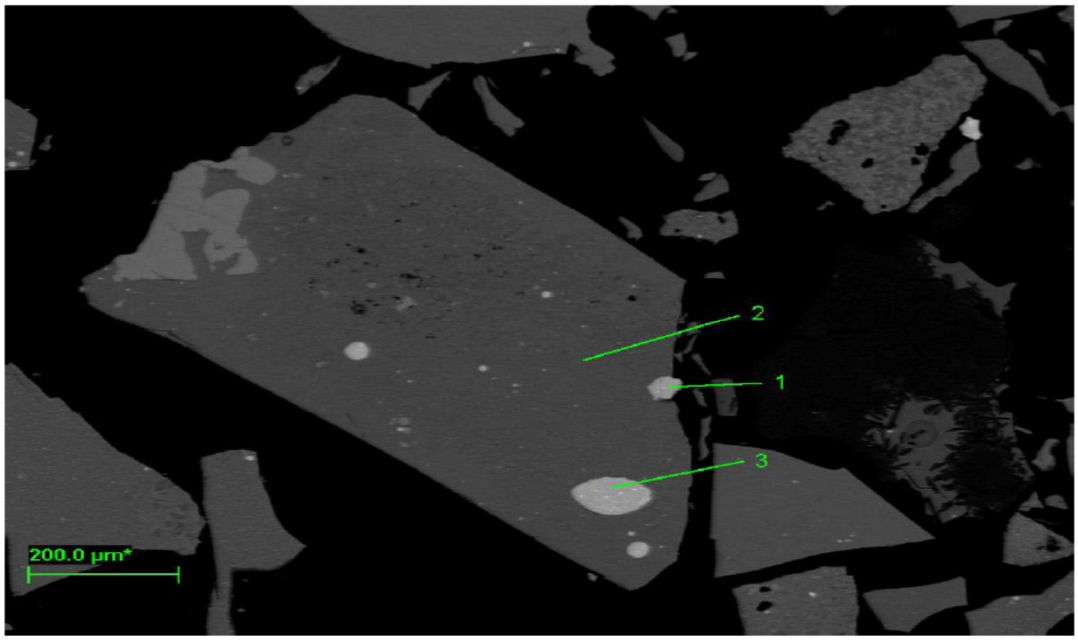


Figure 4.19 Reverb Slag: SEM microphotograph of diopside grain (2) with locked and partially exposed bornite inclusions (3 and 1 respectively).

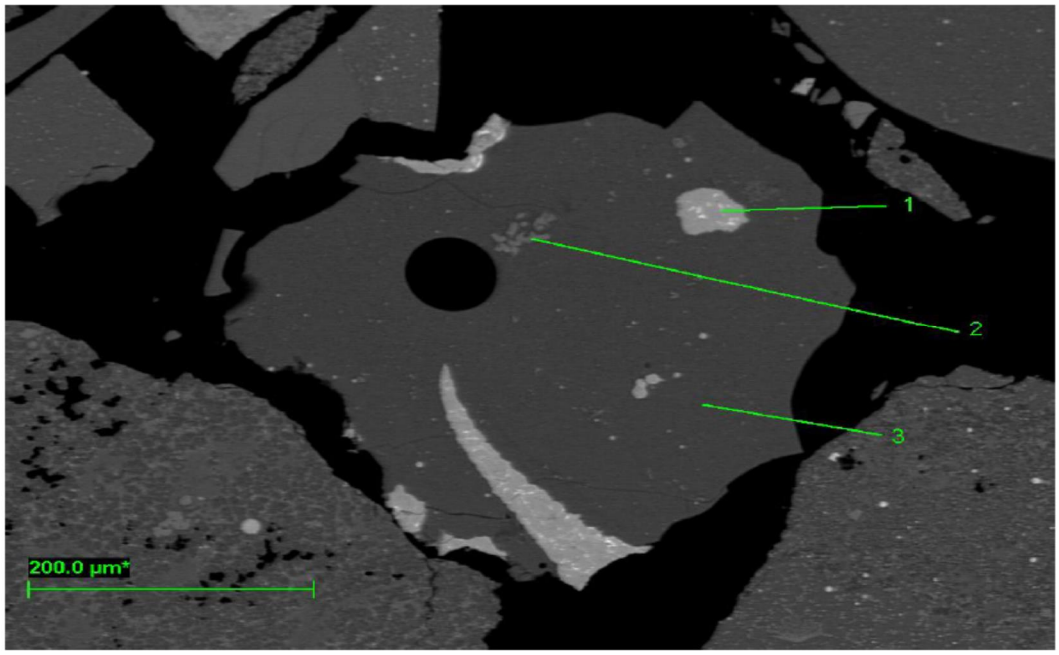


Figure 4.20 Reverb Slag: SEM microphotograph of diopside grain with inclusions of locked and partially exposed chalcopyrite (1) as well as magnetite (2).

