

OPTIMISATION OF THE FROTH FLOTATION PROCESS OF
CHINGOLA REFRACTORY ORES (CRO) BY RELEASE
ANALYSIS.

By

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A dissertation submitted in partial fulfillment of the requirements for the degree
of Master of Mineral Science in Metallurgy and Mineral Processing.

The University Of Zambia.

April, 2017.

ABSTRACT

Release analyses were done on the Chingola Refractory Ores (CRO), which is a mixture of refractory oxides and sulphide copper minerals with an average grade of 1.37% total copper (TCu) with the goal of optimising the froth flotation process of Chingola Refractory Ores. Cupriferous mica, chalcocite, bornite, chalcopyrite, malachite and pseudomalachite were the significant copper minerals in the ore.

The influence of mesh of grind of feed, collector and sulphidiser dosages on the flotation of CRO was investigated. The effect of grinding upon the liberation characteristics of the ore was also investigated. Bench scale flotation tests were carried out on samples ground for 2, 4, 8 and 16 minutes. Sodium isopropyl xanthate (SIPX) collector dosages of 30 grams per ton (gpt), 50 gpt and 70 gpt were used. The effect of a sulphidiser, Sodium hydrogen sulphide (NaHS) on the flotation of CRO was also investigated. Bench scale flotation tests were carried out at sulphidiser dosages of 200 gpt and 300 gpt.

The liberation of copper in CRO increased with increasing grinding time as evidenced by the decrease in release coefficient 'a' and the increase in release coefficient 'b' of the modified Hall equation. However, the flotation tests showed that there was an increase in the loss of copper as particle size decreased. Increasing the collector dosage increased the copper recovery. Increasing sulphidiser dosage decreased copper recovery. The best flotation performance was obtained by using SIPX at a dosage of 70 gpt on a sample ground for 2 minutes, where, a concentrate of 15.9% TCu was obtained with 17.8% recovery. Use of sodium hydrogen sulphide resulted in an increase in recovery for the fine sizes. The best results were achieved by using NaHS at 200 gpt, where, a concentrate with 28% TCu was obtained with a recovery of 13.5% from a sample ground for 16 minutes. Low recoveries and concentrate grades were attributed to the unfavourable flotation properties of the cupriferous micas. In addition, the presence of fast floating non-copper bearing micas in the gangue affected the recovery of the floatable copper minerals in the ore.

Going by the above findings, it is recommended to incorporate a sulphidisation stage in the flotation process. This would ensure that the process will recover both the copper oxide and sulphide minerals, thus, increasing the total copper obtained in the final concentrate. However, the sulphidisation stage should employ Sodium Sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) as the sulphidising agent. From literature $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ has yielded higher copper recoveries than NaHS. Additionally, it is recommended that flotation experiments be done using alkyl hydroxamates/ chelating reagents as collectors to improve the grade/recovery. The study also highlighted the importance of understanding the ore mineralogy in the development of a flotation procedure since all copper minerals respond differently to different flotation conditions. Further intensive study of the cupriferous mica is recommended to gain a better understanding of the nature of the copper in the mica structure.

Keywords: *Refractory ores, cupriferous mica, flotation.*

DECLARATION OF ORIGINALITY.

This is to certify that the work is entirely my own and not of any person, unless explicitly acknowledged (including citation of published and unpublished sources). The work has not been previously submitted in any form to the University of Zambia or any institution for any other purposes.

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CERTIFICATE OF APPROVAL.

This dissertation of Tinashe Oswald NDORO submitted to the Directorate of Research and Graduate Studies of the University of Zambia through the School of Mines, Department of Metallurgy and Mineral Processing was approved as fulfilling part of the requirements for the award of the degree of Master of Mineral Sciences in Metallurgy and Mineral Processing.

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ACKNOWLEDGEMENTS.

I wish to give praise and thanks to the Almighty God for taking me this far.

Special thanks goes to my supervisor Dr. L. K. Witika, for his encouragement, support, patience and contribution to my understanding of various aspects in this work and Dr. E. Siame, Head of Department, Metallurgy and Mineral Processing, School of Mines, University of Zambia for affording me an opportunity to use various facilities in the School.

I would also extend my special thanks to Mr. Pyokera Kawonga, Concentrator Manager – Nchanga Integrated Business Unit (NIBU), Konkola Copper Mines, Mr. Krassner Mandanji, Assistant Plant Manager Technical, Mr. Richard Chibulu, Assistant Plant Manager Technical, Ms. Zyola Nambeye, Plant Metallurgist Technical, Mr. Evans Chomba, Plant Metallurgist Technical, Mr. Edmond Miyaji, Plant Metallurgist Technical and all the Nchanga Concentrator Laboratory staff, for the permission to use their mine ore samples and to carry out part of my work in their laboratories.

My gratitude also goes to my colleagues Takunda Joseph Mhandu and Tichaona Mukono for their brotherly love and encouragement.

Lastly and most importantly, I wish to express my heartfelt thanks and appreciation to my lovely family, Oswald T.P. Ngoro, Junior Ngoro, Tafadzwa Ngoro, Takudzwa Ngoro and my love Felisters Zvavamwe for their love, support and patience over the long journey. I am forever grateful.

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LIST OF ABBREVIATIONS.

AICu	Acid insoluble copper
ASCu	Acid soluble copper
C1	Concentrate 1
Cu	Copper
CRO	Chingola Refractory Ores
KCM	Konkola Copper Mines
NaHS	Sodium Hydrogen Sulphide
NIBU	Nchanga Integrated Business Unit
SIPX	Sodium Isopropyl Xanthate
SP12	Stockpile 12
%TCu	Total copper percentage
Micron (µm)	Micrometres

CHAPTER ONE.

1.0. INTRODUCTION.

The high demand for metals coupled with the advancement of technology has led to the exploitation of low-grade ore deposits around the world, and particularly in Zambia. The treatment of low-grade and complex mineral deposits and the high demand for metals have resulted in the need for large throughput plants to deliver increased productivity, increased utilisation and reduced operational cost. The Zambian Copperbelt presents a typical example of increased treatment of low-grade deposits, where, in the 1960s to the early 1980s, most of the copper mines treated ores with grades approximately 2.5% TCu and stockpiled what was considered as low-grade ore (**Guilbert & Park, 1986; Sondashi, 2015**). However, by 2006 some of the mines were treating low-grade refractory ores with grades as low as 1% TCu (**Sondashi, 2015**).

Nchanga mine is situated on the Zambian Copperbelt in Chingola. The Copperbelt is a north-west trending zone 150km long by 50km wide, extending from the Luanshya mine in the south to the Konkola mine near the town of Chililabombwe in the north. Together with the Copperbelt of the Democratic Republic of Congo (DRC) situated across the border immediately to the north, the Zambian Copperbelt constitutes one of the world's great mining regions, characterised by the size and quality of its copper and cobalt deposits.

1.1. BACKGROUND OF STUDY.

Cupriferous mica ores, now referred to as the Chingola Refractory Ores (CRO), were identified in Chingola in the early 1950's. In the years following, it became evident that vast reserves of low-grade micaceous ores, in which the majority of the copper is incorporated in a mica-type structure, existed in the Chingola area. Owing to their poor response to conventional metallurgical treatment methods and to the difficulties of visual recognition, the full significance of these deposits was not appreciated until after 1954, when mining of the Nchanga pit commenced.

The cupriferous mica deposits at Chingola occur in separate stratigraphic units adjacent to normal mixed oxide-sulphide orebodies and extend down to depths in excess of 300m. The largest deposits of low-grade cupriferous mica are located in the gently sloping south limb of the main Nchanga syncline and occur in the Dolomitic Schist and Upper and lower Banded Sandstone formations. The rock is generally soft and poorly coherent. The cupriferous micas are associated with small quantities of conventional oxide copper minerals: malachite,

pseudomalachite and chrysocolla. In some areas these minerals contribute significantly to the total copper content. The oxide-sulphide mineralogical composition of these ores is shown below in Table 1.1.

Table 1.1: Nchanga Chingola Refractory Ores oxide-sulphide mineralogical composition.

Ore Mineralogical Composition	
Chalcopyrite	CuFeS_2
Bornite	Cu_5FeS_4
Chalcocite	Cu_2S
Pyrite	FeS_2
Carrollite	$\text{Cu}(\text{Co}, \text{Fe}, \text{Ni})_2\text{S}_4$
Native Copper	Cu
Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
Pseudo malachite	$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$
Chrysocolla	$(\text{Cu}, \text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4\text{nH}_2\text{O}$

Owing to their poor response to conventional methods of metallurgical treatment, the refractory ore was stockpiled separately from waste during the mining of the Nchanga Open Pit (NOP) as it was considered to be uneconomic to treat at that time. However, the partially refractory low-grade ore is now being reclaimed from the stockpiles and being treated by conventional flotation methods to produce an oxide-sulphide concentrate to be treated in Nchanga Smelter. However, only 5% of the total copper in the ore has been recovered. This has prompted the technical staff to embark on carrying out a lot of work in an attempt to come up with various ways of optimising the flotation process of these ores but, unfortunately, no conclusive results have been obtained as yet. The Concentrator Technical Staff hence proposed to carry out various test-works at laboratory scale, in an effort to optimise the concentrate recoveries and grades of the CRO. Preliminary laboratory flotation test-works have given rougher concentrates of grades ranging between 1-2% TCu against a target of concentrates of grades ranging between 3-4% TCu, which guarantees that after cleaning on the plant, a minimum grade of at least 15% TCu is obtained as a final concentrate grade.

1.2. AIM OF STUDY.

This study aims at optimising the froth flotation process of CRO by using release analysis.

1.3. STATEMENT OF THE PROBLEM.

Despite carrying out a lot of work, in an effort to find ways of optimising the plant recoveries and concentrate grades of the CRO, inconclusive results have been obtained so far. Preliminary conventional laboratory scale flotation tests have failed to give the target rougher concentrate grades ranging 3-4% TCu. As a result, the plant has failed to produce a final cleaner concentrate of grades ranging 15-16% TCu, which is ideal for the Nchanga Smelter. Thus, there is need to carry out various laboratory test-works, to optimize the plant recoveries and concentrate grades of Nchanga Chingola Refractory Ores (CRO) by release analysis.

1.4. OBJECTIVES OF THE STUDY.

The long term aim of the research is to establish the optimum concentrate recoveries and grades when treating the Chingola Refractory ores. The main objective of the study is to provide a comprehensive review of literature and industry practices in relation to flotation of copper minerals and optimise the froth flotation process of the CRO. Particularly, the study has the following sub-objectives:

- i. To determine the flotation response of CRO with Sodium Isopropyl Xanthate (SIPX).
- ii. To investigate the effect of Sodium Hydrogen sulphide (NaHS) on the flotation of CRO.

1.5. APPLICABILITY OF RESEARCH.

The variability of feedstock quality delivered to flotation plants in mining operations can present a lot of challenges to the Technical Staff, in attempting to achieve targeted plant recoveries and concentrate grades. When faced with variable ore, the plant operators are often required to implement operational parameter changes to maintain process efficiency. This research, therefore, seeks to improve the understanding of the factors affecting the flotation of mixed copper oxidic-sulphidic ores and providing some possible solutions to these challenges.

CHAPTER TWO.

LITERATURE REVIEW.

2.0. INTRODUCTION.

This review of literature begins with the background of froth flotation fundamentals. The use of flotation reagents, such as collectors, frothers and modifiers is provided. Copper sulphide flotation is reviewed as it is assumed to be similar to the behaviour of sulphidised oxide mineral particles as applied in the flotation of refractory copper ores. Previous studies of refractory copper ores flotation are reviewed. Finally, release analysis is reviewed as a method of characterising the flotation response of a given ore, under specific conditions.

2.1. FROTH FLOTATION FUNDAMENTALS.

Froth flotation is defined as a physico-chemical process which exploits the differences in the electrochemical properties of mineral surfaces, that is, between hydrophobic and hydrophilic surfaces, which either occur naturally or are artificially induced by chemical reagents (**Yuan et al, 1996; Sripiya et al, 2003; Bulatovic, 2010**). Figure 2.1 shows the principle of froth flotation.

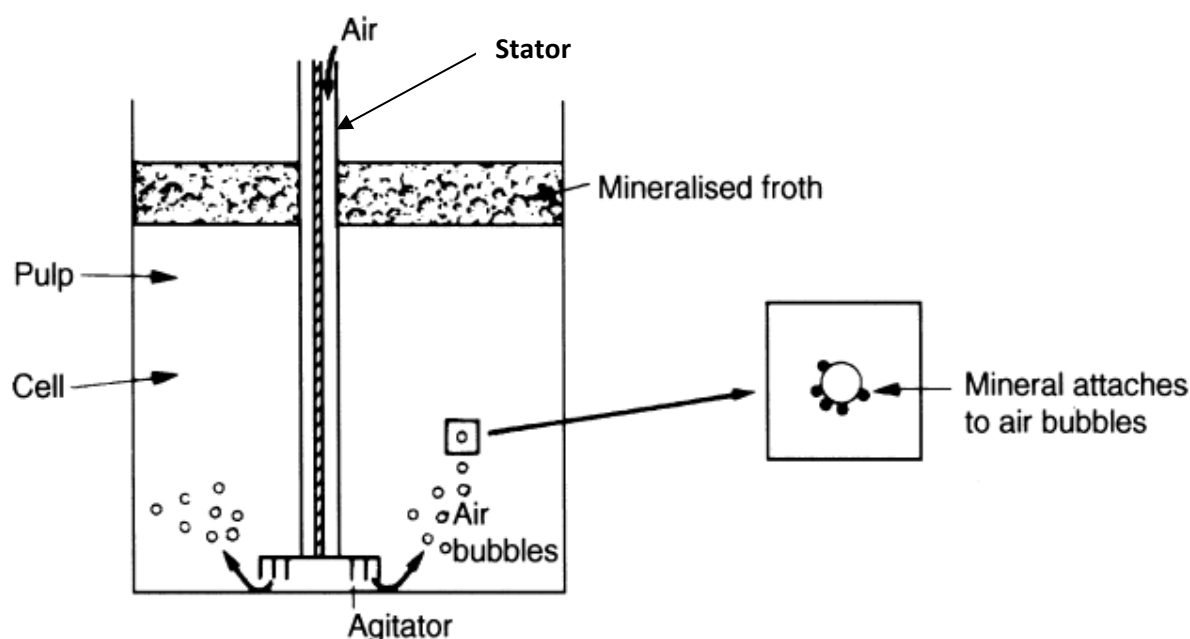


Figure 2.1: Principle of flotation (Wills and Napier-Munn, 2006).

Froth flotation can be regarded as a system, with various sub-processes and interactions (**Klimpel, 1995**). For flotation to take place, an air bubble must be able to attach itself to a

particle in the mineral suspension known as flotation pulp. For this to happen, the particle should be small enough to adhere and be carried by the bubble to the surface into the froth layer, otherwise the particle will drop off the bubble, when the bubble starts to rise. As such, froth flotation is mainly used in the separation of fine particles.

Therefore, froth flotation pulps consist of mixtures of solid particles in an aqueous solution, with small additions of surface active agents and air bubbles. The active agents are either inorganic or organic reagents. Hence, in any flotation pulp all three phases, solid, liquid and gaseous are present. The properties of the bulk phases influence and determine the characteristics of the interfaces formed between the adjoining phases (Sondashi, 2015).

In the three-phase system created, three interfacial tensions are present as shown in Figure 2.2: the solid-air (γ_{sa}) tension, solid-liquid (γ_{sl}) tension and liquid-air (γ_{la}) tension. These interfacial tensions develop an angle between the mineral surface and the bubble surface.

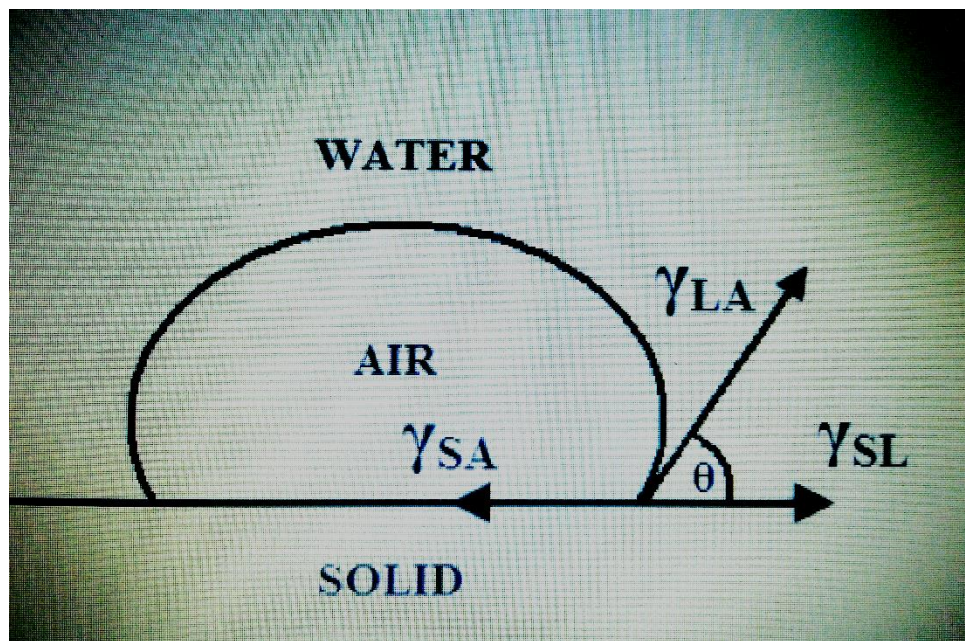


Figure 2.2: Contact angle between bubble and particle in an aqueous medium (Numprasanthai, 2013).

At equilibrium these forces give a relationship frequently referred to as the Young's modulus equation;

$$\cos \theta = \frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} \dots \dots \dots (2.1)$$

where, γ_{sa} , γ_{sl} and γ_{la} are the surface tensions between solid-gas, solid-liquid and liquid-gas respectively and θ is the contact angle between the mineral surface and the bubble.

On the other hand, the force required to break the particle-bubble interface, called the work of adhesion, is equal to the work required to separate the solid-gas interface and to produce separate gas-liquid and solid-liquid interfaces was derived by Dupre as;

$$W_{sa} = \gamma_{la} + \gamma_{sl} - \gamma_{sa} \dots \dots \dots (2.2)$$

Combining equations 2.1 and 2.2 gives;

$$W_{sa} = \gamma_{la}(1 - \cos \theta) \dots \dots \dots (2.3)$$

From equation 2.3 it can be seen that the hydrophobicity of a mineral increases with the contact angle; minerals with a high contact angle are said to be aerophilic, that is, they have a higher affinity for air than for water (**Wills and Napier-Munn, 2006**).