Figure 4.19 and 4.20 show the SEMs for the reverb slag. From the images it is evident that there is very little copper mineral content in this particular slag confirming the XRD results. In other words the reverb furnace is efficient in its recovery of copper and other values to the matte phase, as it produces a clean slag.

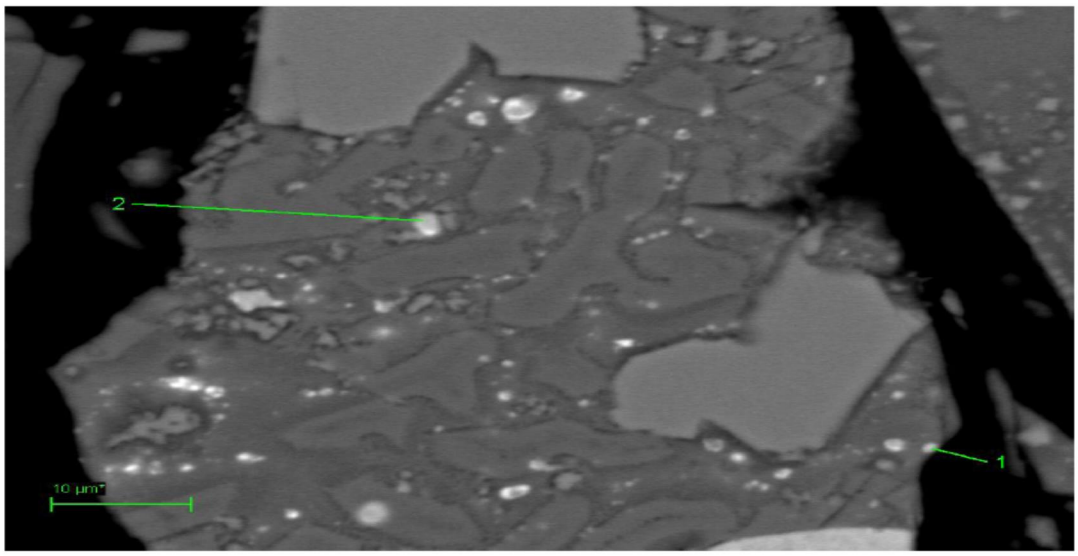


Figure 4.21 Final Tailings (after flotation): SEM microphotograph illustrating tiny, locked inclusions of chalcopyrite (1) and bornite (2).

Figure 4.21 is an SEM of the final tailings. Very tiny inclusions of chalcopyrite which were finely disseminated in the slag matrix were detected. Chalcopyrite was also found to be the only copper mineral present according to the XRD results. Chalcopyrite could not be floated because it is in form of inclusions that are not liberated.

4.5 Discussion summary

The milling studies revealed that different particle size classes contain different amount of the copper minerals and the trend showed that the smaller the size of particles the higher the amount of copper present. The highest copper content was found in particles < 45µm i.e.20.5% in converter and reverb slag, and 28.1% in TSL slag, in fact over 40% of the copper minerals in the slags are concentrated in the size classes -45µm and 75-45µm. This suggests that particles in this size range are the most liberated with respect to the copper minerals, i.e. the grain size of the copper minerals themselves are in that size range. In order to maximize liberation of the slag material in preparation for the flotation process, the milling requirements were therefore, set to 75% passing 45µm. It was also observed that TSL and converter slags produce coarser particles than the reverb slag for the same level of crushing. During the milling tests, two hours of milling time was required to achieve 75% passing 45µm for both TSL and converter slags while the reverb slag only required 1 hour and 40 minutes to achieve the same size distribution criterion. This suggests that the reverb slag is generally softer or has a lower Bond work index than the TSL and the converter slag. This may be due to the fact that the reverb slag has very little or no copper mineral value in it as seen in the mineralogical studies, this proves that a matrix made of largely gangue material is more friable and easier to mill.

Tests were done to study the mineralogical composition of the 3 types of slags and the final tailings. The XRD scans revealed that the three slags are different in terms of copper mineral types present, which is expected since the slags were produced from different smelting operations. The gangue phases across the slags was however fairly consistent.

In converter slag, chalcocite (Cu_2S) was the only copper bearing mineral identified and in TSL slag, chalcocite (Cu_2S), digenite (Cu_9S_5) and bornite (Cu_5FeS_4) were detected in equal abundances (3-10%). The XRD scans did not reveal the presence of copper minerals in reverb slag, suggesting that the reverb smelting process is more efficient as it leaves very little or no residual value minerals in the slag phase. SEM images confirmed the presence of all minerals detected by XRD scans for each slag tested indicating the validity and agreement of both these techniques in identifying different minerals present in the slag materials. Additional minerals detected by SEM in converter slag were bornite and galena, which appear finely disseminated in a chalcocite grain and chalcopyrite ($CuFeS_2$) in TSL slag and reverb slag. Copper minerals are both free (liberated) and locked in gangue phases.

Flotation tests were divided into two phases, the first phase involved flotation of all slag materials after milling the slags to 75% passing 45µm, using different reagents as spelt out in the objectives of the studies and shown in the experimental matrix given in Table 3.2. The reverb slag produced the lowest recoveries of copper minerals (less than 15%) while the TSL and converter slags produced the highest recoveries which were consistently above 70%. The greatest recoveries were obtained using the flotation reagents FC 4146, FS 100 and 10% Na_2S. Phase 2 of the flotation tests involved regrinding and floating tailings from phase 1 tests in order to further liberate and recover additional copper minerals. Additional copper recoveries were attained, bringing the cumulative copper recoveries to above 80% on average across the TSL and converter slag flotation. Converter slag produced the highest recovery (90%) with reagent FC 4146. The same reagent also produced the highest recovery (86%) when the two slags (converter and TSL slags) were mixed in a 1:1 ratio. TSL slag produced the highest recovery (89%) with reagent FC 7245.

The current flotation practice at the Namibia Custom Smelters was optimized with respect to reagents in this work and the test clearly showed that the recovery performance is much better when the slags are floated separately than combined. Further improvements in the recoveries recorded in the test-work of this study after regrinding and flotation of flotation tailings has generated significant interests in the company and the cost benefit analysis of re-designing the current circuit is under consideration.

5. Conclusion

The mineralogical analysis of all the slags used at the slag mill plant showed that no copper oxide minerals exist as previously envisaged, hence the preliminary acid solubility test cannot be used as a test that validates the presence of copper oxide minerals, the dissolution of the copper could have been from the sulphide copper before passivation. The main copper bearing minerals found were chalcocite in the converter slag; chalcocite, digenite and bornite in the TSL slag. The reverb slag was found to have insignificant amounts of copper minerals in it. The final tailings contained low quantities of finely divided chalcopyrite which could not be detected in the parent slags.

The milling test work demonstrated that best liberation is obtained when particles are of sizes less than 45 microns, hence the milling of the bulk samples were done to 75% passing 45 microns. Regrinding and flotation of plant tailings has shown to be a more suitable route to treat smelter slags. Up to 92.2% recovery was obtained with converter slag, using the reagent FC 4146, which is of the thionocarbamate family. The lowest tailings grade of 0.25% copper was obtained with TSL slag, using reagent FC 7245 of the mercaptan family. Lower, yet economical concentrate grades are attained when regrinding and flotation is done. Regrinding further liberates the trapped minerals but this also makes the gangue float with relative ease by means of entrapment, thereby reducing the concentrate grades. Nonetheless, in a typical flotation plant, the concentrate can be sent to a cleaning stage to increase the grade. The lowest grade obtained was 11.1% copper, with the reagent FC7245. The highest concentrate grade achieved was with Na_2S, yielding 19.8% copper.

It is advisable for each slag type to be treated alone, as maximum recoveries will be achieved, TSL slag yields greatest recovery with FC 7245 and converter slag with FC 4146. In the plant set up, the concentrate may be cleaned to produce a slightly enriched concentrate. The current and the recommended flow sheets are illustrated in Figure 6.1 and 6.2 respectively.