Successful industrial practice of flotation (**Kohad, 1998; Wills and Napier-Munn, 2006**) involves knowledge and optimisation of four important components of flotation process, namely:

- i. Mineralogical characteristics of the ore (mineral association, liberation size, presence of slime particles and soluble species contributed by the ore).
- ii. Surface colloid and reagent chemistry which determines selectivity of separation (collectors, frothers, activators, depressant, modifiers and dispersant).
- iii. Process engineering (feed preparation (size reduction), cell design and control system).
- iv. Operating parameters such as aeration rate, temperature, Eh/pH, ionic strength and flotation circuit configuration.

Also overall separation (**Kohad, 1998; Wills and Napier-Munn, 2006**) efficiency in flotation is dependent on:

- i. Surface chemistry factors such as bubble attachment, mineral reagent interactions and reagent chemistry. These factors are related to equilibrium considerations contributing selectively to separation.
- ii. Hydrodynamics factors which contribute to the kinetics of flotation such as agitation, air flow rate, dispersion and cell design control recovery of minerals.

In the flotation process a number of physico-chemical variables are important. According to **Kohad, (1998)** and **Wills and Napier-Munn, (2006)**, the important physico-chemical variables in flotation are:

- i. Role of mineral/water interface.
- ii. Surface charge on the minerals.
- iii. Effect of hydrocarbon length of the collector.
- iv. Effect of neutral molecules.
- v. Role of polar functional group of the collector.
- vi. Role of solution chemistry of the collector.
- vii. Role of inorganic ions (activator and depressant).
- viii. Effect of temperature.
- ix. Ore properties such as grade, mineralogy, degree of oxidation and liberation of minerals.

2.2. FLOTATION REAGENTS.

Reagents are the most important part of the flotation process (**Bulatovic, 2007**). The selection of reagents is of great importance for the process to give the most effective separation and concentration results. Thus, in commercial plants, the control of reagent additions is the most important part of the flotation process. Flotation reagents can be categorised into three main classes, on the basis of the function of a particular reagent. They are divided into collectors, frothers and modifiers.

2.2.1. COLLECTORS.

Collectors are basically organic chemical compounds, which differ in chemical composition and function. The basic purpose of the collector is to selectively form a hydrophobic layer on a given mineral surface in the flotation pulp and thus provide conditions for attachment of the hydrophobic particles to air bubbles and recovery of such particles in the froth product. Collectors can be divided into distinct groups according to their ability to dissociate in water. Figure 2.3 shows the classification of collectors.

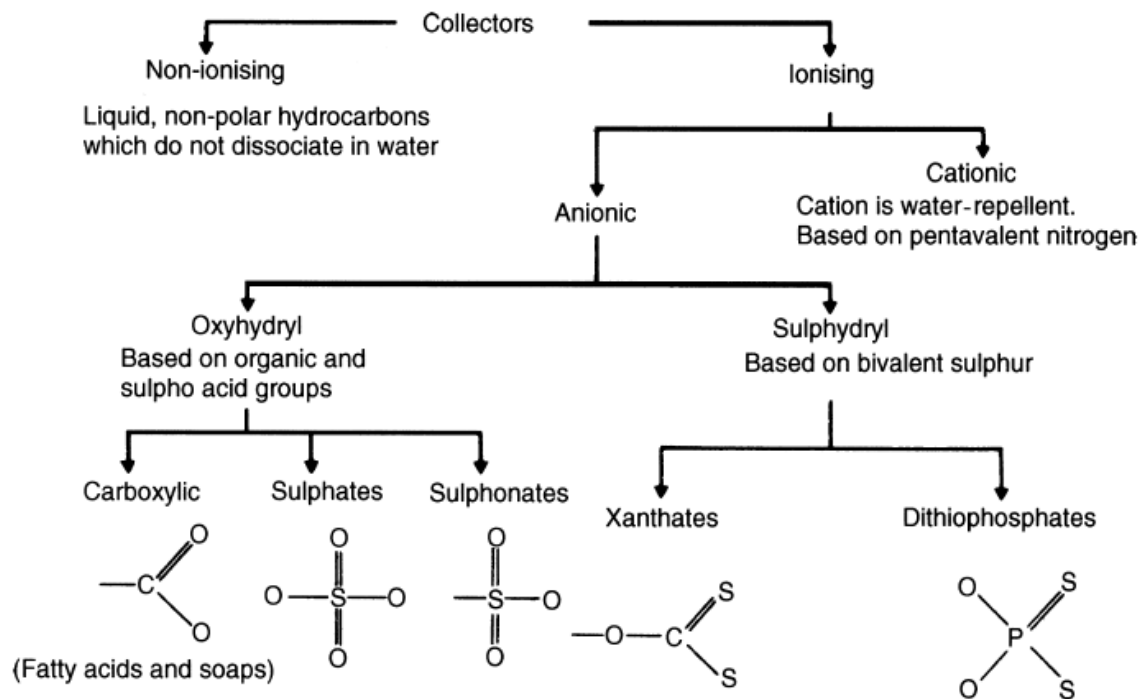


Figure 2.3: Classification of collectors (Wills and Napier-Munn, 2006).

2.2.2. FROTHERS.

Frothers are heteropolar surface-active compounds that lower the surface tension of water and have the ability to adsorb onto the air bubble–water interface. Their presence in the liquid phase increases the film strength of the air bubbles, thus providing better attachment of hydrophobic particles to the bubbles. The heteropolar structure of the frother makes the non-polar group to orientate towards air and the polar group towards water as shown in Figure 2.4.

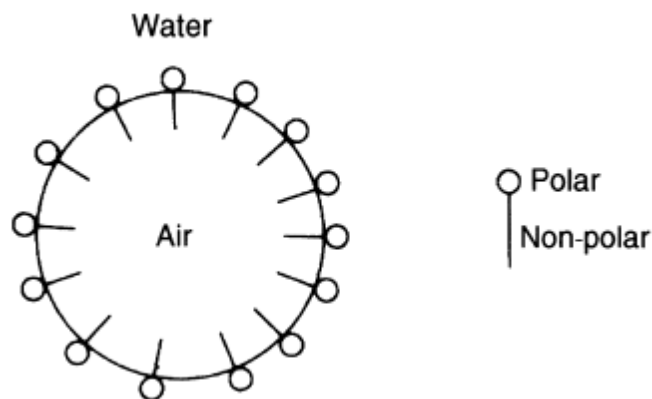


Figure 2.4: Action of Frother (Wills and Napier-Munn, 2006).

A good frother should have no collecting power but should be able to ensure that the floated minerals are transferred from the float cell to a collecting launder (**Hughes, 2005; Wills and Napier-Munn, 2006**). Frothers must be to some extent soluble in water so that they are evenly distributed in an aqueous solution, to ensure that their surface active properties are effective (**Wills and Napier-Munn, 2006; Bulatovic, 2007**). The effectiveness of frothers is dependent on their composition and Figure 2.5 shows the respective groups.

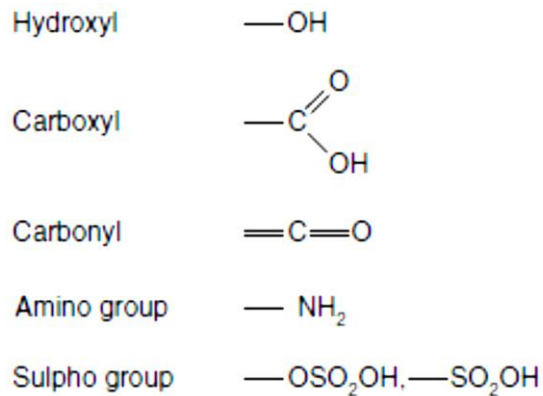


Figure 2.5: Functional groups in effective frothers (Wills & Napier-Munn, 2006).

The most widely used frothers include natural chemicals such as pine oil, cresylic acid, and synthetic reagents such as methyl isobutyl carbinol (MIBC) and polyglycol ethers (**Bulatovic, 2007; Numprasanthai, 2013; Sondashi, 2015**). However, alcohols (OH) are the most commonly used, since they have no collector properties and in this respect are preferable to other frothers such as carboxyls, which are also powerful collectors.

2.2.3. MODIFIERS.

Modifiers are chemicals used extensively in flotation to modify the action of the collector, making collector action more selective towards certain minerals (**Wills and Napier-Munn, 2006; Bulatovic, 2007**). Modifiers can be classed as activators, depressants and pH modifiers. Activators react with the mineral surface so that they become hydrophobic due to the action of the collector, depressants increase the selectivity of flotation by rendering certain minerals hydrophilic and pH modifiers regulate the ionic composition by changing the ion concentration of the hydrogen ion in the pulp (**Bulatovic, 2007**). Table 2.1 shows some of the modifiers used in sulphide and non-sulphide mineral flotation.

Table 2.1: Modifiers used in sulphide and non-sulphide flotation (Nagaraj and Ravishankar, 2007; Bulatovic, 2007).

Inorganic	Small organic	Polymeric molecules
Ammonium sulphide (sporadic)	Mercaptoethanol (sporadic)	Carboxymethylcellulose (CMC)
Ca, Mg, Al and Fe salts	Organic dyes (sporadic)	Dextrin
Copper sulphate	Polyamines (diethyleneamine [DETA], triethyleneamine [TETA])	Guar gum
Hydrofluoric acid	Sodium thioglycolate and its thiocarbonate derivative (sporadic)	Modified guar
Lead nitrate	Surfactants (mostly non-ionic and anionic; sporadic in sulphides, more regular in non-sulphide)	Lignin sulphonates
Lime	Tannins or quebracho (sporadic in sulphide, more regular in non-sulphide)	Polyacrylates
Phosphoric acid		Synthetic functionalised polymer
Sodium and zinc cyanide		
Sodium ferro-cyanide (sporadic)		
Sodium hypochlorite		
Sodium meta and polyphosphates		
Sodium metasilicate		
Sodium sulphide and hydrosulphide		
Sodium sulphide and sulphur dioxide		
Sulphuric acid		
Zinc sulphate		

2.3. FLOTATION OF SULPHIDE ORES.

Sulphide ores are the major sources of base metals like Copper, Lead, Zinc, Nickel and Cobalt (**Bulatovic, 2007; Newell et al, 2007**). Beneficiation of these base metal sulphide minerals is predominantly through the froth flotation technique.

Some of the most important sulphide minerals are: Galena (PbS), Sphalerite (ZnS), Chalcocite (Cu₂S), Covellite (CuS), Chalcopyrite (CuFeS₂), Pyrite (FeS₂) and Molybdenite (MoS). According to **Kohad, (1998)** distinguishing features of these minerals are:

- i. The minerals are covalently bonded compounds and possess very low solubility; each of these minerals has a definite solubility product in water.
- ii. Sulphide minerals are meta-stable and are prone to surface oxidation in the presence of water and oxygen.
- iii. Minerals are electronic semi-conductors which can act as a source or sink for electrons and therefore can support electrode reaction at the surface.
- iv. Most of the sulphide minerals are regularly charged in working range of pH and therefore the electrical double layer interaction oppose the adsorption of commonly used anionic reagents.
- v. Some of the sulphides have feeble natural hydrophobicity. Some of these are capable of rapid and complete flotation in the absence of conventional collectors.
- vi. One of the important consequences of the electrochemical nature of the surface reaction is the galvanic interaction between the grinding media and the sulphide minerals.
- vii. Sulphide ore minerals are generally floated using thiol type reagent xanthates and dithio-phosphates. Oxidised minerals do not respond to these collectors and hence require surface modifying treatment.

Sulphide copper ores are considered easy to treat provided that the main copper mineral is chalcopyrite (**Bulatovic, 2007; Muganda et al, 2011**). However, in case the ore contains secondary copper minerals, such as chalcocite, bornite and covellite, the depression of pyrite may be a problem because the pyrite can be activated by copper ions generated during the grinding operation (**Bulatovic, 2007**). Some copper sulphide ores can be partially oxidized, also influencing the selection of a reagent scheme. Copper sulphide ores are normally finer grained than porphyry copper ores and require finer grinding (i.e. 70–80% less than 200 mesh) (**Bulatovic, 2007**).

2.3.1. REAGENTS USED IN THE FLOTATION OF SULPHIDE ORES.

Commonly used reagents in industrial flotation plants are Collector, Frother, Activator, Depressants and pH modifiers. Of the above, collectors are the most important reagents which play a critical role in sulphide flotation. Sulphydryl or thiol type collectors which in general consist of the “SH” group in combination with an organic radical have extensive application

Extensive research has been carried out to understand surface chemistry and interaction between collectors and sulphides (**Fuerstanaue et al, 2000; Bulatovic, 2007**). Some of the important aspects as listed by **Kohad, (1998)** are:

- i. Interaction between sulphide minerals and thiol collectors takes place by a corrosion type mixed potential mechanism involving simultaneous electrochemical reactions at mineral water interface.
- ii. Potential difference of the mineral solution interface is the most important parameter determining the rates of reactions causing flotation which is termed as Redox Potential (Eh). By monitoring oxidation/reduction environment of the pulp, Eh can be controlled and can be used as one of the on-line control parameters of flotation process in the plant for naturally or weakly floatable sulphide minerals.
- iii. In order to enhance the selectivity of collection, many modifying agents like activators and depressors are used for soluble sulphide minerals.

However, it has been reported that flotation kinetics/selectivity of many soluble sulphides, for example, sphalerite and pyrrhotite requires activation under normal flotation conditions. Longer chained xanthates are generally used for improving selectivity (**Rickelton, 1972**) and research work has confirmed a relationship between carbon number, flotation response and solubility product of corresponding metal xanthates. Xanthate collectors are not capable of recovering ultra-fine particles (less than 10 μ m) and significant losses can occur in the fine fraction. They are not selective with respect to iron sulphide. The average consumption of xanthate is reported to be relatively high, ranging from 50 to 150 grams per mega tonnes (**Kohad, 1998**). Therefore, a mixture of two or three types of xanthates at different stages of collection also in combination with dithio-phosphates and certain nitril compounds, are being used in many sulphide flotation plants.

The choice of collector also depends on the nature and occurrence of copper and associated sulfides. In most cases, xanthate collectors are used alone or in combination with dithiophosphates or thionocarbamates (**Bulatovic, 2007**). Dithiophosphates and thionocarbamates are normally used when secondary copper minerals are present in the ore or when the copper flotation is carried out at lower pH (**Bulatovic, 2007**).

Another important parameter which has a remarkable effect on the flotation of sulphide minerals is pH. It is established that xanthates decompose in acidic environment and hence, resulting in lower flotation recovery (**Kohad, 1998**). Thus, through proper pulp pH control selective flotation of one sulphide from another can be achieved.

As regards other reagents used in sulphide flotation, depressants like Sodium Cyanide, Zinc Sulphate and Sodium Meta bi-sulphide are common (**Kohad, 1998; Nagaraj and Ravishankar, 2007**). Cyanide has been used as a depressant and deactivator in the flotation of sulphide minerals (**Wang & Forssberg, 1996; Bulatovic, 2007; Nagaraj and Ravishankar, 2007**). However, the actual effect of cyanide in the flotation process is still not clear and depends greatly on solution chemical conditions and the reaction time. It has been reported that cyanide activates, rather than depresses flotation under some cases (**Glembotskii et al, 1963; Vreugde, 1982; Nagaraj and Ravishankar, 2007**). The effectiveness of a depressant depends on the concentration and selection of collector(s) (**Kohad, 1998; Bulatovic, 2007**).

Pine oil, Methyl isobutyl carbinol (MIBC) and Cresylic acid are commercially used as frothers in sulphide flotation depending upon overall economics and the nature of frothers, whether brittle or hard, and froth bubble size required (**Kohad, 1998**). Frother choice varies from (**Bulatovic, 2007**) one ore type to the other and most commonly, an alcohol-type frother is used. The exception is when clay slimes are present in the ore; then a mixture of two frothers or a glycol-type frother is employed.

If the sulphide is associated with oxides and oxide minerals, the ore is subjected to sulphidising by sodium sulphide, followed by flotation with xanthate or metacaptobenzols and mecarptans (**Kohad, 1998; Bulatovic, 2007; Dianwen, et al., 2012**). The sulphidising process needs to be monitored carefully, generally done in stages and preferably through control of pulp Eh. Chelating agents and cationic collectors are also used for flotation of oxidised minerals (**Fuerstanau et al, 2000; Bulatovic, 2007**).

2.4. FLOTATION OF OXIDE COPPER MINERALS.

Oxide copper minerals are an important copper resource (**Lee et al., 1998; Hope et al, 2012; Xiong and Zheng, 2013; Mao et al, 2014**). The oxide copper minerals are found in weathered regions of most copper sulphide ore bodies (**Lee et al., 1998; Mulaba and Bell, 2005**). The overlaying oxide ore is usually stockpiled after it is removed from the sulphide lode and left unprocessed as the sulphide ore is simpler to recover by conventional flotation procedures and thus, more attractive to the plant operator. Oxide ore can be concentrated using flotation or, if it has a low acid demand, it may be economic to acid heap leach the stockpile (**Lee et al., 1998; Mulaba and Bell, 2005; Phetla and Muzenda, 2010**).

The concentration of oxidised copper minerals by flotation has been extensively studied (**Glembotskii et al, 1963; Coelho, 1972; Lee et al., 1998; Hope et al, 2012; Xiong and Zheng, 2013; Mao et al, 2014**). Flotation of oxidised copper minerals has been applied in Central Africa, especially Congo (**Kongolo et al, 2003; Bulatovic, 2007; Phetla and Muzenda, 2010**). However, oxide copper minerals do not generally respond well to traditional concentration methods using known sulphide copper collectors. **Marabini et al. (1991)** noted that surface properties of copper oxide minerals are a significant factor in their problematic recovery. **Barbaro et al., (1997)** highlighted that copper oxide minerals are prone to dissolution, lack mechanical strength and possess strongly hydrophilic surfaces, which are difficult to transform into hydrophobic surfaces. Conventional sulphide copper collectors fail to adhere to the oxides, resulting in excessive collector consumption, limited selectivity and poor recovery (**Numprasanthai, 2013**). Additionally, the mineral assemblage in oxidised copper zones contains gangue that also creates slimes, detrimental to recovery, grade and frothing conditions (**Poling, 1973**). Thus, their recovery in a froth flotation circuit requires special treatment. The flotation process used has two most common approaches:

- i. Fatty acid flotation of oxide copper minerals from siliceous ore (**Deng and Chen, 1991; Lee et al, 1998; Lee et al, 2009; Mulaba and Bell, 2005**).
- ii. Sulphidisation of oxide minerals using sodium sulphide (Na_2S), sodium hydrosulphide (NaHS), or ammonium sulphide ($(\text{NH}_4)_2\text{S}$) followed by flotation using xanthate or other sulphide collectors (**Saquet, 1962; Dianwen, et al., 2012**).

Although a number of other methods have been proposed for the flotation of these ores, only a few have advanced beyond the laboratory stage. However, the flotation of most oxidised copper minerals is difficult.