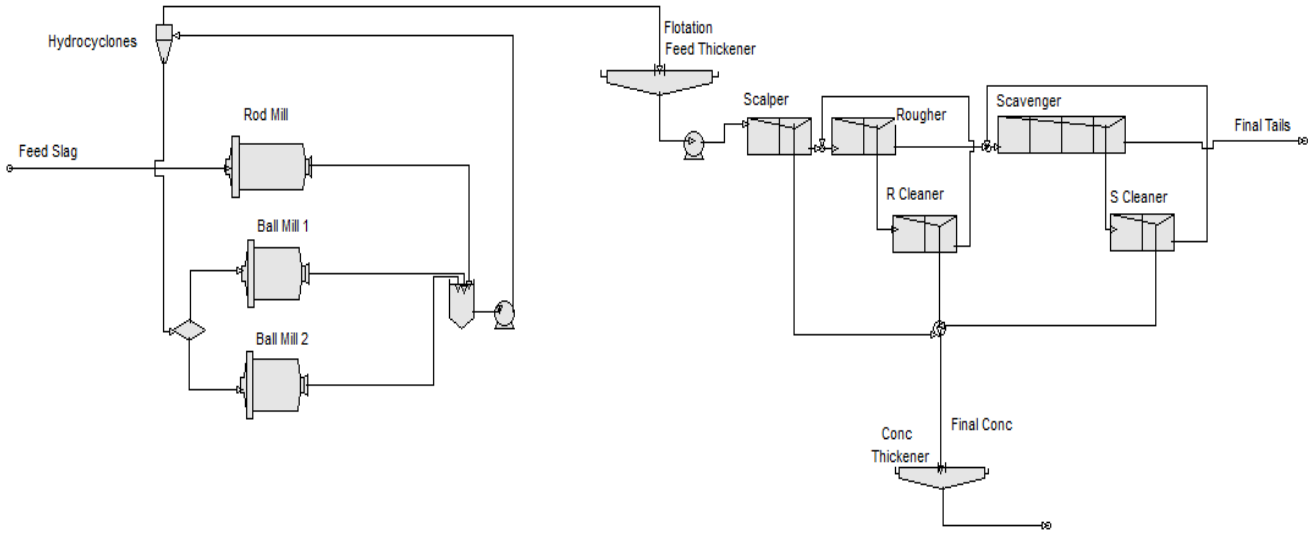


Figure 5.1 Current plant set up.

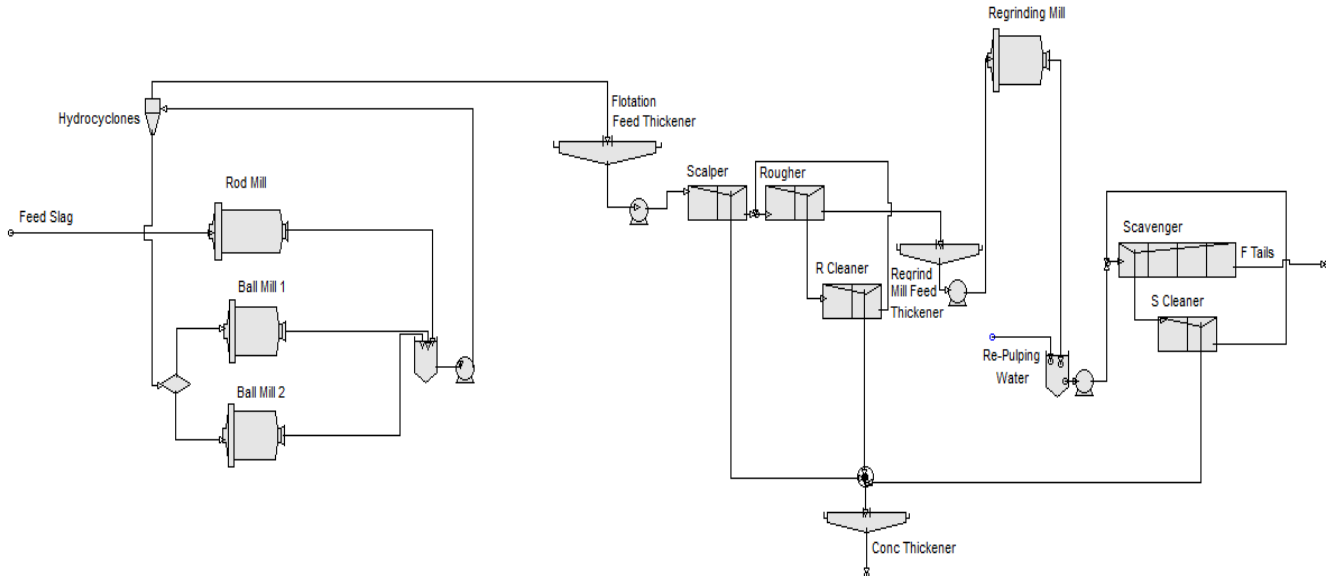


Figure 5.2 Proposed plant set up.

6. References

Abek-Hady, M.S., Atef, M. R., Mohamed R.M., 2008. "Beneficiation of Egyptian Abu-Swayel copper ore by flotation". *Physiochemical Problems of Mineral Processing,* vol. 42, pp. 119-130.

Aplan, F.F., Fuersentau, D.W., 1984. "The Flotation of Chrysocolla by Mercapatan", International Journal of Mineral Processing, vol. 13, pp. 105-115.

Arakatsu, A., Hajime, N., Hiroshi,. N., 1977. "Flotation Process for Copper Ores and Copper Smelter Slags". *United States Patent,* 4022686.

Bradshaw, D.J., Harris, P.J., O'Connor, C.T., 2005. "The effect of Collectors and Their Interactions with Depressants on the Behaviour of the Froth Phase Flotation". *Centenary of Flotation Symposium,* pp. 329-332.

Bruckard, W.J., Somerville, M., Hao, F.,2004. "The recovery of copper, by flotation, from calcium-ferrite-based slags made in continuous pilot plant smelting trials". *Minerals Engineering* Vol. 17, pp. 495–504.

Carr, D., Harbort G., Lawson, V., 2003."Expansion of the Mount Isa Mines copper concentrator phase one cleaner circuit expansion". *Eighth Mill Operators' Conference*, July 21–23, 2003. Townsville, Queensland.

Cordoba, E.M., Munoz, J.A., Blazquez, M.L., Gonzalez, F., Ballester, A., 2009.ôPassivation of chalcopyrite during its chemical leaching with ferric ion at 68 °Cô. *Minerals Engineering*. Vol. 22, pp. 229-235.

Davenport, W.G., King, M., Schlesinger, M., Biswas, A.K., 2002. *Extractive metallurgy of copper,* 4th edition, Pergamon.

Ferriera, B.K., 2004. Electrochemical reactors for PGM recovery. Master of Science dissertation, University of the Witwatersrand.

Grosso, M., Rigamonti, L., Biganzoli, L., Schiona, G., 2010. ôMetals recovery from incineration bottom ashes: Future opportunities in Italyô. *2nd International Conference on Hazardous and Industrial Waste Management*, 5ï 8 October 2010, Chania, Crete, Greece.

Jackman, R.B., Hayward, C.R., 1933. ôForms of Copper Found in Reverberatory Slagô. *The American Institute of Mining, Metallurgical, and Petroleum Engineers.* Papers ï Smelting, pp. 11.

King R.P., 1976. ôModel for the Design and Control of Flotation Plantsô. *Journal of the South African Institute of Mining and Metallurgy.*

King, R.P., 2000. *Modeling & Simulation of Mineral Processing Systems, Butterworth-Heinemann*, Great Britain.

Lee, K., Archibald, D., Mc Lean, J., Reuter, M.A., 2008. ôFlotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectorsô *Minerals Engineering*, doi: 10.1016/j.mineng.2008.11.005.

Mackey, P.J., 1982. ôThe Physical Chemistry of Copper Smelting Slags ï A Review.ô *Canadian Metallurgy Quarterly*, vol 21, No. 3, pp 221 ï 260.

Michigan Technology University, 2010, *Flotation Fundamentals*, Department of Chemical Engineering, Michigan, USA, viewed 6 April 2012, <http://www.chem.mtu.edu/chem_eng/faculty/kawatra/Flotation_Fundamentals.pdf>

Mihailova, I., Mehandjiev, D., 2010. óCharacterization of fayalite from copper slags.ô *Journal of the University of Chemical Technology and Metallurgy*, vol. 45, No. 3, pp 317-326.

Mounsey, E.N., Li, H., and Floyd, J.W. 1999. ôThe design of the Ausmelt technology smelter at Zhong Tiao Shan's Houma smelterô. *Copper 99-Cobre 99 Proceedings of the Fourth International Conference*, Vol. 5 Smelting Operations and Advances.

Nel, E., Theron, J., Martin, C., Raabe, H., 2004. ôPGM Ore Processing at Impalaôs UG-2 Concentrator in Rustenburg, South Africaô *SGS Minerals Services,* Technical paper 2004-02.

Nyakudarika, T., Makumbe, S., Rule, S., 2012. óFully Autogenous Grinding at Unki Mine Concentrator-A case of successful value engineeringô. *Journal of the South African Institute of Mining and Metallurgy.*

Pecqueur G., Crignon C., Quénée B., 2001.óBehaviour of cement-treated MSWI bottom ashô. *Waste management* 21, pp. 229-233.

Peterson, H.D., Fuerstenau, M.C., Rickard, R.S., Miller, J.D., 1965. óChrysocolla flotation by the formation of insoluble surface chelatesô. *Society of Mining Engineers*, pp. 388-392.

Phetla, T.P., Muzenda, E., 2010. óA Multistage Sulphidisation Procedure for Low Grade Malachite copper Oreô. *World Academy of Science, Engineering and Technology*, vol. 69, pp. 255-261.

Risberg. A., 2006. Industrial Wastewater in Chile ï Identification of Problems and Suggestions for Improvement. Master of Science dissertation, Uppsala University.

Simba, K.P, 2010. Effects of mixture of grinding media of different shapes on milling kinetics, Master of Science Dissertation, University of the Witwatersrand, Johannesburg.

Srdjan, M.B., 2010. *Handbook of flotation reagents*, 1st edition, Elsevier Ltd.

Tilsley, P. (2014, January 08). New gold rush flattens Johannesburg's famous mining dumps. *Fox News.* Retrieved from http://www.foxnews.com

Twidle, T.R., Engelbrecht, P.C., 1984. "Developments in the flotation of copper at Black Mountain". *Journal of the South African Institute of Mining and Metallurgy.* Vol. 84, no 6, pp. 164-178.

Voijtech, E., Zdenek, J., Bohdan, K., Ondrej, S., Martin, M., 2009. "Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia". *Applied Geochemistry.* Vol. 24, pp. 1-15.

Wang, X., Geysen, D., Padilla T., D'Hoker H.D., Huang,S., Jones, P.T., Van Gerven, T., Blanpain, B., 2011. "Fayalite Based Slags: Metal Recovery and Utilization". *Second International Slag Valorization symposium*. April 18-20, 2011. Leuven, Belgium.