One of the major problems with flotation of copper oxide minerals, at industrial scale is that the floatability from natural ores depends largely on the mineralogy of the ore and the gangue composition (**Bulatovic, 2007**). As such, the floatability of copper oxide minerals that are present in the ore containing carbonaceous and dolomitic gangue is significantly different from the flotation properties of oxide copper containing siliceous gangue minerals.

Direct flotation of ores containing carbonaceous and ferruginous gangue gives poor results because of the non-selectivity of collection. The presence of various types of clay in the ore has a significant effect on flotation properties of oxide minerals (**Coelho, 1972; (Bulatovic et al, 1979; Bulatovic, 2010)**). According to **Coelho, (1972)** prior de-sliming may permit successful flotation of malachite and azurite ores. In some cases, treatment of the pulp with flocculants such as acrylic acid polymers may be used as a substitute for the de-sliming step (**Bulatovic, 2007**).

Long chain carboxylic collectors such as oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$) or their salts, in the pH range of 8 to 10.5, have been known to give good recovery of malachite and azurite but mediocre recovery of cuprite and tenorite (**Coelho, 1972**).

It has also been reported that sulphhydryl compounds are also effective collectors for the carbonates of copper but excessive amounts of these reagents are required for good recoveries if used alone. Sulphidisation (using Na_2S , H_2S or molten sulphur) can reduce collector consumption. However, the amount of sulphidising agent is critical because a slight excess leads to lack of floatability (**Lee et al, 2009**). Hence, stepwise sulphidisation is becoming the standard procedure (**Bulatovic, 2007; Phetla and Muzenda, 2010**).

2.4.1. OXIDE COPPER ORES AND MINERALS.

Of the 120 oxide-containing minerals identified mainly from the Central and South African regions, only a few have any economic value. Some of the most important copper oxide minerals (**Bulatovic, 2010**), are listed in Table 2.2.

Table 2.2: Economically valuable copper minerals (Bulatovic, 2010).

Mineral	Chemical formula	Copper content (% TCu)	Specific Gravity (SG)	Colour
Cuprite	Cu_2O	88.8	5.9	Brick red
Tenorite	CuO	80.0	6.5	Black
Malachite	$\text{Cu}_2(\text{OH})\text{CO}_3$	57.4	3.9	Green
Azurite	$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	55.3	3.7	Blue
Bronchantite	$\text{Cu}_4(\text{OH})_6\text{SO}_4$	56.6	3.9	Emerald green
Atacamite	$\text{Cu}_2(\text{OH})_2\text{Cl}$	44.6	3.8	Green, blue
Antlerite	$\text{Cu}_3(\text{OH})_2\text{SO}_4$	54.0	3.9	Emerald green
Chrysocolla	$\text{CuO} \cdot \text{SiO}_2$	10 – 36	2.2 – 4	Blue
Chaecantite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	25.5	2.2	Deep blue

The most significant industrially beneficiated copper minerals among the oxide copper ores listed in Table 2.2 are Malachite and Azurite, whereas Chrysocolla and Cuprite are the less important (Glembotskii et al, 1963; Bulatovic, 2010). Most of the known copper oxides deposits are located in the Republic of Congo (Katanga) and Zambia whereas only a few deposits are located in Chile, Peru, Canada and the United States.

Usually, oxide copper ores contain more than one copper oxide mineral, and also contain mixtures of copper sulphide/ oxide minerals. According to Bulatovic (2010), the copper oxide ores can be divided into the following five groups:

- i. **Copper oxide ores** – ore is predominantly malachite with significant quantities of cobalt. The ores can be further sub-divided into two main groups on the basis of mineral composition: (a) oxide ore that contains carbonaceous gangue minerals (carbonate, dolomite) with little or no silica; and (b) oxide ore, where silica is the predominant gangue mineral. The gangue composition of the ore plays a decisive role in selection of reagent scheme for the beneficiation of the ore. These ores also contain cobalt minerals, mainly carrolite (Co_2CuS_4) and cobaltite (CoAsS).
- ii. **Copper oxide mixed ore (Type I)** – the main copper minerals found in these ores include malachite, pseudo-malachite, chrysocolla and some tenorite. Ores may also contain mainly siliceous gangue minerals, including sphaerocobaltite as the main

cobalt minerals. The carbonaceous types also contain an appreciable amount of clay slime minerals.

- iii. ***Copper oxide mixed ore (Type 2)*** – in contrast to Type 1, this ore type contains cuprite, malachite and azurite as the main copper oxide minerals. Predominantly contains carbonaceous gangue, and usually, significant amounts of clay-like slimes.
- iv. ***Mixed copper sulphide/oxide ores*** – these contain varieties of both sulphide and oxide minerals, and are the most complex copper-bearing ores from a beneficiation point of view. The major copper minerals present in this ore type include bornite, chalcocite, covellite, malachite, cuprite, and chrysocolla. Significant amounts of cobalt minerals may also be present in this ore.
- v. ***Copper oxide gold ores*** – this ore type is not abundant but is of significant value because it contains gold. The few known deposits are in Brazil and Australia. Copper in these ores is represented by cuprite, native copper, antlerite and tenorite. The gold is associated with cuprite, as an auricupride and several sulphosalts. The major problem associated with treatment of this ore type is the presence of large amounts of clay slimes in the form of iron hydroxide and illite.

2.4.2. FLOTATION PROPERTIES OF INDIVIDUAL COPPER MINERALS AND MIXTURES.

According to **Bulatovic (2010)** the flotation characteristics of copper oxide minerals from natural ore are dependent on a number of factors, some of which include:

- 1) Chemical composition and physical structure of the copper oxide minerals and the ionic composition of the slurry phase. The oxide minerals are often porous and in some cases, water soluble. Some of the oxide minerals tend to slime during grinding, and flotation of fine oxide minerals is to a greater extent difficult.
- 2) The gangue constituents and their nature are sometimes determining factors in the selection of a treatment process for beneficiation of oxide copper ores. Highly weathered ores usually contain a fairly large amount of slimes, which has a negative effect on the floatability of copper oxide minerals. Also, there is an appreciable difference in floatability between oxide minerals from carbonaceous and siliceous ores.
- 3) The mechanical strength of the surface layers of many of the copper oxide minerals is weak. Therefore, flotation of copper oxide ores using sulphidisation method, can improve by reducing turbulence and attrition within the flotation cell.

Floatability of malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) is one of the most important aspects for production of copper from oxide ores using flotation. Various flotation methods have been examined by a number of researchers (**Normand, 1974; Saquet, 1975; Phetla and Muzenda, 2010**). In a number of oxide ores, cuprite (Cu_2O) is present as a secondary mineral together with sulphides, malachite and tenorite. Cuprite can be floated using either sulphidisation or anionic flotation methods. The flotation properties are to a less extent different from those of malachite. For example, using a sulphidisation method for flotation of cuprite requires higher dosages of the sulphidiser. Laboratory studies conducted on these types of ore indicated that improved metallurgical results can be achieved by using the sulphidisation method with an ester-modified xanthate (**Bulatovic, 1996**).

Tenorite (CuO) is usually present in mixed copper oxide/sulphide ore. The flotation properties of tenorite are similar to those of cuprite. Azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$) usually appears in small quantities together with malachite in a number of deposits in Zambia and the Democratic Republic of Congo. Plant and laboratory data showed that azurite has similar flotation properties as malachite (**Bulatovic, 2010**).

Chrysocolla (CuO_xSiO_2) is the most studied of all the copper oxide minerals (**Bulatovic, 2010**). Numerous researchers have carried out extensive laboratory studies (**Castro et al, 1976; Gonzales, 1978; Hope et al, 2012**). Laboratory research work has shown that chrysocolla can be floated using the sulphidisation method, as shown in Figure 2.6 or by hydroxamate collectors.

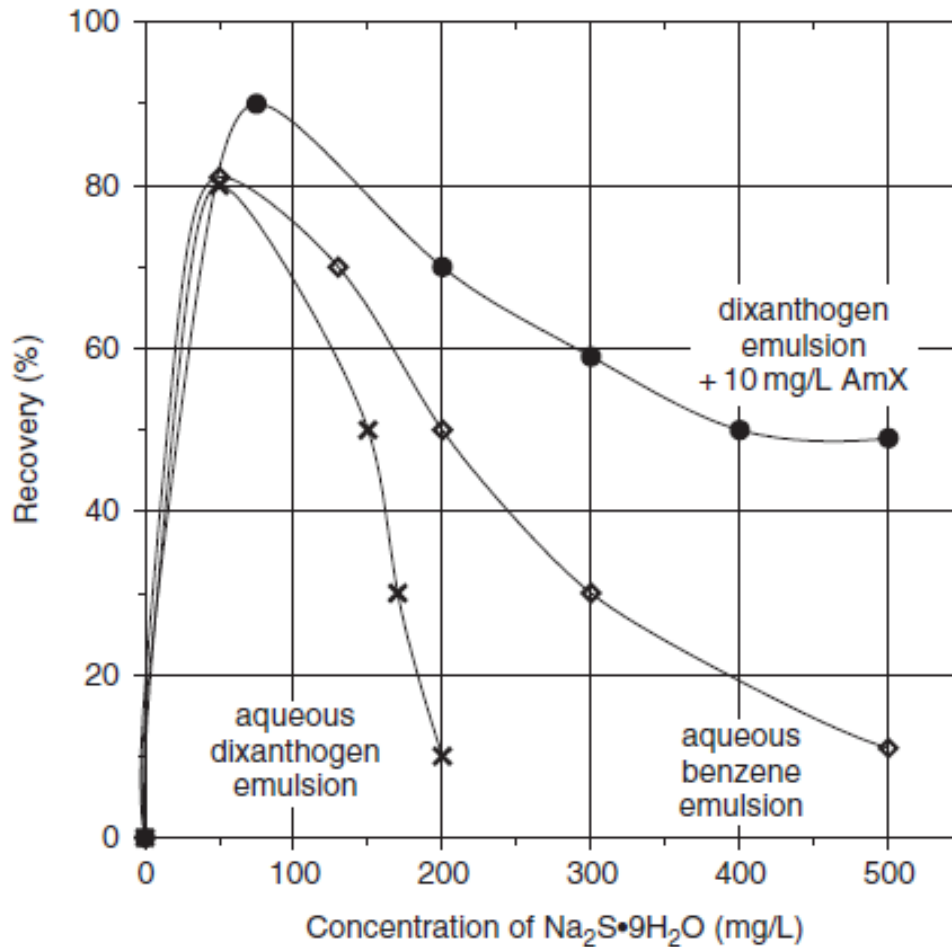


Figure 2.6: Effect of Na_2S on the flotation of Chrysocolla (Bulatovic, 2010).

2.4.3. FLOTATION PRACTICE IN THE BENEFICIATION OF OXIDE COPPER MINERALS.

The selection of a reagent scheme for the beneficiation of oxide copper ores depends on a number of factors and some of the important ones are:

- 1) Type of oxide copper minerals present in the ore.
- 2) Type of gangue minerals - some ore types contains silicate gangue free of slimes, which are the most amenable to flotation. Ores with dolomitic gangue can be beneficiated using sulphidisation only. In general, each ore type requires a selection of different reagent schemes.
- 3) Degree of liberation - the relatively fine-grained ores are more amenable to flotation than the finely disseminated ones, which require finer grinding.

- 4) Chemical composition and physical structure of the copper minerals play an essential role in the floatability of oxide copper minerals (**Aplan and Fuerstanau, 1962; Bulatovic, 2007**).

From plant practice, the treatment of oxide copper and copper cobalt ores is being carried out by the following methods: a) Sulphidisation flotation method, b) The carboxylic/fatty acid process and c) The use of alkyl hydroxamates/ chelating reagents.

2.4.3.1. The sulphidisation process.

This process was first applied on lead carbonate ores and is now the most widely used method in the beneficiation of oxide copper-bearing ores. The reagent schemes used to treat oxide copper ores, mixed copper sulphide oxide ores and oxide copper/cobalt ores varies from one ore type to the next, mainly by type of collector and sulphidiser used. The choice of reagent scheme depends largely on the type of natural ore to be treated. The three main reagents used in beneficiation of oxide copper and copper cobalt ores include sulphidisers, collectors and modifiers/depressants (**Ray, 1979; Phetla and Muzenda, 2010; Bulatovic, 2010**). It is reported to be preferable to other processes like the fatty acid process as it is more selective and not limited to certain types of gangue minerals.

The most preferred sulphidiser used in flotation of oxide copper minerals is $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. Other sulphidisers used in operating plants include NaHS and $(\text{NH}_4)_2\text{S}$. Previous studies have reported that higher dosages of NaHS are required to achieve activation of malachite. The consumption rate of sulphidiser also depends on the type of collector used. When using xanthate only, the sulphidiser rate is much higher than when using certain secondary collectors, such as dithiophosphates.

Bulatovic (2010) noted that the selection of a sulphidiser is based on the consumption required for flotation of oxide copper from particular ore types. Figure 2.7 shows the effect of different sulphidisers.

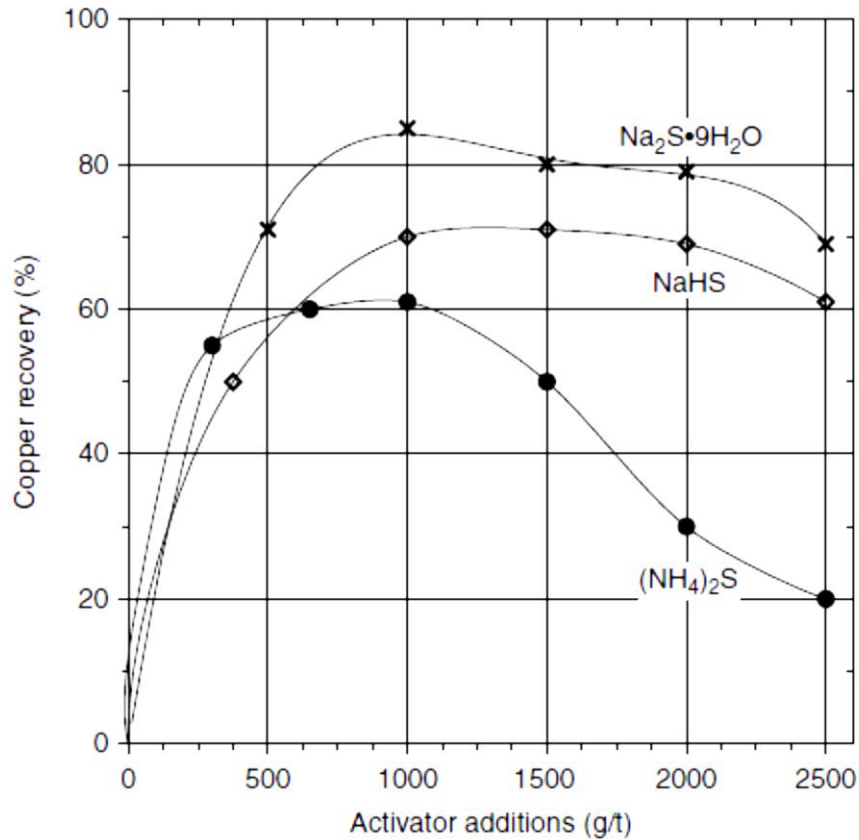


Figure 2.7: Effect of levels of different sulphidisers on copper flotation from the Kolwezi open pit (Congo, Africa) (Bulatovic, 2010).

Figure 2.7 showed that the highest copper recovery was achieved by using $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ as the sulphidiser. As such, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ is the most preferred sulphidiser used in the flotation of oxide copper minerals.

Dispersion of the gangue is normally realised by conditioning the feed with sodium silicate (Na_2SiO_3). However, in the past two decades, new depressants have been developed and introduced into a number of operating plants. Some of these depressants include: a mixture of sodium phosphate and lignin sulphonate (depressant 3XD), a mixture of low-molecular-weight acrylic acid and sodium silicate (depressant 2D) and hydrosol based on the reaction of sodium silicate with alumina sulphate (depressant SD). These depressants were extensively examined on copper oxide ores from the Nchanga mine in Zambia (Bulatovic, 2010). Figure 2.8 shows the grade-recovery relationship using the different depressant combinations.

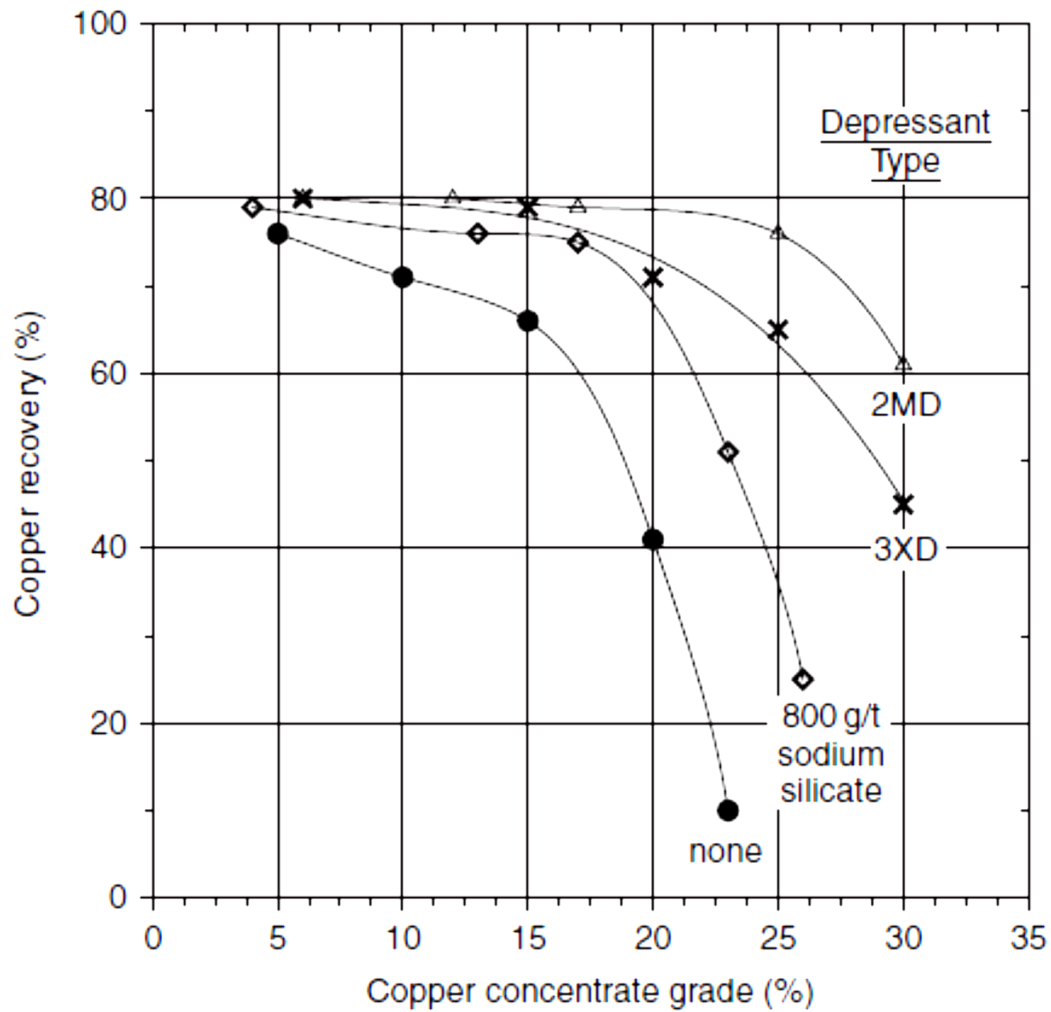


Figure 2.8: *Effect of levels of various depressants on copper grade-recovery relationship from Nchanga open pit ore (Bulatovic, 2010).*

From the graphs, depressants 3XD and 2MD showed excellent dispersion of gangue.

Crozier (1992) reported that sulphidisation in the treatment of oxide ores was first developed with industrial success on Pb-Zn oxide ores in Australia. The method involves multistage addition of sodium sulphide (Na_2S), sodium hydrosulphide (NaHS), or ammonium sulphide ($(\text{NH}_4)_2\text{S}$), together with xanthate collectors such as potassium amyl xanthate (PAX) (**Mwema and Mpoyo, 2001**). When induced in the slurry, the sulphidiser dissociates into the species H_2S , HS^- or S^{2-} depending on the pH. These ions react with the copper oxide minerals, to form a sulphide layer on the surface of the mineral particles.

Kongolo et al, (2003) investigated the efficiency of copper/cobalt oxide ores flotation by combination of sulphidisers. Sodium hydrosulphide and ammonium sulphide, were used as sulphidisers to enhance flotation selectivity of copper and cobalt towards the gangue minerals. The investigation showed that sodium hydrosulphide exhibited a good selectivity of copper and cobalt flotation towards gangue minerals. On the other hand, ammonium sulphide induced higher metal recoveries with very low selectivity. However, a controlled addition of a 1/1 combination of sodium hydrosulphide and ammonium sulphide showed the best sulphidising effect in regard to the quality of produced concentrates and the related recovery of valuable metals, that is, 80% of copper and cobalt were recovered with a concentration ratio of 3.5. Potassium amyl xanthate (PAX) was used as the main collector, strengthened by a secondary collector, an emulsion of a mixture containing 90wt% gasoil and 10% hydrolysed palm oil. Sodium carbonate was added in the proportion of 10% of the gasoil quantity in order to stabilize the emulsion.

Newell et al, (2007) showed that sulphidisation restored the floatability of three oxidised sulphide minerals: chalcopyrite, pyrrhotite and pentlandite. At optimum sulphidisation potential of -650 mV, the flotation recovery of chalcopyrite was found to be significantly greater than that of the pyrrhotite, which in turn was found to be better than that of the pentlandite.

Zhan-fang et al, (2009) reported that sodium sulphide and butyl xanthate flotation obtained a concentrate with 19.01% TCu and a recovery of 35.02% from a mexican copper ore. The ore was a mixed ore containing mainly copper oxide and some copper sulphide that responded well to flotation.

Phetla and Muzenda (2010) carried out a study to develop a flotation procedure for an oxide copper ore from Central Africa. The study aimed at producing a copper concentrate of grade 18% TCu from a 4% TCu feed grade. The best recovery achieved with the multistage sulphidisation procedure at high temperature and extended residence time, was 48% and 50% Cu and Co respectively. The best concentrate grade achieved was 13% TCu after de-sliming.

Dianwen et al, (2012) in their study on the sulphidisation promotion effect of ammonium sulphate on flotation of copper oxide ore, showed that flotation recovery increased by 12.28% when ammonium sulphate was added in the presence of sodium sulphide. The highest

recovery was obtained when ammonium sulphate and sodium sulphide were in the same dosages.

Wen et al, (2012) reported that there was an improvement in the flotation indexes of a refractory copper oxidised ore with a copper content of 1.45% TCu, from Jinping, China. The study used a combination of ethylenediamine phosphate and ammonium bicarbonate as the activator, sodium sulphide as sulphidising agent, isoamyl xanthate as collector and pine oil as frother. A closed-circuit flotation test yielded a copper recovery of 76% with a concentrate grade of 21.65% TCu.

Wang et al, (2013) reported on the flotation of a Yunnan copper oxide ore using a combination of sodium sulphide and ethylenediamine as activators with ordinary xanthate. A closed circuit flotation test yielded a flotation concentrate with a grade of 16.01% TCu and recovery of 74.38%.

Wang et al, (2013) carried out flotation tests on a copper oxide ore in Dali, containing 0.69% TCu copper and 11.24 gpt of silver. The ore was beneficiated by the sulphidisation-xanthate flotation method. The reagents used in the study were sodium sulphide as the sulphidising agent, and butyl xanthate and ammonium dibutyl dithiophosphate as the combined collectors. Closed circuit flotation tests yielded a copper concentrate of grade 18.34% TCu and a recovery of 70.13%.

Mao et al, (2014) employed the sulphidisation flotation process on a refractory copper oxidised ore from Honghe mine. The flotation tests yielded a concentrate grade of 3.93% TCu and concentrate recovery of 64.36% with sodium sulphide consumption at 200 gpt, sodium isobutyl xanthate at 150 gpt, ethylenediamine phosphate (activator) at 60 gpt and pine oil at 75 gpt. A closed circuit flotation test then yielded a copper recovery of 57.41% with a concentrate grade of 10.85% TCu.

2.4.3.2. The carboxylic/fatty acid process.

A number of different collectors have been evaluated for oxide copper flotation without sulphidisation. These include organic complexing agents, fatty acids, fatty amines and petroleum sulphonates (**Nagaraj, 1987; Deng and Chen, 1991; Fuerstman et al, 2000**).

Despite showing promise in the laboratory tests, all these collectors have had limited success when applied to a plant situation (**Lee et al, 1998; Deng & Chen (1991)** reported that the limitation of some of these collectors is their lack of selectivity over carbonate gangue

minerals, such as dolomite, and calcite. In addition, it was noted that some of the gangue minerals even float preferentially over the copper oxide.

The carboxylic acid process has been in use in Africa for over 50 years and has been referred to as the “palm oil” process (**Phetla and Muzenda, 2010**). It has been reported that around 5 million tonnes of copper oxide ores are beneficiated annually by this process, producing 25% of the copper concentrates.

A copper producer in Central Africa has been reported to use a fatty acid collector, consisting of palm oil at 75% acidity (expressed as oleic acid). It is mixed with gas oil (diesel) at a ratio of 3:1 (palm oil: gas oil). Its consumption is reported to be in the order of 1200g/t for a 6% TCu feed. The other reagents used in this process are soda ash for alkalinity and sodium silicate for gangue dispersion and depression. However, the main concern with palm oil is its lack of selectivity, particularly when the ore contains carbonate gangue minerals such as calcite and dolomite. These are collected by the fatty acid even preferentially to valuable copper minerals such as malachite. Thus, the use of the fatty acid process must be strictly limited to the treatment of siliceous ore containing only traces of carbonate gangue minerals (**Phetla and Muzenda, 2010**).

2.4.3.3. The use of alkyl hydroxamates/ chelating reagents in the flotation of oxide copper minerals.

Popperle (1940) first introduced the use of hydroxamic acid or their salts as collectors in ore flotation. **Fuerstanau and Peterson (1969)** used alkyl hydroxamates for the flotation of chrysocolla and suggested that flotation was as a result of the formation of an insoluble complex between surface metal ions and hydroxamate.

Evrard and DeCuyper (1975) reported the use of alkyl hydroxamate for copper-cobalt oxide ores flotation as being advantageous. **Danilova et al, (1975)** noted the benefits of using alkyl hydroxamates to recover chrysocolla without prior sulphidisation. **Lenormand et al, (1979)** discussed the mechanism of adsorption of potassium octyl hydroxamate on malachite.

Lee et al, (1998) provided relevant practical aspects and guidelines to facilitate the successful application of hydroxamates in operating plants. They reported that alkyl hydroxamates are excellent collectors for well defined copper minerals such as, malachite, cuprite, tenorite, azurite, atacamite, and chrysocollas with high copper content, without any prior sulphidisation or activation. In addition, they highlighted that hydroxamates have a number of advantages over most other collectors and methods such as sulphidisation flotation,

developed for recovery of oxide copper. Some of these advantages are: no special controls are needed; application is straight forward; flexibility in addition point; ease of handling and simplified flowsheet.

Laboratory flotation tests with AERO®6493 Promoter (alkyl hydroxamate) conducted by plant metallurgists of a Canadian mining company (British Columbia), on an ore assaying 0.61%TCu showed a 10% increase in total copper recovery resulting from a 30% increase in ASCu recovery. Typical ASCu recovery in the absence of alkyl hydroxamate was less than 1%. After a plant trial was conducted with AERO®6493 Promoter, trial results confirmed that 20-30% of the ASCu could be recovered using 75 gpt of the collector. Best results were achieved when hydroxamate was stage added to the rougher, scavenger and first cleaner.

Fuerstanau et al, (2000) in a study on the applicability of chelating agents as universal collectors for copper minerals, reported that potassium octyl hydroxamate, a water-soluble reagent, exhibited unusual potential for the flotation of oxide copper minerals.

Lee et al, (2009) showed that using n-octyl hydroxamate (AM28 made by Ausmelt Limited) in conjunction with traditional sulphide collectors (PAX) and methyl iso-butyl carbinol (MIBC) as a frother can successfully simultaneously recover copper sulphides and oxides by flotation from blended ore minerals. The blend used in this laboratory scale investigation was 70% sulphide ore and 30% oxide ore on a weight basis. The copper sulphides present in the blend were bornite and chalcopyrite, while the oxides were malachite and minor azurite. Study showed that AM28 successfully recovered malachite and minor azurite, which were present in Minto's oxide ore without adversely affecting the sulphide recovery for the blend composite.

Parker et al, (2012) utilised electrochemistry, vibrational spectroscopy and x-ray photoelectron spectroscopy to investigate the interaction of KH n-octahydroxamate with sulphide minerals chalcocite, pyrite, chalcopyrite, covellite and bornite. Each of the techniques showed that a multilayer of cupric hydroxamate formed on chalcocite, bornite and chalcopyrite conditioned in the hydroxamate collector, and visual inspection revealed that the multilayer had rendered the minerals hydrophobic. Consumption of hydroxamate by non-target minerals (such as oxidised pyrite) was also observed. These minerals also reported to the concentrate and this indicated a possible application of hydroxamates in the flotation of mixed sulphide oxide ores.

Xiong et al, (2013) used a hydroxamate collector in conjunction, with potassium amyl xanthate (PAX) in the flotation of low-grade copper oxide ores from Dong Chuan mine. From the series of laboratory scale rougher flotation tests conducted, the highest copper recovery obtained was 78.9% at a concentrate grade of 2.5% TCu using AM28 dosage of 740 g/t and PAX dosage of 20 gpt with one stage of cleaning, the copper grade increased to 9.6% TCu with the copper recovery at 64.9%.

Xiong et al, (2013) conducted a series of bench-scale flotation tests on refractory oxide copper ores from Yangla Mine. Potassium amyl xanthate was used as the sulphide collector and a chelating reagent, hydroxamate AM28 was used as the oxide collector. It was reported that AM28 successfully recovered all the discrete copper oxide minerals from the Yangla ore. The rougher flotation tests yielded an average copper recovery of 38.4% with a concentrate grade of 3.19% TCu.

Numprasanthai (2013) investigated on chrysocolla flotation using n-octahydroxamate collector. Dry chrysocolla grinding yielded a copper recovery of over 97% and wet chrysocolla grinding yielded copper recovery of up to 99.1%.

From the above discussion, the sulphidisation process and the use of alkyl hydroxamates/chelating reagents have shown great potential in the flotation of oxide copper minerals.

2.5. RELEASE ANALYSIS: THEORY AND PRACTICE.

2.5.1. THE RELEASE ANALYSIS CONCEPT.

The purpose of a release analysis is to achieve the perfect separation of a ground ore sample into a number of fractions, using the flotation properties of the sample constituents to effect the separation (**Rickelton, 1972**). Release analysis is analogous to the float and sinks analysis technique encountered in dense medium separation techniques, where the specific gravity properties of the sample are utilised to achieve a perfect separation (**Dell, 1964**).

Any suitable laboratory cell may be used to conduct a release analysis. The weight of the sample used should be sufficiently high to allow the separation of floatable material into fractions whose weights can be readily and accurately determined, that is, weigh at least several grams. A 6kg sample was found suitable in this case. A wet grinding method should be used to prevent the occurrence of surface oxidation.

Reagent dosage is important in the release analysis procedure. To obtain the maximum amount of information about the sample, it is necessary to float as much of the mineral bearing particles as possible (**Rickelton, 1972**). As such, excess collector dosages are used and maintained throughout the procedure. However, the addition of frothing agents should be carefully controlled, to avoid the production of a highly stable froth, which could result in excessive gangue entrainment in the flotation concentrate.

2.5.2. THE TREE RELEASE ANALYSIS PROCEDURE.

This technique was developed in 1983 (**Nicol and Bensley, 1983**) as an alternative procedure due to the possible experimental biases associated with release analysis. The procedure was based on the concept of fractionating a sample by progressively refloating the concentrate and tailings such that the test branches out in the form of a tree. Figure 2.9 shows a schematic flow-sheet of the tree release analysis.

According to the tree analysis procedure, a sample is initially floated at some arbitrary set of flotation conditions (i.e. impeller speed, aeration rate, and flotation time) and is split into a concentrate and a tailings fraction (**Nicol & Bensley, 1983**). These fractions are then refloated under the same flotation conditions, and their subsequent concentrate and tailings fractions are refloated. This procedure is continued until the final products contain less than 2% of the initial feed mass or until the desired flotation level is reached. The final products are then analysed and sorted in order of decreasing grade. These results are then used to construct a release curve.

The tree analysis procedure is reported to be probably the simplest of the release analysis procedures in concept, however, it is also tedious since it may require 4-5 levels to span the appropriate grade-recovery range. In theory, the tree analysis procedure should provide the best separation since both the tailings and concentrate are refloated numerous times to ensure that all of the material is properly fractionated according to grade (**Nicol and Bensley, 1983**).

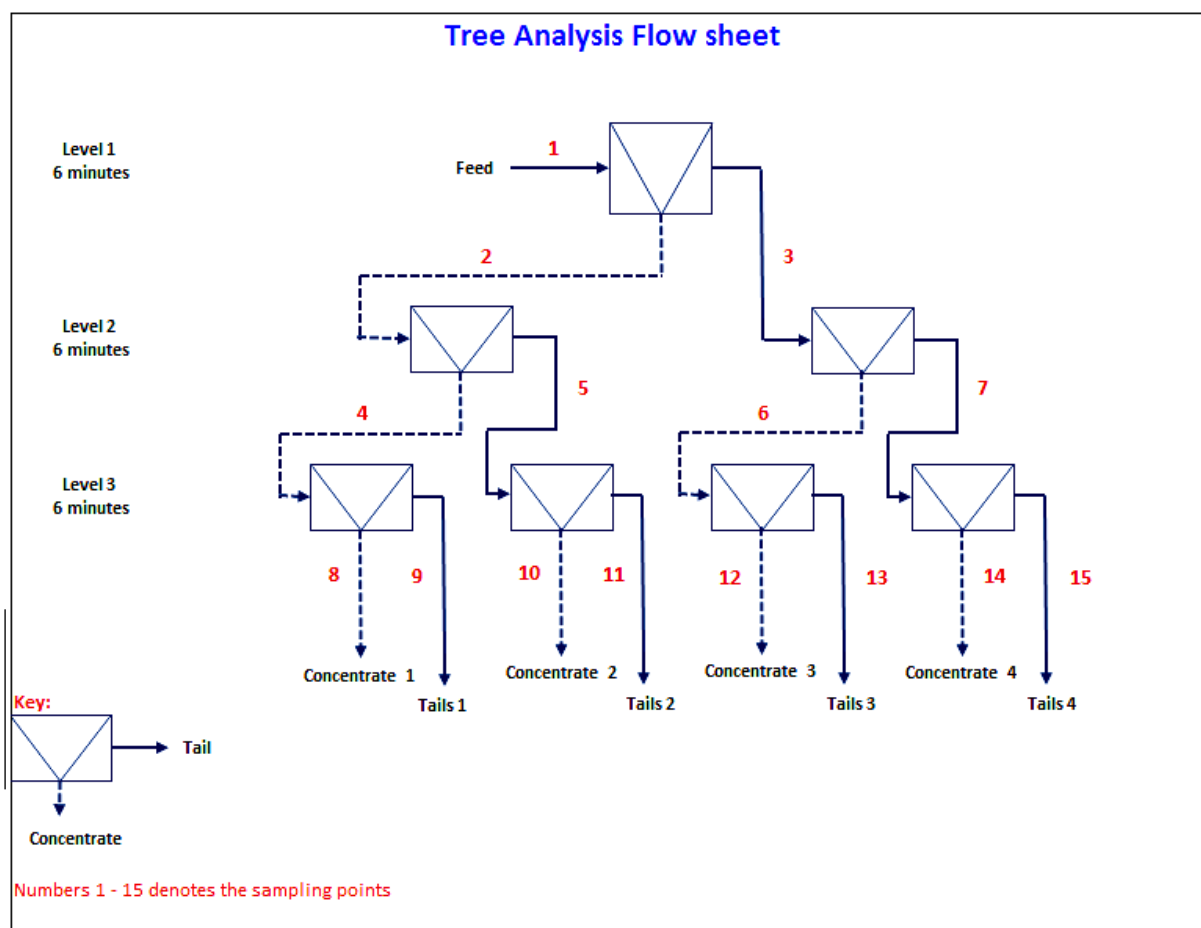


Figure 2.9: Schematic diagram of the tree analysis procedure (Nicol and Bensley, 1983).

2.5.3. RELEASE CURVES AND THE GRADE-GRADIENT PLOT.

Rickelton (1972) has described the treatment and presentation of results obtained from a release analysis test. The data obtained from such a test consists of tailings and concentrate weights and their subsequently determined assays. A 'release curve' may be derived from these results. There are a number of ways of plotting release curves, for example, as recovery versus concentrate grade, recovery versus concentrate weight or the grade-gradient plot. The grade-gradient plot is particularly advantageous and was adopted in this research as a standard technique.