Wills, B.A., 2006. *Mineral Processing Technology: an introduction to the practical aspects of the ore treatment and mineral recovery*, 7th edition, Elsevier Ltd.

Zhang, W. and Poling, G.W. (1991). "Sulphidization promoting effects of ammonium sulphate on sulphidized xanthate flotation of malachite". *Proc. XVII Int. Min. Proc. Cong., Dresden*, Vol. IV, pp. 187.

Ziemkiewicz, P., 1998. ‘Steel slag: applications for AMD control’. *Proceedings of the 1998 conference on Hazardous Waste Research*. May 19-21, 1998. Snow Bird, Utah.

7. Appendices

7.1. Tables of flotation results (Phase 1)

7.1.1. Converter slag

Table 7.1 Converter slag results (Phase 1).

Test	Reagents			Time	Feed	Concentrate	Sulfidized Conc	Total Conc	Tailings	Enrichment Ratio	Cu Recovery
	PAX (300 g/t)	Flotanol CO 7	Secondary collector (200g/t)		% Cu	% Cu	% Cu	% Cu	% Cu		
Test 1	10% PAX (3ml)	Frother (4 drops)	FC 7245 (0.179ml)	15 min	2.39	9.61		9.61	0.86	4.02	70.3%
Test 2	10% PAX (3ml)	Frother (4 drops)	FC 4132 (0.2)	15 min	2.39	9.35		9.35	0.78	3.91	73.5%
Test 3	10% PAX (3ml)	Frother (4 drops)	FC 5473 (0.19)	8min PAX, 7 min FC 5473	2.39	12.05	1.19	8.79	0.74	3.68	73.6%
Test 4	10% PAX (3ml)		FC 4146 (0.18ml)	15 min	2.39	10.73		10.73	0.75	4.49	73.8%
Test 5	10% PAX (3ml)		FC 7412 (0.208ml)	15 min	2.39	10.8		10.80	0.75	4.52	73.7%
Test 6	10% PAX (3ml)	Frother (4 drops)	E 703 (0.2ml)	15 min	2.39	10.33		10.33	0.75	4.32	74.0%
Test 7	10% PAX (3ml)	Frother (4 drops)	M91 (0.2ml)	15 min	2.39	8.4		8.40	0.84	3.51	72.1%
Test 8	10% PAX (3ml)	Frother (4 drops)	FS-2 (0.2ml)	15 min	2.39	9.26		9.26	0.89	3.87	69.4%
Test 9	10% PAX (3ml)	Frother (4 drops)	FS-100 (0.2ml)	15 min	2.39	5.74		5.74	0.76	2.40	78.6%
Test 10	10% PAX (3ml)	Frother (4 drops)	$(NH_4)_2S$ (0.2ml)	8 min PAX, 7 min $(NH_4)_2S$	2.39	12.78	3.69	10.05	0.86	4.21	68.6%
Test 11	10% PAX (3ml)	Frother (4 drops)	10% NaHS (5ml)	8 min PAX, 7 min NaHS	2.39	11.46	1.27	8.40	0.75	3.52	73.4%
Test 12	10% PAX (3ml)	Frother (4 drops)	10% Na_2S (5ml)	8min PAX, 7 min Na_2S	2.39	14.99	15.74	15.22	0.64	6.37	76.5%
Test 13	10% PAX (3ml)	Frother (4 drops)	10% NaHS, $(NH_4)_2SO_4$	8 min PAX, 7 min NaHS; $(NH_4)_2SO_4$	2.39	16.04	3.34	12.23	0.71	5.12	73.5%

7.1.2. TSL slag

Table 7.2 TSL slag results (Phase 1).

Trial	Reagents			Time	Feed	Concentrate	Sulfidized Conc	Total Conc	Tailings	Enrichment Ratio	Cu Recovery
	PAX (300 g/t)	Flotanol CO 7	Secondary collector (200g/t)		% Cu	% Cu	% Cu	% Cu	% Cu		
Test 1	10% PAX (3ml)	Frother (4 drops)	FC 7245 (0.179ml)	15 min	2.27	7.16		7.16	0.82	3.15	72.1%
Test 2	10% PAX (3ml)	Frother (4 drops)	FC 4132 (0.2)	15 min	2.27	5.81		5.81	0.67	2.56	79.7%
Test 3	10% PAX (3ml)	Frother (4 drops)	FC 5473 (0.19)	8min PAX, 7 min FC 5473	2.27	7.99	2.22	6.259	0.67	2.76	76.9%
Test 4	10% PAX (3ml)		FC 4146 (0.18ml)	15 min	2.25	6.32		6.32	0.77	2.81	74.9%
Test 5	10% PAX (3ml)		FC 7412 (0.208ml)	15 min	2.25	8.47		8.47	0.7	3.76	75.1%
Test 6	10% PAX (3ml)	Frother (4 drops)	E 703 (0.2ml)	15 min	2.43	5.97		5.97	0.74	2.46	79.4%
Test 7	10% PAX (3ml)	Frother (4 drops)	M91 (0.2ml)	15 min	2.43	5.46		5.46	0.78	2.25	79.2%
Test 8	10% PAX (3ml)	Frother (4 drops)	FS-2 (0.2ml)	15 min	2.24	7.69		7.69	0.67	3.43	76.8%
Test 9	10% PAX (3ml)	Frother (4 drops)	FS-100 (0.2ml)	15 min	2.24	4.82		4.82	0.61	2.15	83.3%
Test 10	10% PAX (3ml)	Frother (4 drops)	$(NH_4)_2S$ (0.2ml)	8 min PAX, 7 min $(NH_4)_2S$	2.24	9.53	1.2	7.031	0.63	3.14	77.0%
Test 11	10% PAX (3ml)	Frother (4 drops)	10% NaHS (5ml)	8 min PAX, 7 min NaHS	2.29	8.45	1.01	6.218	0.76	2.72	73.4%
Test 12	10% PAX (3ml)	Frother (4 drops)	10% Na_2S (5ml)	8min PAX, 7 min Na_2S	2.29	3.56	3.22	3.458	0.67	1.51	87.1%
Test 13	10% PAX (3ml)	Frother (4 drops)	10% NaHS, $(NH_4)_2SO_4$	8 min PAX, 7 min NaHS; $(NH_4)_2SO_4$	2.29	7.81	1.16	5.815	0.77	2.54	73.6%

7.1.3. Reverb slag

Table 7.3 Reverb slag results (Phase 1).

Trial	Reagents			Time	Feed	Concentrate	Sulfidized Conc	Total Conc	Tailings	Enrichment Ratio	Cu Recovery
	PAX (300 g/t)	Flotanol CO 7	Secondary collector (200g/t)		% Cu	% Cu	% Cu	% Cu	% Cu		
Test 1	10% PAX (3ml)	Frother (4 drops)	FC 7245 (0.179ml)	15 min	1.09	2.87		2.87	1.02	2.63	10.0%
Test 2	10% PAX (3ml)	Frother (4 drops)	FC 4132 (0.2)	15 min	1.09	2.89		2.89	0.99	2.65	14.0%
Test 3	10% PAX (3ml)	Frother (4 drops)	FC 5473 (0.19)	8min PAX, 7 min FC 5473	1.07	3.79	1.06	2.97	0.98	2.78	11.3%
Test 4	10% PAX (3ml)		FC 4146 (0.18ml)	15 min	1.07	2.35		2.35	1.00	2.20	11.4%
Test 5	10% PAX (3ml)		FC 7412 (0.208ml)	15 min	1.07	2.96		2.96	1.05	2.77	2.9%
Test 6	10% PAX (3ml)	Frother (4 drops)	E 703 (0.2ml)	15 min	1.07	2.34		2.34	1.03	2.19	6.7%
Test 7	10% PAX (3ml)	Frother (4 drops)	M91 (0.2ml)	15 min	1.07	2.63		2.63	1.00	2.46	10.6%
Test 8	10% PAX (3ml)	Frother (4 drops)	FS-2 (0.2ml)	15 min	1.07	2.35		2.35	1.05	2.20	3.4%
Test 9	10% PAX (3ml)	Frother (4 drops)	FS-100 (0.2ml)	15 min	1.07	3.50		3.50	1.05	3.27	2.7%
Test 10	10% PAX (3ml)	Frother (4 drops)	$(NH_4)_2S$ (0.2ml)	8 min PAX, 7 min $(NH_4)_2S$	1.07	4.61	1.43	3.66	1.06	3.42	1.2%
Test 11	10% PAX (3ml)	Frother (4 drops)	10% NaHS (5ml)	8 min PAX, 7 min NaHS	1.07	3.18	1.51	2.68	1.03	2.50	5.5%
Test 12	10% PAX (3ml)	Frother (4 drops)	10% Na_2S (5ml)	8min PAX, 7 min Na_2S	1.07	8.05	1.15	5.98	0.97	5.59	10.6%
Test 13	10% PAX (3ml)	Frother (4 drops)	10% NaHS, $(NH_4)_2SO_4$	8 min PAX, 7 min NaHS; $(NH_4)_2SO_4$	1.07	3.49	1.18	2.80	0.94	2.61	16.6%

7.1.4. Mixed slag

Table 7.4 Mixed slag results (Phase 1).