The ordinate of the plot is 'cumulative percentage recovery of metal' and the abscissa is a quantity termed 'unit weight' which is defined as the 'cumulative weight of concentrate per 100 units of metal in the feed'. When these coordinates are used, a definite relationship exists between the gradient of the curve and the grade of the concentrate represented by the curve, hence the term 'grade-gradient' plot. The advantages of the grade-gradient plot may be illustrated with the help of Figures 2.10 and 2.11. Figure 2.10 shows the results of a release

analysis test plotted as a curve whose coordinates are cumulative percentage recovery, and cumulative percentage weight of concentrate. These coordinates can be expressed mathematically in terms of the mass and material balance equations:

$$F = C + T - \text{Mass Balance} \dots\dots\dots (2.4)$$

$$Ff = cC + tT - \text{Material Balance} \dots\dots\dots (2.5)$$

Where F = weight of feed (g)

C = weight of concentrate (g)

T = weight of tails (g)

f = assay of feed (%)

c = assay of concentrate (%)

t = assay of tails (%)

Hence, at any point P, on the curve,

$$\text{Cumulative percentage recovery} = \frac{cC}{fF} \times 100 \dots\dots\dots (2.6)$$

$$\text{Cumulative percentage weight of concentrate} = \frac{C}{F} \times 100 \dots\dots\dots (2.7)$$

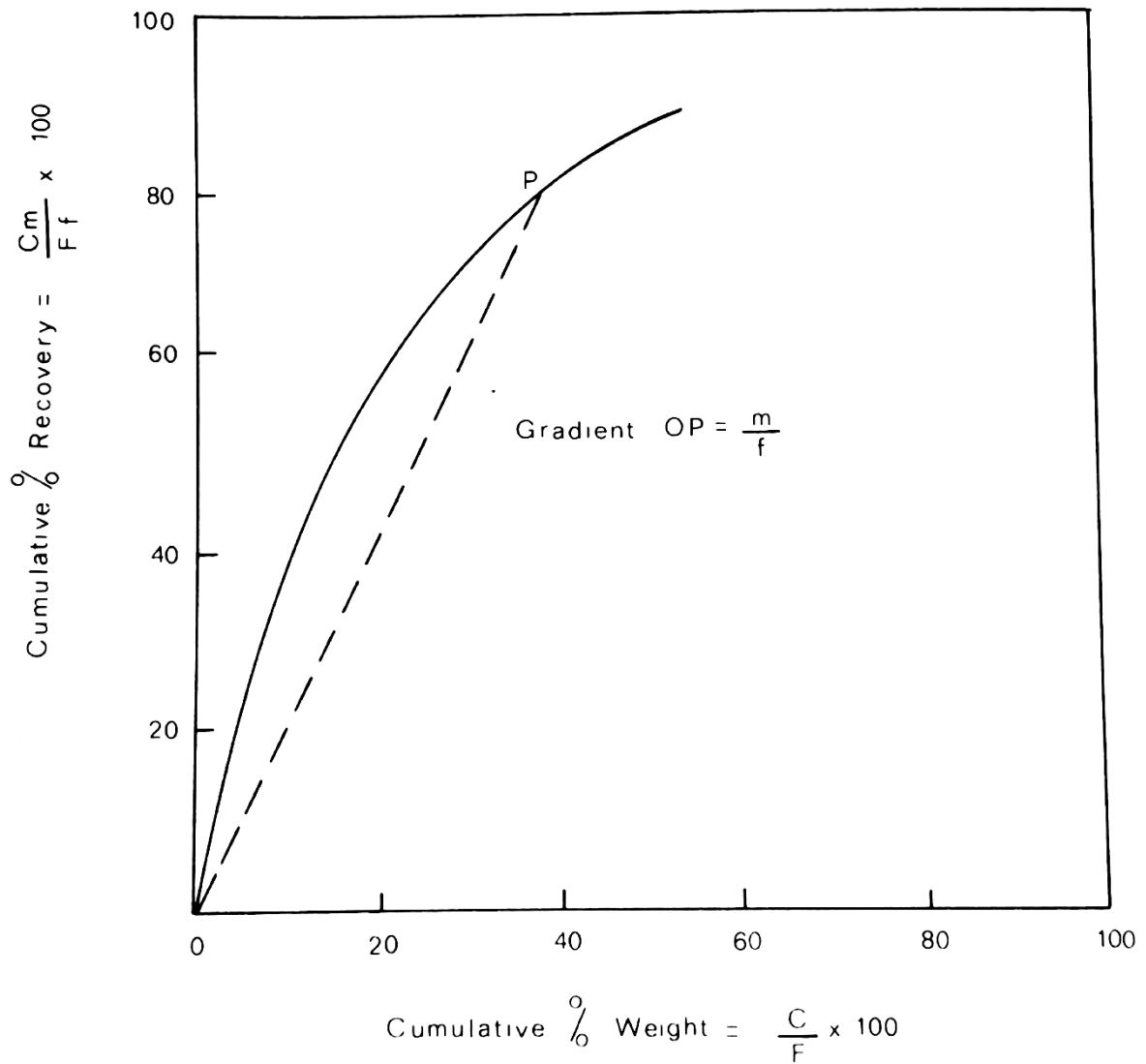


Figure 2.10: Recovery-weight of concentrate plot (Rickelton, 1972).

$$\text{Gradient of } OP = \frac{cC}{fF} \times \frac{F}{c} = \frac{c}{f} \dots\dots\dots (2.8)$$

Therefore, the gradient of the curve is a function of feed grade as well as concentrate grade.

Figure 2.11 shows release analysis results, plotted with grade-gradient coordinates.

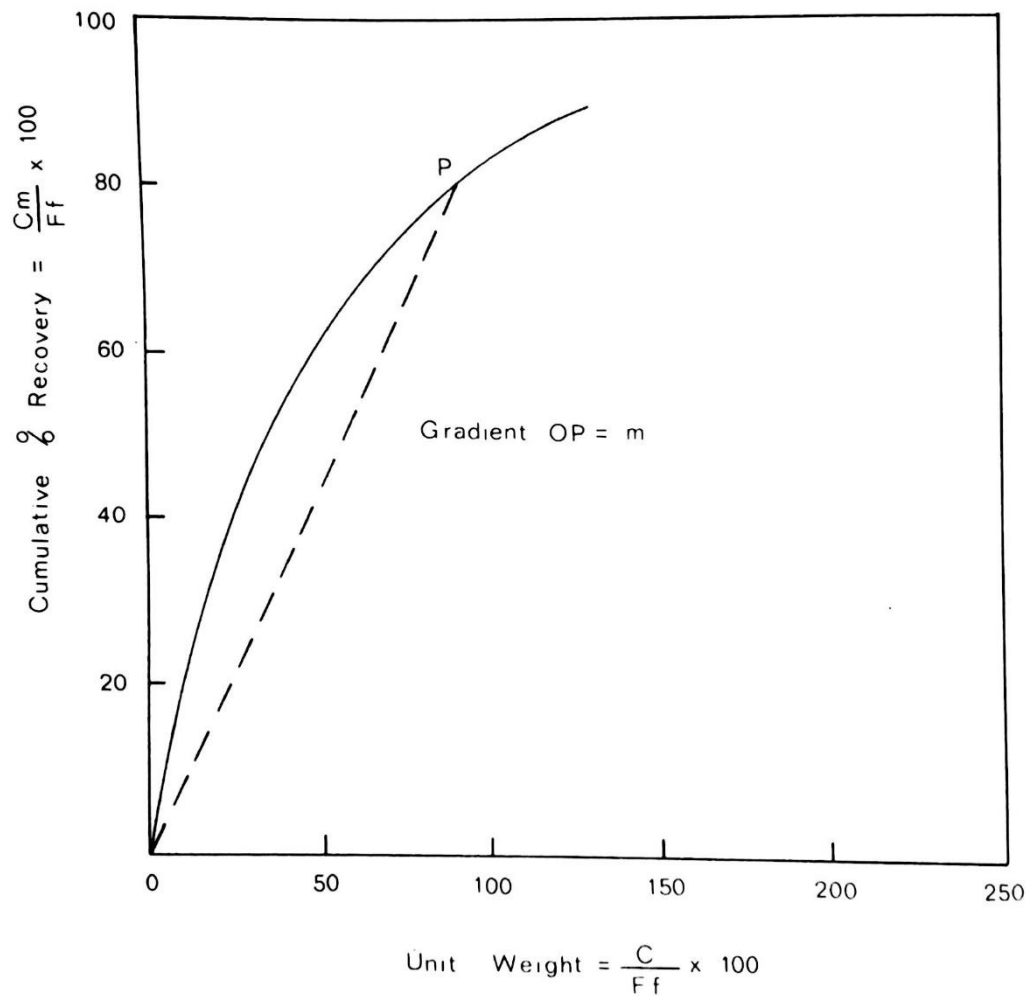


Figure 2.11: Grade-gradient plot (Rickelton, 1972).

$$\text{Gradient of } OP = \frac{cC}{fF} \times \frac{fF}{c} = c \dots\dots\dots (2.9)$$

The gradient of the line OP is, thus, numerically equal to the grade of the concentrate, represented by the point P, on the curve.

2.5.4. DEFINITION OF RELEASE CURVES.

Release analysis data can be presented in different ways (**Rickelton, 1972**), and imperfect separations may be plotted with grade-gradient coordinates. In an effort to avoid the confusion that could arise from this situation, an unambiguous definition of release curves was adopted.

A ‘release curve’ is the graphical representation of ‘release analysis’ data using the ‘grade-gradient’ system of coordinates (**Rickelton, 1972**). Thus, the graphical representation of flotation test data which does not satisfy this definition may not be termed a release curve.

2.5.5. MATHEMATICAL EXPRESSION OF RELEASE CURVES.

The degree of liberation of a ground ore sample determines the extent to which a floatable mineral may be physically separated from the gangue. Release curves may, therefore, be used to quantitatively describe liberation as they represent the best possible separation which can be achieved by flotation. **Rickelton (1972)** reported that it was desirable to condense the release curve data into the form of two parameters, enabling the degree of liberation of a flotation plant feed to be mathematically defined and opening up the possibility of on-line plant control.

This research adopted the modified Hall equation derived by **Rickelton (1972)** as the most suitable method of deriving liberation parameters from release curve data. Thus, in this research, the modified Hall mathematical model (equation 2.10) was used in the derivation of uniquely defined release curves;

$$\frac{1}{R} = \frac{a}{M - \frac{100R}{W}} + b \dots\dots\dots (2.10)$$

Where R= cumulative % recovery, ‘a’ and ‘b’ = release coefficients, M = pure mineral grade and W= unit weight.

The coefficients, ‘a’ and ‘b’, are constant for a given release curve, making the equation linear in $\frac{1}{R}$ and $\frac{1}{M - \frac{100R}{W}}$. Figure 2.12 shows the linearised form of a release curve.

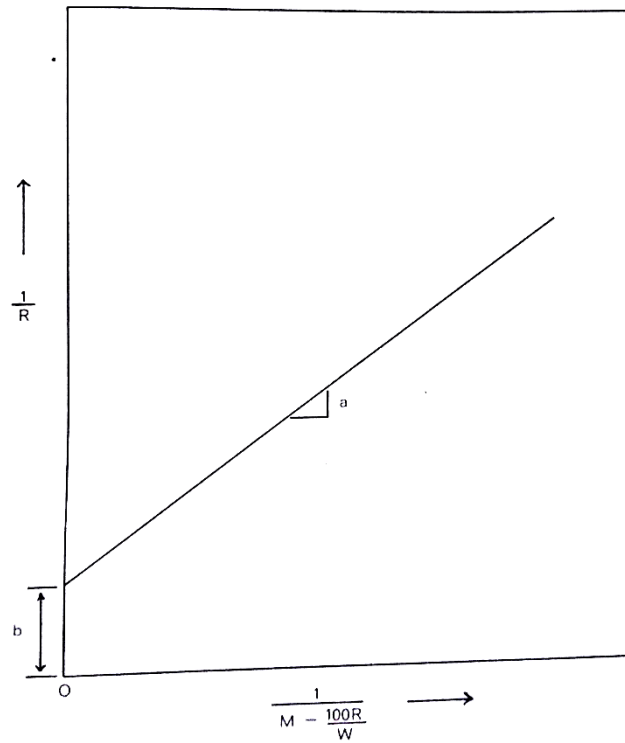


Figure 2.12: Linearised form of a release curve (Rickelton, 1972).

From the graph in figure 2.12, gradient of the straight line is 'a', and the intercept on the $\frac{1}{R}$ axis is 'b'. The coefficients 'a' and 'b' may be determined by subjecting the release curve coordinates to a simple linear regression analysis, which may then be used to define the release curve. An example will be used to illustrate the method of calculation of 'a' and 'b', and the accuracy of fit obtained from the modified Hall equation.

CHAPTER THREE.

MATERIALS AND METHODS.

3.0 INTRODUCTION.

This chapter describes the steps followed in the laboratory flotation of CRO. It includes sample preparation and flotation procedures. The research design was generally of quantitative nature and involved carrying out several bench scale flotation experiments by testing SIPX (three different dosages) and a combination of SIPX at standard plant dosage with NaHS at different dosages (two dosages) on Chingola Refractory Ore which is a mixture of oxidic and sulphidic copper minerals in nature in order to establish the flotation response of the ores and the liberation characteristics of the ore.

3.1. SAMPLE PREPARATION AND GRINDING.

In this study two differently sized laboratory roll crushers were used to reduce the particle size of the ore to less than 2 mm. Two hundred and fifty 1 kg samples were then prepared from the crushed ore using the grid method. Prior to flotation, each of the 1 kg ore samples was ground for an appropriate length of time in a batch laboratory ball mill. In this case, grinding times of 2, 4, 8 and 16 minutes were used to achieve a grind size of 50%, 60%, 70% and 80% passing 75 μ m respectively. The following mill charge was adopted in each case,

- i. 1 kg of dry ore.
- ii. 650ml of tap water.

3.2. FLOTATION EXPERIMENTS.

Eighty flotation tests were performed in order to determine the influence of various flotation parameters. Parameters studied were the grind size of feed, dosages of collector (SIPX) and dosage of NaHS. The flotation test work was done using the Denver D12 laboratory flotation machine with 1, 2 and 5 litre cells.

The following chemical reagents were used in the flotation tests:

- i. Sodium Isopropyl Xanthate (SIPX) – collector (dosages of 30gpt, 50gpt and 70gpt).
- ii. Sodium Hydrogen Sulphide (NaHS) – sulphidising agent (dosages of 200gpt and 300gpt).
- iii. FZN 245 – an alcoholic frother.

3.2.1 Flotation conditions.

Flotation tests under different conditions were undertaken. The flotation conditions were compared in terms of SIPX single dose additions with booster collector additions at each of the subsequent stages. The flotation tests on combinations of 50gpt SIPX and NaHS at two different dosages of 200gpt and 300gpt were also investigated. The NaHS was added as a single dose in the second stage of flotation to the rougher tails.

3.3. RELEASE ANALYSIS.

To enable a study of the effect of different flotation parameters, a release analysis was performed on the individually ground samples. The schematic flow-sheet of the flotation procedure followed is shown in Figure 2.9.

3.4. ASSAYING AND RELEASE CURVE COMPUTATION.

After the completion of each release analysis, the concentrate and tailings samples were filtered, dried, weighed and assayed for copper, as described in Appendix 1.

3.5. THE COMPUTATION OF RELEASE CURVE COORDINATES FROM RELEASE ANALYSIS DATA.

The method used to calculate release curve coordinates from raw release analysis data, is shown in Table 3.1.

Table 3.1: The calculation of release curve coordinates.

Sample fraction	Weight of fraction (g)	%TCu in fraction	Weight of Cu in fraction (g)	% Recovery of copper		Unit weight	
				Fractional	Cumulative	Fractional	Cumulative
a	b	c	$d = \frac{bc}{100}$	$e = \frac{100d}{\sum d}$	$f = \sum e$	$g = \frac{100b}{\sum d}$	$h = \sum g$
Conc. 1	26.16	3.41	0.89	1.3	1.3	38.1	38
Conc. 2	8.52	2.07	0.18	0.3	1.6	12.4	50
Conc. 3	11.7	1.51	0.18	0.3	1.8	17.0	68
Conc. 4	101.95	1.15	1.17	1.7	3.5	148.5	216
Tails	5761.55	1.15	66.26	96.5	100.0	8389.5	8606
Total	5909.88	1.16	68.68	100.0		8605.5	

3.6. SAMPLE CALCULATION OF RELEASE COEFFICIENTS.

The modified equation (2.10) was solved using the following procedure:

- i. From the experimentally determined values of cumulative recovery (%), R and unit weight, W, the terms $\frac{1}{R}$ and $\frac{1}{M - \frac{100R}{W}}$ were constructed (Table 3.2). The determination of M was defined by Hall as being equal to the grade of the concentrate which would be recovered, by flotation, if the minerals were fully liberated from gangue impurities. In this case $M = 5.08\%TCu$.

- ii. The terms $\frac{1}{R}$ and $\frac{1}{M - \frac{100R}{W}}$ were then subjected to a linear regression (method of least squares) to determine the coefficients 'a' and 'b', where, if $y = \frac{1}{R}$, $x = \frac{1}{M - \frac{100R}{W}}$ and

$n = \text{number of sets of data points,}$

$$a = \frac{n \sum xy - (\sum x)(\sum y)}{n \sum x^2 - (\sum x)^2} \dots\dots\dots (3.1)$$

$$b = \frac{\sum y - a \sum x}{n} \dots\dots\dots (3.2)$$

Table 3.2: The computation of linearised release curve coordinates.

Sample	Cumulative % Recovery (R)	Unit Weight (W)	$\frac{1}{R}$	$\frac{1}{M - \frac{100R}{W}}$
Concentrate 1	1.3	38	0.769855	0.602792
Concentrate 2	1.6	50	0.642775	0.531915
Concentrate 3	1.8	68	0.551569	0.411025
Concentrate 4	3.5	216	0.284074	0.289048

It was noted that the best curve fit was obtained when co-ordinates corresponding to high recovery values were used. In this example, the data corresponding to the third and fourth concentrates was used (The linear relationship between $\frac{1}{R}$ and $\frac{1}{M - \frac{100R}{W}}$ is illustrated in Figure 2.12).

The computed coefficients were as follows,

$$a = 2.193134$$

$$b = -0.349856$$

Substituting ‘a’ and ‘b’ into the equation 2.10, the equation of the release curve was found to be,

$$\frac{1}{R} = \frac{2.193134}{M - \frac{100R}{W}} - 0.349856 \dots \dots \dots (3.3)$$

iii. The accuracy of the curve fitting procedure was tested in two ways, as follows.

a. Equation 3.3 was rearranged to,

$$W = \frac{100R}{5.08 - \frac{2.193134}{\frac{1}{R} + 0.349856}} \dots \dots \dots (3.4)$$

Equation 3.4 was used to compute W for set values of R. the experimental and computed points are shown in Figure 3.1. A high accuracy of fit is evident.

b. A correlation coefficient (r) was obtained from the linear regression analysis

data, where $r = \frac{n \sum(xy) - (\sum x)(\sum y)}{\sqrt{[n \sum x^2 - (\sum x)^2][n \sum y^2 - (\sum y)^2]}}$

For this example, $r = 1$. This indicates that the regression line represents all of the data. This high value is an indicator of the accuracy of the curve fitting technique.