Trial	Reagents			Time	Feed	Concentrate	Sulfidized Conc	Total Conc	Tailings	Enrichment Ratio	Cu Recovery
	PAX (300 g/t)	Flotanol CO 7	Secondary collector (200g/t)		% Cu	% Cu	% Cu	% Cu	% Cu		
Test 1	120	Frother (4 drops)	FC 7245 (0.179ml)	15 min	2.35	12.48		12.48	0.79	5.31	70.9%
Test 2	120	Frother (4 drops)	FC 4132 (0.2)	15 min	2.35	11.48		11.48	0.8	4.89	70.9%
Test 3	120	Frother (4 drops)	FC 5473 (0.19)	8min PAX, 7 min FC 5473	2.35	14.05	2.11	10.47	1.02	4.45	61.0%
Test 4	120		FC 4146 (0.18ml)	15 min	2.35	18.73		18.73	0.71	7.97	72.5%
Test 5	120		FC 7412 (0.208ml)	15 min	2.35	18.33		18.33	0.77	7.80	70.2%
Test 6	120	Frother (4 drops)	E 703 (0.2ml)	15 min	2.35	11.66		11.66	0.72	4.96	73.9%
Test 7	120	Frother (4 drops)	M91 (0.2ml)	15 min	2.35	14.73		14.73	0.72	6.27	72.9%
Test 8	120	Frother (4 drops)	FS-2 (0.2ml)	15 min	2.35	10.13		10.13	0.76	4.31	73.1%
Test 9	120	Frother (4 drops)	FS-100 (0.2ml)	15 min	2.35	12.58		12.58	0.78	5.35	71.2%
Test 10	120	Frother (4 drops)	$(NH_4)_2S$ (0.2ml)	8 min PAX, 7 min $(NH_4)_2S$	2.35	17.37	5	13.66	0.68	5.81	74.0%
Test 11	120	Frother (4 drops)	10% NaHS (5ml)	8 min PAX, 7 min NaHS	2.35	22.12	2.78	16.32	1.07	6.94	57.2%
Test 12	120	Frother (4 drops)	10% Na_2S (5ml)	8min PAX, 7 min Na_2S	2.35	21	2.86	15.56	0.64	6.62	75.1%
Test 13	120	Frother (4 drops)	10% NaHS, $(NH_4)_2SO_4$	8 min PAX, 7 min NaHS; $(NH_4)_2SO_4$	2.35	21.12	2.62	15.57	0.78	6.63	69.4%

7.2. Tables of flotation results (Phase 2)

Table 7.5 Phase two results.

Trial	Reagents			Time	Feed	Concentrate	Sulfidized Conc	Total Conc	Tailings	Enrichment Ratio	Cu Recovery	Conc mass Fr
	PAX (300 g/t)	Flotanol CO 7	Secondary collector (200g/t)		% Cu	% Cu	% Cu	% Cu	% Cu			
Test 1	10% PAX (3ml)	Frother (4 drops)	FC 7245 (0.179ml)	15 min	0.99	4.63		4.63	0.47	4.67	58.6%	0.068
Test 2	10% PAX (3ml)		FC 4146 (0.18ml)	15 min	0.99	5.21		5.21	0.33	5.25	71.3%	0.074
Test 3	10% PAX (3ml)	Frother (4 drops)	10% Na_2S (5ml)	8min PAX, 7 min FC Na_2S	0.99	3.77	1.21	3.00	0.48	3.03	59.2%	0.187

TSL Salg												
Trial	Reagents			Time	Feed	Concentrate	Sulfidized Conc	Total Conc	Tailings	Enrichment Ratio	Cu Recovery	Conc mass fr
	PAX (300 g/t)	Flotanol CO 7	Secondary collector (200g/t)		% Cu	% Cu	% Cu	% Cu	% Cu			
Test 1	10% PAX (3ml)	Frother (4 drops)	FC 7245 (0.179ml)	15 min	0.46	2.44		2.44	0.25	5.25	51.2%	0.092
Test 2	10% PAX (3ml)		FC 4146 (0.18ml)	15 min	0.46	3.14		3.14	0.30	6.77	38.0%	0.053
Test 3	10% PAX (3ml)	Frother (4 drops)	10% Na_2S (5ml)	8min PAX, 7 min FC Na_2S	0.46	3.65	0.87	2.81	0.42	6.06	10.1%	0.016

Mixed Slag												
Trial	Reagents			Time	Feed	Concentrate	Sulfidized Conc	Total Conc	Tailings	Enrichment Ratio	Cu Recovery	Conc mass fr
	PAX (300 g/t)	Flotanol CO 7	Secondary collector (200g/t)		% Cu	% Cu	% Cu	% Cu	% Cu			
Test 1	10% PAX (3ml)	Frother (4 drops)	FC 7245 (0.179ml)	15 min	0.87	4.13		4.13	0.59	4.75	38.0%	0.074
Test 2	10% PAX (3ml)		FC 4146 (0.18ml)	15 min	0.87	3.48		3.48	0.54	4.00	45.0%	0.103
Test 3	10% PAX (3ml)	Frother (4 drops)	10% Na_2S (5ml)	8min PAX, 7 min Na_2S	0.87	2.10	2.86	2.33	0.72	2.68	27.0%	0.088