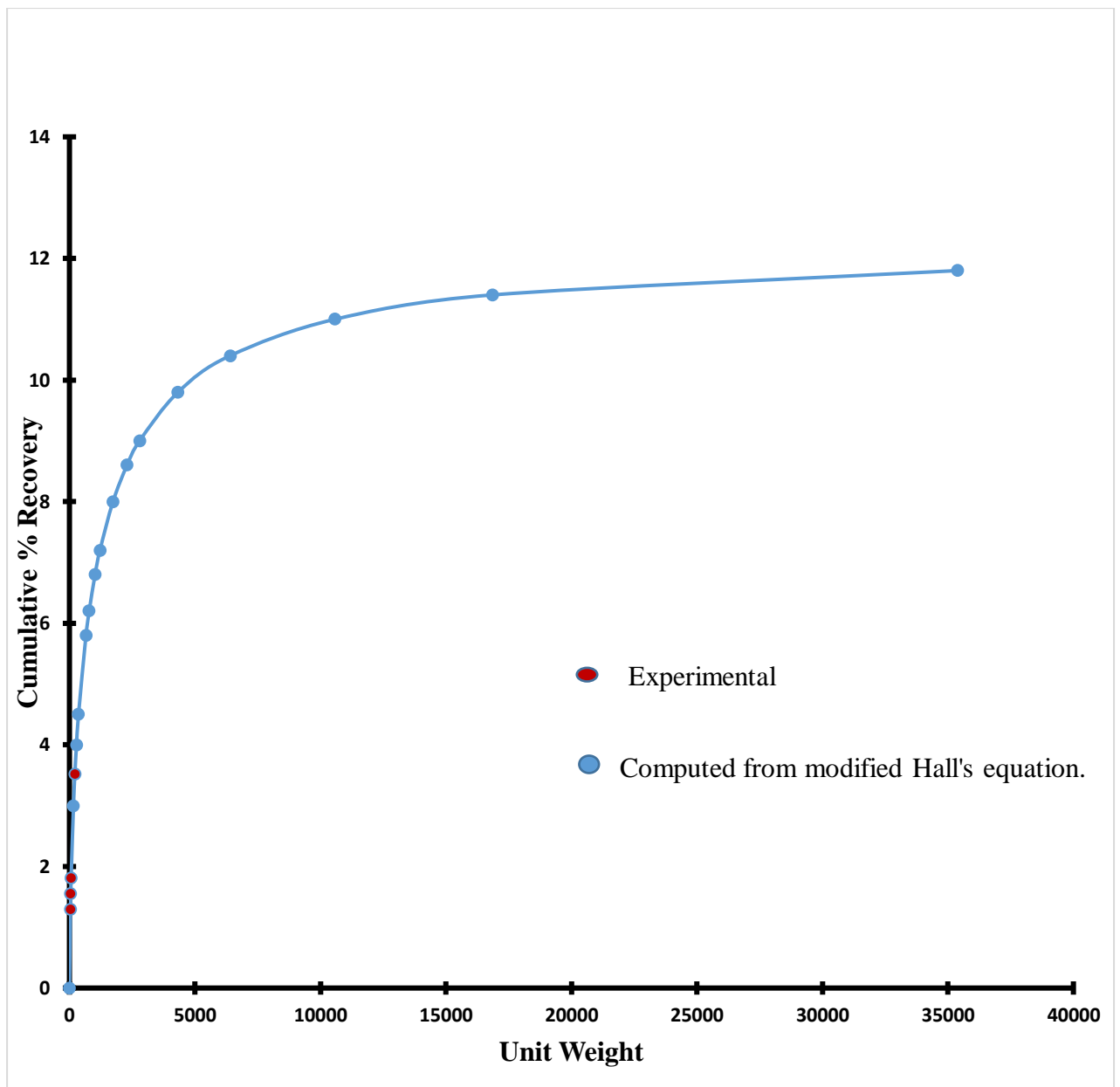


Figure 3.1: Curve fitting accuracy.

3.7. SUMMARY.

Release coefficients were derived from release curve data using the modified form of the procedure developed by Hall. The modified equation of the release curve was written as,

$$\frac{1}{R} = \frac{a}{M - \frac{100R}{W}} + b \dots\dots\dots (2.10)$$

where, R = cumulative recovery (%)

W = unit weight

M = pure mineral grade (% TCu)

‘a’ and ‘b’ = release coefficients.

This equation enabled the release curves to be defined in terms of one known ore parameter (M) and two release coefficients (a and b). The use of release coefficients to quantify and describe the effects of grinding and ore characteristics upon liberation is fully discussed Chapter 4.

CHAPTER FOUR.

RESULTS AND DISCUSSION.

4.0. INTRODUCTION.

This chapter includes the summarised mineralogical analysis of CRO (SP12 ore) and the flotation test results. The flotation tests have been categorised into two stages of investigation:

- i. Flotation with SIPX at 30, 50 and 70 gpt.
- ii. Sulphidisation flotation with SIPX and NaHS where the SIPX was maintained at 50 gpt and NaHS was dosed at 200 gpt and 300 gpt.

4.1. GENERAL DESCRIPTION OF CRO MINERALOGY.

A detailed mineralogical description of CRO is given in Appendix 1. Microscopic examination of polished briquettes of CRO sample showed that the ore was micaceous material rich in cupriferous micas which account for about 35% and about 49% of the TCu and AICu respectively. Reflected light microscopy showed that the copper sulphides were scantily distributed. Chalcocite (Cu_2S) was the main copper sulphide mineral with minor quantities of bornite (Cu_5FeS_4) and chalcopyrite (CuFeS_2). The main sulphide was seen to be 72% liberated. The acid soluble copper was mainly from malachite with pseudo malachite and cupriferous micas contributing lesser amounts. The contribution from chrysocolla was found to be negligible. Table 4.1 shows a summary of the mineralogical analysis of CRO.

Table 4.1: Mineralogical composition of CRO.

MINERALS	SP 12 Ore			
	Wt%	% TCu	% ASCu	F : L
Chalcopyrite	0.015	0.005	-	100:0
Bornite	0.018	0.011	0.000	100:0
Chalcocite	0.430	0.343	0.005	72:28
Pyrite	0.035	-	-	100:0
Native Copper	0.015	0.015	-	100:0
Malachite	0.610	0.351	0.351	98:2
Pseudomalachite	0.274	0.151	0.151	100:0
Chrysocolla	0.033	0.012	0.012	100:0
Cupriferous Mica	12.000	0.480	0.120	-
Gangue	86.569	-	-	-
TOTAL	100.000	1.370	0.640	-
Assays by: ASD NIBU		1.37	0.64	

4.2. SIZE ANALYSIS.

In order to correlate release parameters with size parameters, a size analysis for each ground sample was carried out. This was achieved by determining the size distribution of samples ground for 2, 4, 8 and 16 minutes respectively, using the standard sieve analysis. Figure 4.1 shows the milling curve obtained from the CRO.

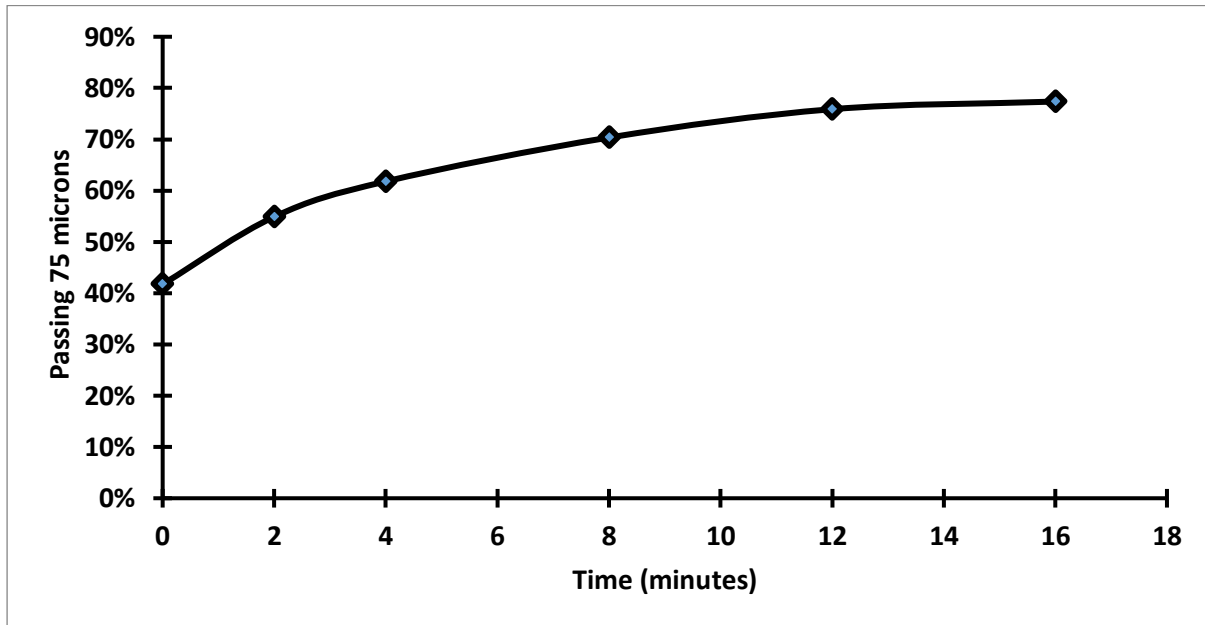


Figure 4.1: Milling curve for CRO.

From Figure 4.1 the time required to achieve the required grind size of 50%, 60%, 70% and 80% passing 75 μ m was determined to be 2, 4, 8 and 16 minutes respectively.

4.3. FLOTATION RESPONSE OF CRO WITH SIPX.

4.3.1. Flotation response of CRO with 30 gpt of SIPX.

The first flotation tests were carried out with 30 gpt SIPX on samples ground for 2, 4, 8 and 16 minutes respectively. The different grinding times used in this test were maintained for all the subsequent tests.

4.3.1.1. The computation of release coefficients.

The release coefficients 'a' and 'b' were calculated from the modified Hall equation (2.10) using the linear regression analysis described in Section 3.6. The pure mineral grade (M) was estimated by assuming that M was equal to the highest concentrate grade obtained from the release analyses. In this case $M = 5.08\%$ TCu, corresponding to the grade of the first

concentrate obtained from the release analysis performed on the sample which was ground for 16 minutes. Figure 4.2 shows the 30 gpt SIPX release curves.

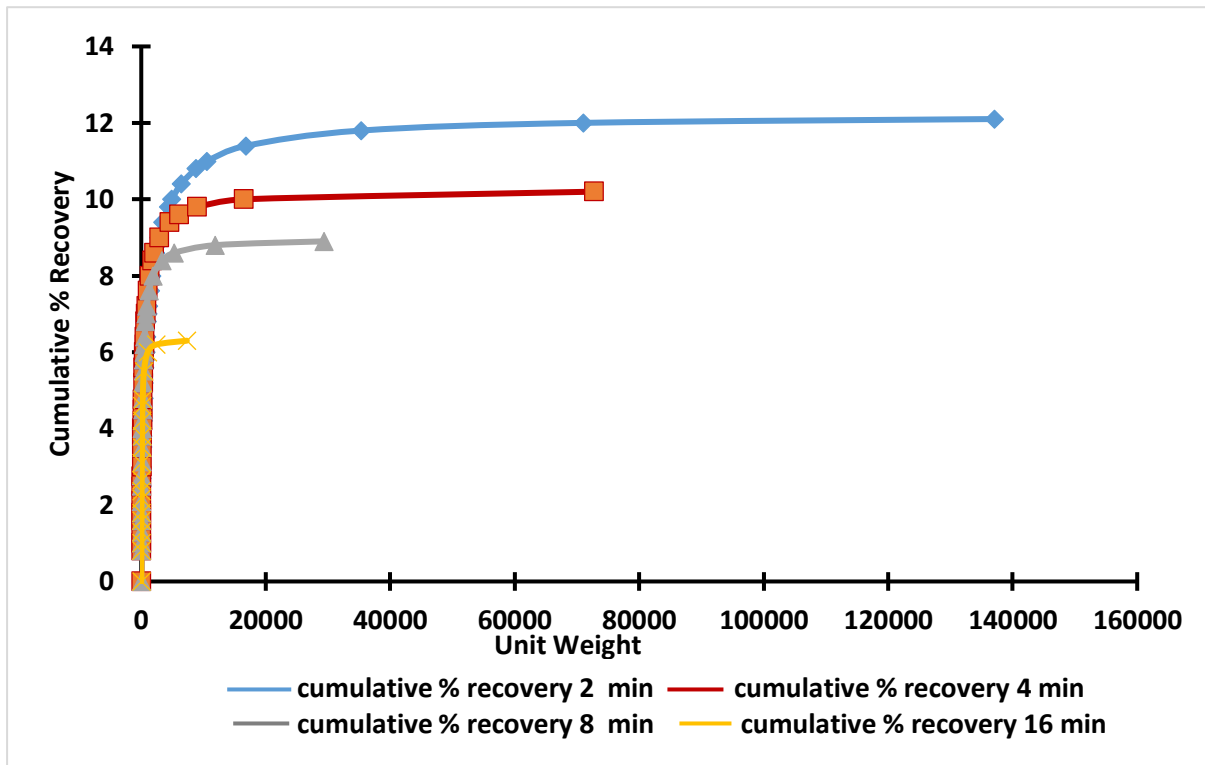


Figure 4.2: Release curves of CRO for 30 gpt SIPX.

From Figure 4.2 CRO exhibited ‘branched’ release curves. **Rickelton (1972)** reported that this behaviour was exhibited by coarse grained ores. The ‘branched’ release curves indicated that the ores were well liberated, when ground to a size suitable for flotation, that is, the large grain to particle size ratio resulted in the production of a comparatively large number of pure, liberated mineral particles as evidenced by the mineralogical analysis of the ore, where chalcocite, the main copper sulphide mineral was reported to be 72% liberated. Further grinding had the result of increasing the grade of the middlings particles resulting in the branched appearance of the release curves.

The release curves are showing a decrease in recovery as particle size decreases. This is inconsistent with the expected increase in liberation of minerals as particle size decreases. The discrepancy may be due to occurrence of fast floating non-copper bearing micas in ore which tend to inhibit the flotation of the conventional sulphide minerals. The highest recovery from the release curves is 11.8%. This low recovery may be attributed to losses in copper which occur mainly in the form of cupriferous mica and oxide copper minerals as

shown by the mineralogical analysis on the flotation tailings which reported that the copper losses were in the form of cupriferous mica, chalcocite, chalcopyrite and acid soluble copper.

4.3.1.2. Liberation characteristics.

The effects of grinding upon the liberation characteristics of the ore were illustrated by plotting graphs of the release coefficients as functions of particle size. The size parameter employed for this purpose was the d_{20} size for each distribution, obtained from the size distribution plots shown in Figure 4.1. All the subsequent flotation tests maintained this size parameter. Figure 4.3 shows the release coefficient-particle size plot for the flotation with 30 gpt SIPX.

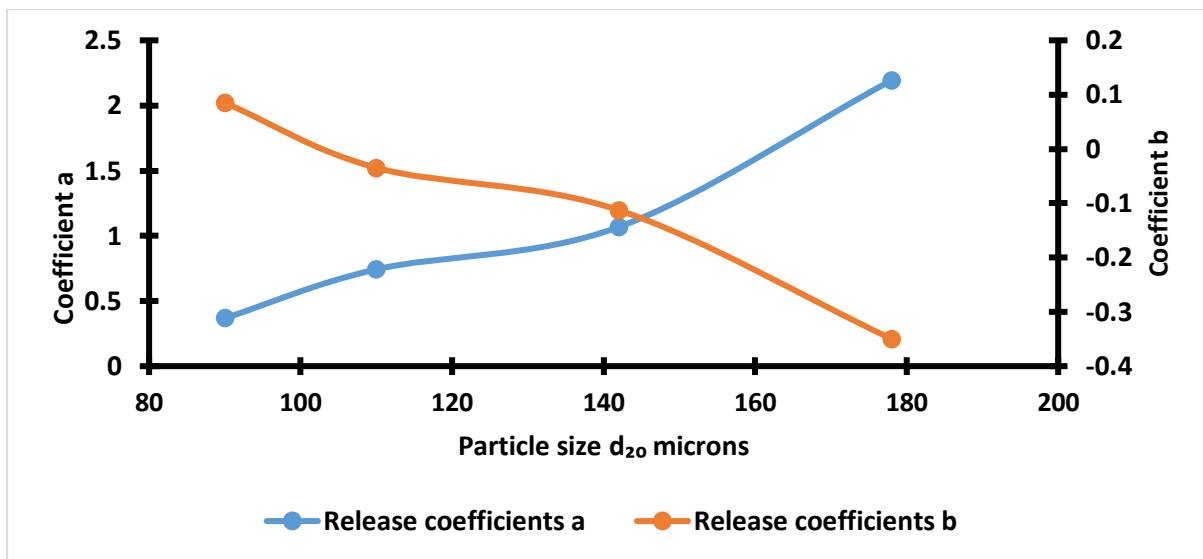


Figure 4.3: Release coefficient – Particle size plots (30 gpt SIPX).

Figure 4.3 showed that the initial effect of grinding was to produce substantial increases in the state of liberation of the ore as shown by the magnitude of the difference between the value of coefficient 'a', 2.5 at 180 microns and 1.1 at 140 microns. Also, a tendency for the increase in liberation to become less pronounced at the finer sizes was noted, that is, 0.7 at 110 microns to 0.4 at 90 microns. Figure 4.3 showed that as grinding proceeds and liberation increases, release coefficient 'a' decreases and release coefficient 'b' increases. The type of relation shown in Figure 4.3 may be useful in plant design to determine the best separation which may be achieved by flotation under a set of economically fixed grinding conditions. This will be illustrated by reference to an example.

4.3.1.3. The use of release coefficients to predict release curves.

Release coefficients may be used to predict the flotation behaviour of a sample whose particle size parameter lie within the tested range of sizes. Say, for example, the optimum size to which an ore must be ground prior to flotation lies between the sizes of the samples corresponding to grinding times of 4 and 8 minutes, the release curve corresponding to the intermediate sample may be determined as follows.

Assuming that the d_{20} size of the optimum sample to be 126 microns. This size will be determined by economic considerations, that is, as grinding proceeds, recoveries and concentrate grades may increase but that increase may not provide a sufficient rise in revenue to offset the additional grinding costs. The release coefficients corresponding to a d_{20} size of 126 microns may be determined from Figure 4.3.

Thus, $a = 0.85$

$b = -0.05$.

The general form of the modified Hall equation is written as,

$$\frac{1}{R} = \frac{a}{M - \frac{100R}{W}} + b \dots \dots \dots (2.10)$$

Substituting for a , b and M ,

$$\frac{1}{R} = \frac{0.85}{5.08 - \frac{100R}{W}} - 0.05 \dots \dots \dots (4.1)$$

Since $M = 5.08\%$ TCu for the CRO with SIPX@30gpt.

Rearranging equation 4.1 will give,

$$W = \frac{100R}{5.08 - \frac{0.85}{\frac{1}{R} + 0.05}} \dots \dots \dots (4.2)$$

Equation 4.2 can then be used to compute W for any value of R . The release curve coordinates computed in this way may then be used to construct the corresponding release curve. The predicted results have been plotted in Figure 4.4 as an illustration.

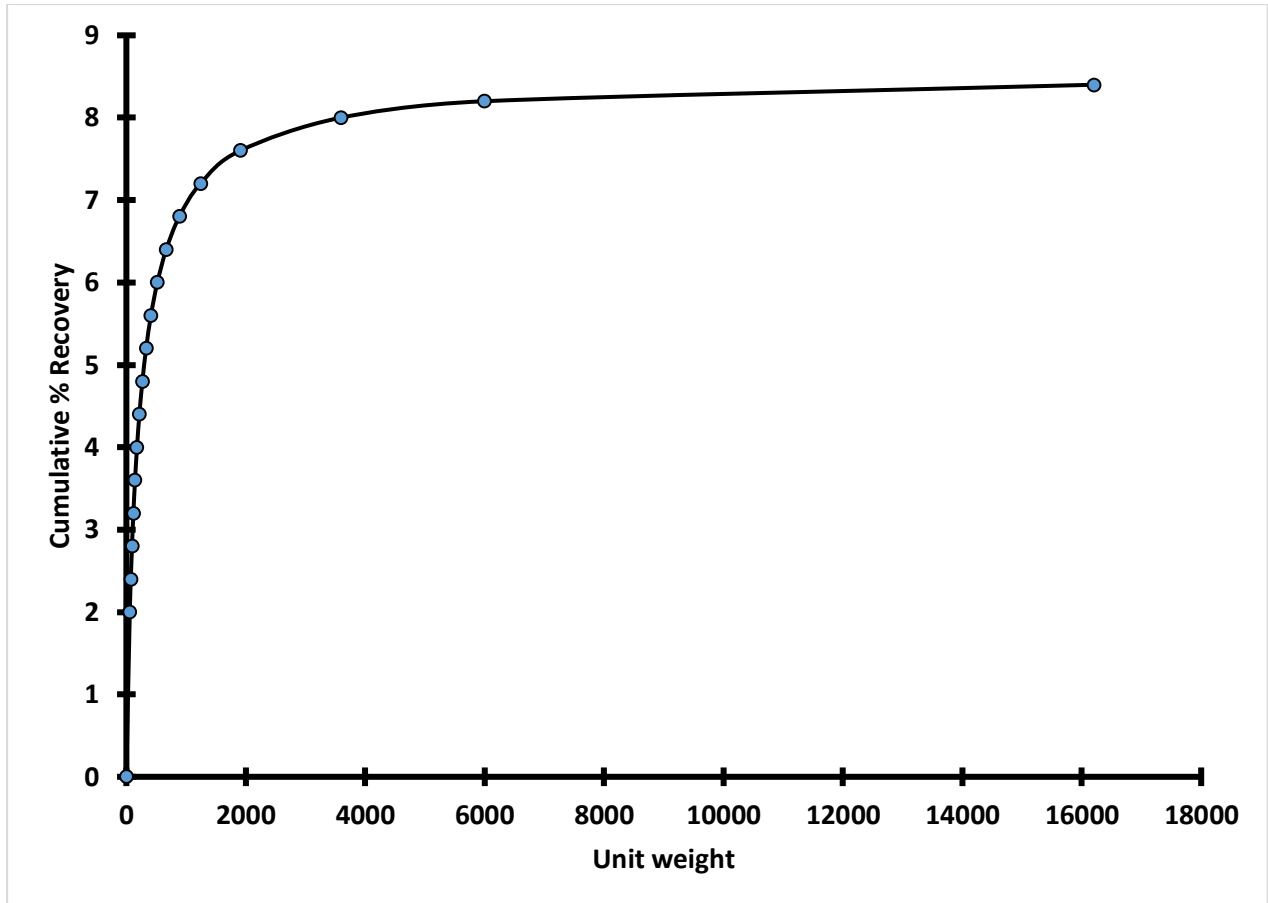


Figure 4.4: Predicted release curve for $d_{20}=126$ microns.

4.3.2. Flotation response of SP12 ore with 50 gpt SIPX.

The second batch of flotation tests were carried out with 50 gpt SIPX.

4.3.2.1. The computation of release coefficients from release curve data.

The release coefficients 'a' and 'b' were calculated from the modified Hall equation (2.10) using the linear regression analysis described in Section 3.6. The pure mineral grade (M) was estimated to be equal to 4.98% TCu, corresponding to the grade of the first concentrate obtained from the release analysis performed on the sample which was ground for 8 minutes. Figure 4.5 shows the release curves for flotation tests carried out with 50 gpt SIPX.

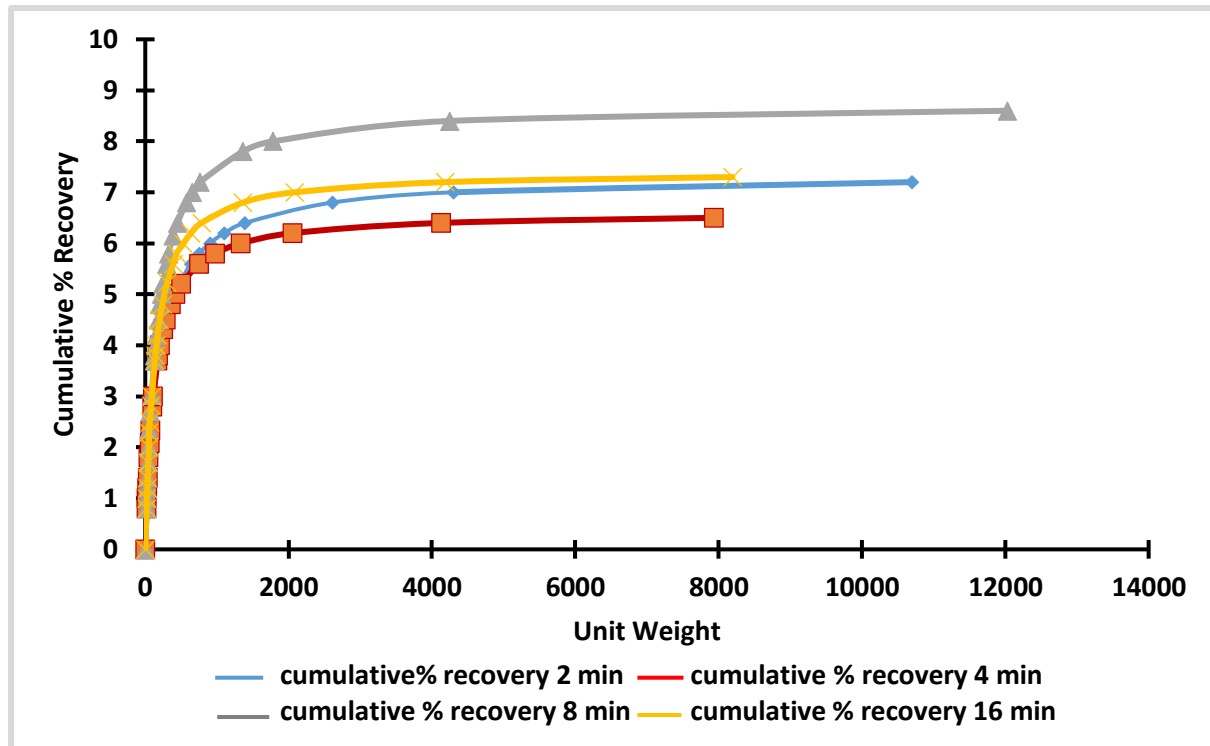


Figure 4.5: Release curves of CRO for 50 gpt SIPX.

Figure 4.5 exhibited ‘branched’ release curves for the tests with 50 gpt SIPX. The curves also showed the expected trend of increasing liberation as particle size decreased. The curves for the samples with grinding times of 8 and 16 minutes respectively yielded high recoveries of 8.6% and 7.3% respectively. This may be attributed to the increase in the collector dosage and therefore, collecting power which was accompanied by an increase in the recovery. However, the curves for this test have shown a decrease in the maximum possible recovery. This discrepancy may be due to variances in the ore mineralogical characteristics.

4.3.2.2. Liberation characteristics.

The effects of grinding upon the liberation characteristics of the ore were illustrated by plotting graphs of the release coefficients as functions of particle size. Figure 4.6 shows the release coefficient-particle size plot for flotation with 50 gpt SIPX.

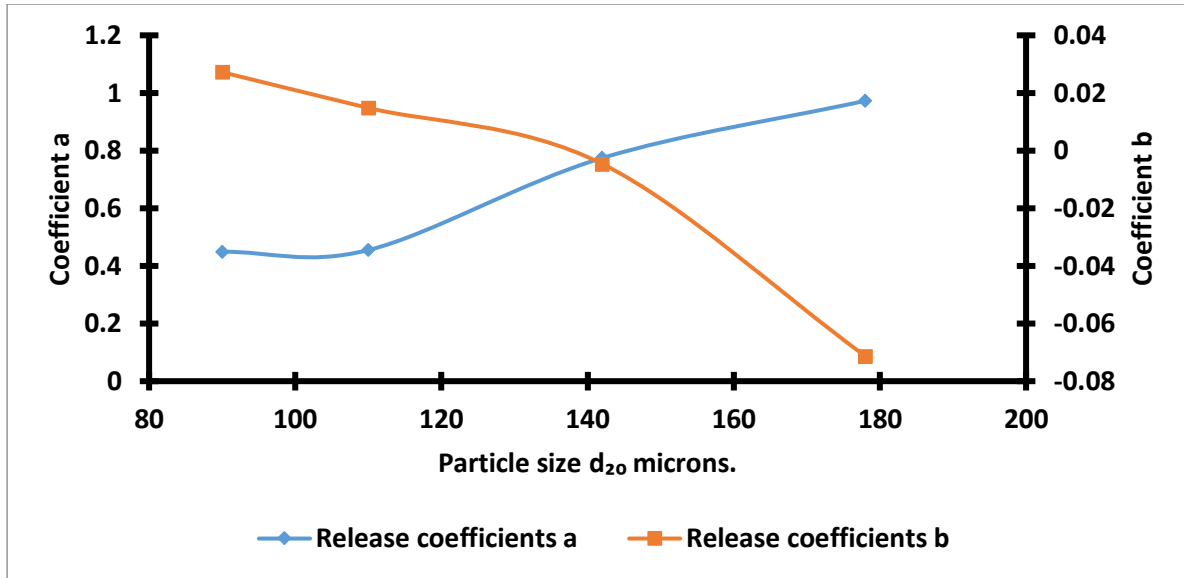


Figure 4.6: Release coefficient – particle size plots (50 gpt SIPX).

Figure 4.6 also showed that as grinding proceeded and liberation increased, release coefficient 'a' decreased and release coefficient 'b' increased. The release coefficients 'a' and 'b' obtained for 50 gpt SIPX were significantly different from those obtained for 30 gpt SIPX. This may be attributed to the different characteristics of the ore in the stockpile.

4.3.3. Flotation response of SP12 ore with 70 gpt SIPX.

The third batch of flotation tests were carried out with 70 gpt SIPX.

4.3.3.1. The computation of release coefficients from release curve data.

The release coefficients 'a' and 'b' were also calculated from the modified Hall equation (2.10) using the linear regression analysis described in Section 3.6. The pure mineral grade (M) was estimated to be equal to 15.9% TCu, corresponding to the grade of the first concentrate obtained from the release analysis performed on the sample which was ground for 16 minutes. Figure 4.7 shows the release curves for 70 gpt SIPX.

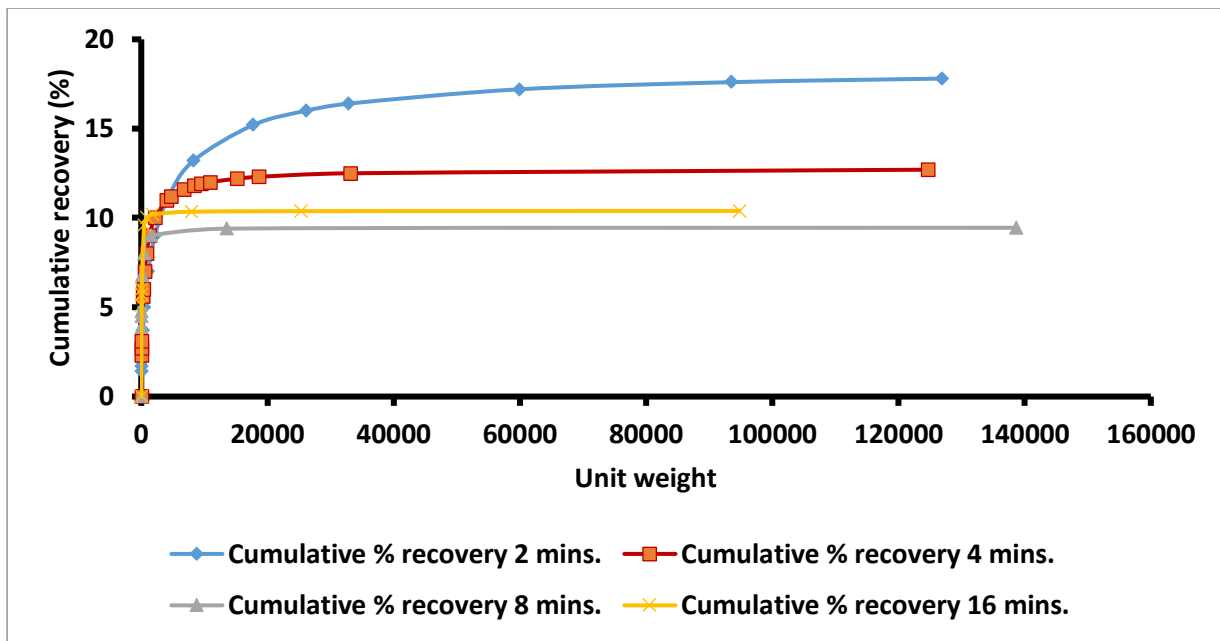


Figure 4.7: Release curves for 70 gpt SIPX.

Figure 4.7 exhibited ‘branched’ release curves for the tests with 70 gpt SIPX. The release curves also showed the unique trend of a decrease in recovery as particle size decreased. This as discussed before may be attributed to the occurrence of fast floating non-copper bearing micas which inhibit the collection of the scantily distributed copper minerals. An increase in the collector dosage is expected to be accompanied with an increase in the recovery. The release curves constructed from the flotation with 70 gpt SIPX were in agreement with this. There was a marked increase in the maximum possible recovery from 11.8% at a dosage of 30 gpt to 17.8% at a dosage of 70 gpt. This may be attributed to increased adsorption of the collector on the mineral surface due to increased collector strength.

4.3.3.2. Liberation characteristics.

The effects of grinding upon the liberation characteristics of the ore were illustrated by plotting graphs of the release coefficients as functions of particle size. Figure 4.8 shows the release coefficient-particle size plot for 70 gpt SIPX.

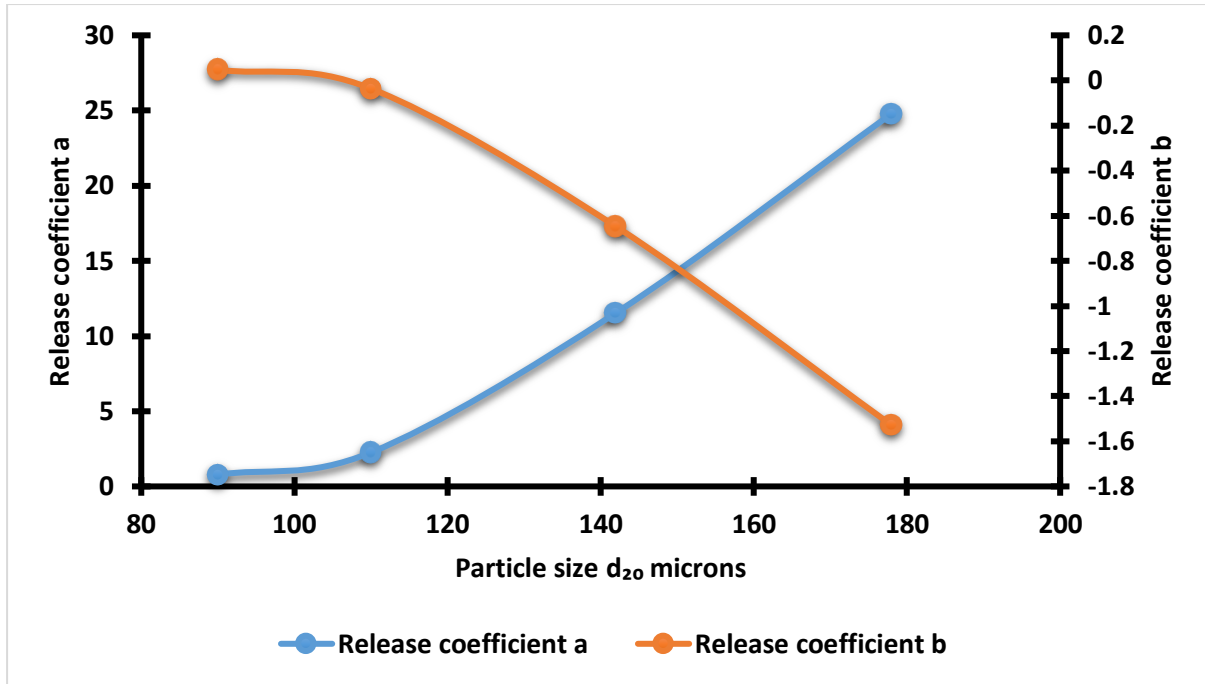


Figure 4.8: Release coefficient – particle size plots (70 gpt SIPX)

Figure 4.8 showed a decrease in coefficient ‘a’ from 25 at 180 microns to 10 at 140 microns as the initial effect of grinding. As grinding proceeded the decrease in coefficient ‘a’ was from 0.3 at 110 microns to 0.05 at 90 microns. This showed that the initial effect of grinding was to produce substantial increases in the state of liberation of the ore with the increase in liberation becoming less pronounced as the finer sizes were produced. There was a significant decrease in coefficient ‘a’ as grinding proceeded.

4.4. FLOTATION RESPONSE OF CRO WITH SIPX AND NaHS.

In the second stage of flotation, sulphidisation flotation was performed by using NaHS as the sulphidiser in an effort to increase the recoveries and concentrate grades.

4.4.1. Flotation response of SP12 ore with 50 gpt SIPX and 200 gpt NaHS.

The first batch of flotation tests was carried out with SIPX being maintained at 50 gpt and 200 gpt NaHS. The NaHS was added as a single dose in the second stage of flotation to the rougher tails to recover the oxide copper minerals.

4.4.1.1. The computation of release coefficients from release curve data.

The release coefficients ‘a’ and ‘b’ were calculated from the modified Hall equation (2.10) using the linear regression analysis described in Section 3.6. The pure mineral grade (M) was estimated to be equal to 28% TCu, corresponding to the grade of the first concentrate

obtained from the release analysis performed on the sample which was ground for 16 minutes. Figure 4.9 shows the release curves for 50 gpt SIPX with 200 gpt NaHS.

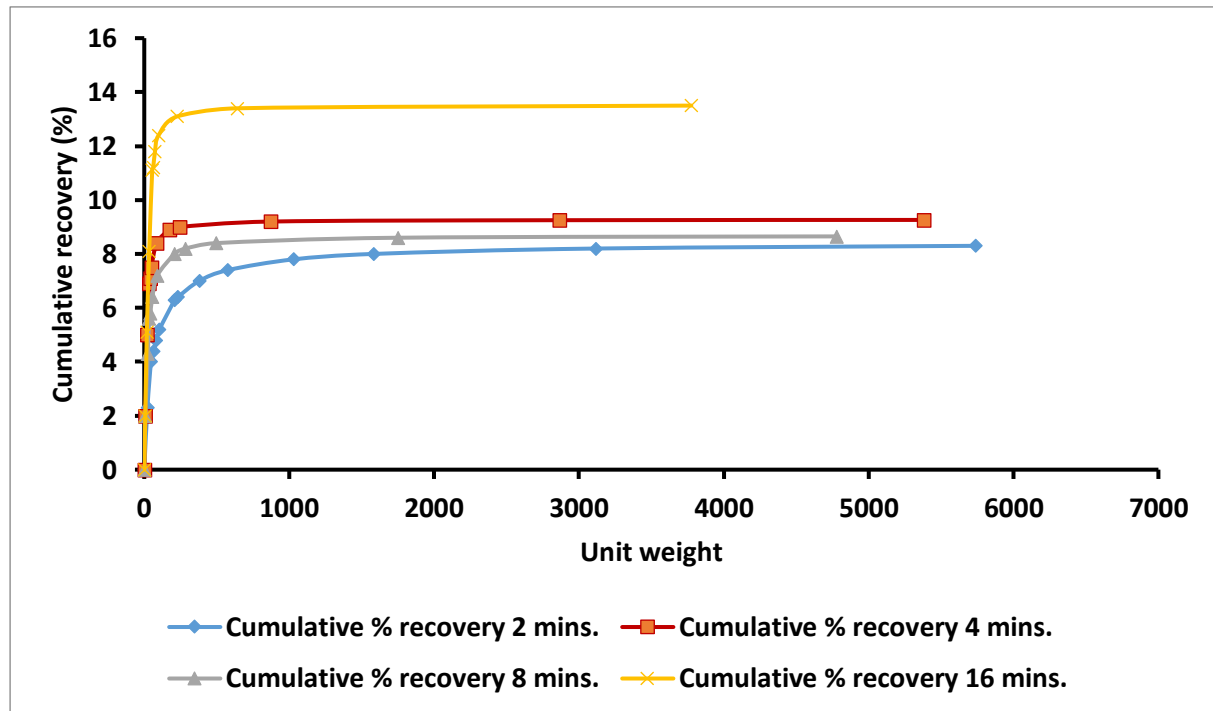


Figure 4.9: Release curves for 50 gpt SIPX and 200 gpt NaHS.

Figure 4.9 showed the expected trend of an increase in recovery with decreasing particle size. The addition of NaHS increased the flotability of the CRO. This may be attributed to the action of NaHS on the surfaces of oxidic copper minerals rendering them amenable to flotation by xanthate. This is in accordance to the observations made by **Freeman, et al. (2000)**. The increase in recovery after addition of NaHS was most apparent for the fine sizes which yielded a recovery of 13.5%. The increase in flotation characteristics of the ore for the fine sizes may be attributed to the added function of the NaHS as a froth stabiliser.

4.4.1.2. Liberation characteristics.

The effects of grinding upon the liberation characteristics of the ore were illustrated by plotting graphs of the release coefficients as functions of particle size. Figure 4.10 shows the release coefficient-particle size plot 50 gpt SIPX and 200 gpt NaHS.

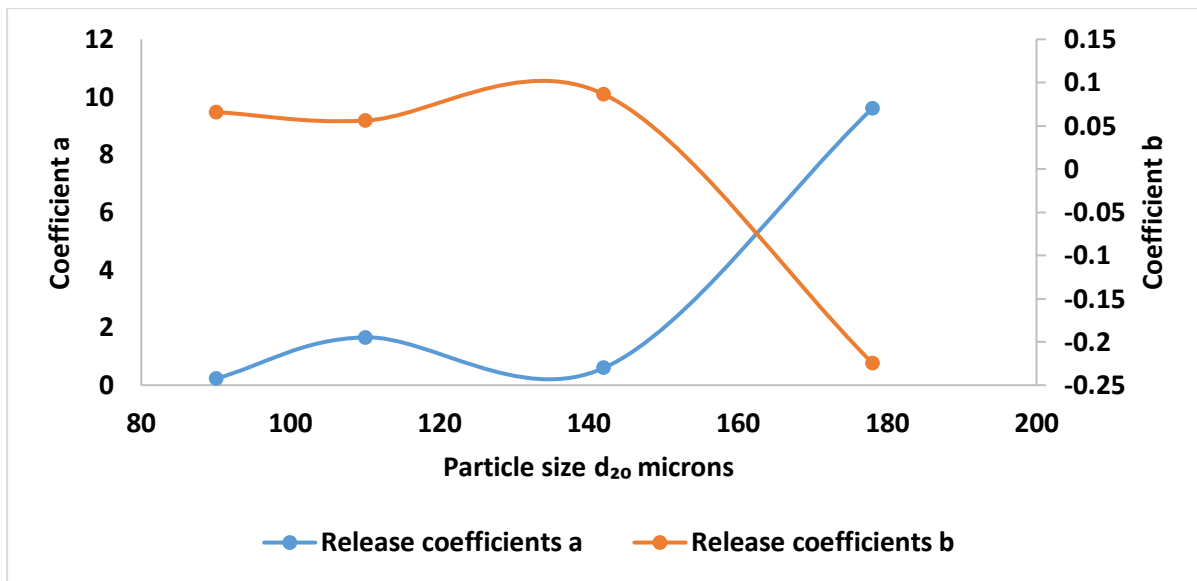


Figure 4.10: Release coefficient – particle size plots (50 gpt SIPX and 200 gpt NaHS).

Similarly, figure 4.10 shows that the initial effect of grinding was to produce substantial increases in the state of liberation of the ore with the increase in liberation becoming less pronounced as the finer sizes were produced. Figure 4.10 shows an anomaly where there was an increase in release coefficient 'a' and a decrease in release coefficient 'b' as particle size was reduced from 140 microns to 120 microns. This is unexpected as a reduction in particle size should be accompanied by a reduction in coefficient 'a' and an increase in coefficient 'b', signifying an increase in liberation of the ore.

4.4.2. Flotation response of SP12 ore with 50 gpt SIPX and 300 gpt NaHS.

The second batch of flotation tests were also carried out with 50 gpt SIPX and an increased dosage of 300 gpt NaHS. The NaHS was added as a single dose in the second stage of flotation to the rougher tails.

4.4.2.1. The computation of release coefficients from release curve data.

The release coefficients 'a' and 'b' were calculated from the modified Hall equation (2.10) using the linear regression analysis described in Section 3.6. The pure mineral grade (M) was estimated to be equal to 27.1% TCu, corresponding to the grade of the first concentrate obtained from the release analysis performed on the sample which was ground for 8 minutes. Figure 4.11 shows the release curves for 50 gpt SIPX and 300 gpt NaHS.

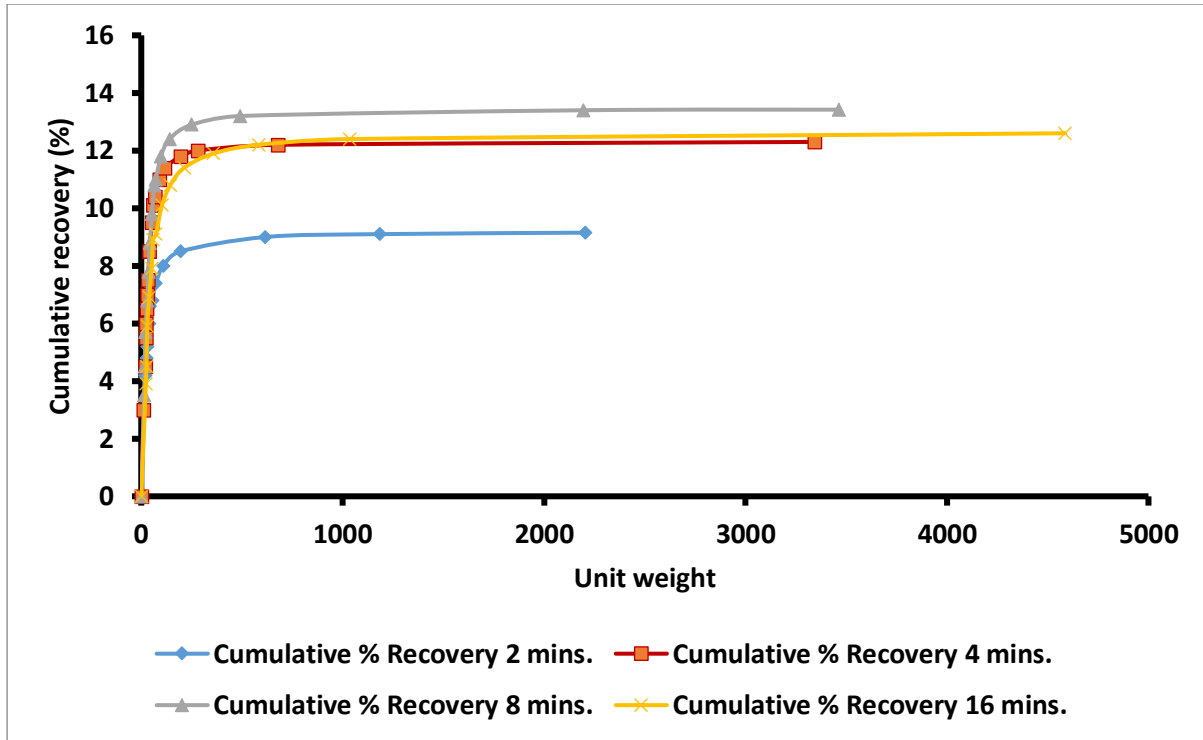


Figure 4.11: Release curves for 50 gpt SIPX and 300 gpt NaHS.

From the release curves in Figure 4.11, there is no apparent improvement in the magnitude of the recovery. The curves are similar to the ones constructed for the test carried out with 50 gpt SIPX only. The addition of NaHS also resulted in the recovery of the finer fractions showing the expected trend of increasing recovery as particle size decreases.

4.4.2.2. Liberation characteristics.

The effects of grinding upon the liberation characteristics of the ore were illustrated by plotting graphs of the release coefficients as functions of particle size. Figure 4.12 shows the release coefficient-particle size plot for 50 gpt SIPX and 300 gpt NaHS.

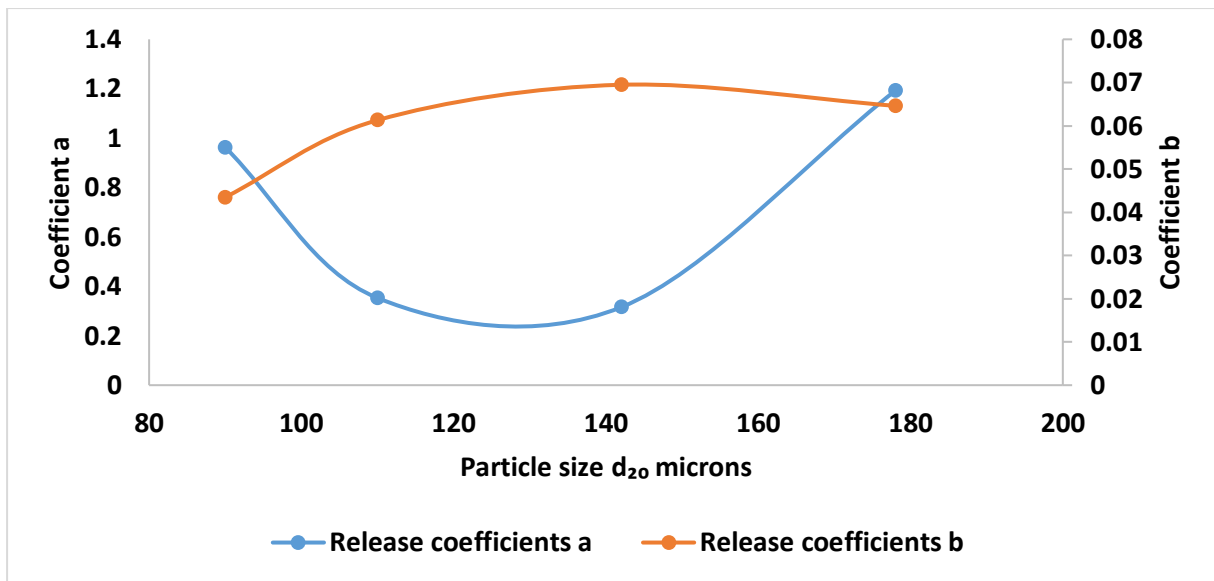


Figure 4.12: Release coefficient – particle size plots (50 gpt SIPX and 300 gpt NaHS).

Figure 4.12 shows a decrease in release coefficient 'a' from 1.2 to 0.3 and increase in release coefficient 'b' from 0.06 to 0.07. This shows that the initial effect of grinding was to produce substantial increases in the state of liberation of the ore. However, as particle size is reduced from 140 microns to 90 microns, there was an increase in release coefficient 'a' and decrease in release coefficient 'b'. This was contrary to the expected trend of decreasing coefficient 'a' and increasing coefficient 'b' as particle size is reduced. This may be attributed to the effect of NaHS on the flotation of CRO. Unlike the other flotation tests, substantial increases in the state of liberation are also evident as we move to finer particle sizes.

CHAPTER FIVE.

5.0 CONCLUSIONS AND RECOMMENDATIONS.

5.1. CONCLUSIONS.

In this study, tree release analysis was used to optimise the froth flotation process of CRO. From the experimental results, the following conclusions can be made;

- CRO is micaceous material rich in cupriferous mica. The main copper minerals in the ore are chalcocite, chalcopyrite and bornite as sulphide minerals and malachite with pseudomalachite and cupriferous mica as the oxide copper minerals.
- Mineralogical analyses revealed that the gangue minerals are mainly in the form of quartz-feldspar with micas, argillite and carbonaceous shale occurring as minor gangue minerals.
- Flotation test results showed that CRO is a coarse grained ore and that cupriferous micas are complex and difficult to float using conventional flotation methods. The liberation of copper in CRO increased with increasing grinding time as evidenced by the decrease in release coefficient 'a' and the increase in release coefficient 'b'. However, the flotation tests showed that there was an increase in the loss of copper as particle size decreased.
- The following are the highest recoveries obtained in the flotation of CRO per each of the reagent dosage used:
 1. For the tests done with SIPX only:
 - a. 30 gpt SIPX yielded a concentrate containing 5.08% TCu with a recovery of 11.8% for a sample of grind size 50% passing 75 microns.
 - b. 50 gpt SIPX yielded a concentrate containing 4.98% TCu with a recovery of 8.6% for a sample of grind size 70% passing 75 microns.
 - c. 70 gpt SIPX yielded a concentrate containing 15.9% TCu with a recovery of 17.8% for a sample of grind size 50% passing 75 microns.
 2. For the tests done at 50gpt SIPX with NaHS:
 - a. 200 gpt NaHS yielded a concentrate containing 28% TCu with a recovery of 13.5% for a sample of grind size 80% passing 75 microns.
 - b. 300 gpt NaHS yielded a concentrate containing 27.1% TCu with a recovery of 13.1% for a sample of grind size 70% passing 75 microns.
- The presence of fast floating non-copper bearing micas in the gangue inhibited the recovery of the floatable copper minerals in the ore.

5.2. RECOMMENDATIONS.

Going by the above findings, it is recommended to incorporate a sulphidisation stage in the flotation process. This would ensure that the process will recover both the copper oxide and sulphide minerals, thus, increasing the total copper obtained in the final concentrate. However, the sulphidisation stage should employ Sodium Sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) as the sulphidising agent. From literature $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ has yielded higher copper recoveries than NaHS. Additionally, it is recommended that flotation experiments be done using alkyl hydroxamates/ chelating reagents as collectors to improve the grade/recovery.

Finally, it is important that an intensive study of the cupriferous mica is done to gain a better understanding of the nature of the copper in the mica structure and therefore, ensure the successful exploitation of this resource.

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7. APPENDICES.

APPENDIX 1: MINERALOGICAL EXAMINATION CRO (SP12) FEED MATERIAL.

1. Introduction

A single sample of SP 12 Feed material was submitted for mineralogical examination. This is for the master's student working on SP 12 Ore for his project. The objective is to investigate and understand the mineralogical composition of the SP 12 Feed material.

2. Method

The samples were mounted in thermoplastic media and the polished briquettes examined using reflected light microscopy to determine the sulphide mineral distribution. Wet screened portions of samples at +38µm were examined using a stereomicroscope to determine the 'oxide' mineral distribution.

3. Results

3.1 Chemical Analyses

The samples were analysed by NchangaASD and gave the following results, Table 1.

Table A1.1: Chemical analyses

SAMPLE DATE	SAMPLE CODE	%TCu	%ASCu	%AICu
21.10.16	SP 12 MATERIAL	1.37	0.64	0.73

3.2 Mineralogical Analysis

Table A1.2: Mineral Data for SP 12 Stockpile sample for Release Analysis Test.

MINERALS	SP 12 STOCKPILE			
	Wt%	%TCu	%ASCu	F : L
Chalcopyrite	0.015	0.005	-	100:0
Bornite	0.018	0.011	0.000	100:0
Chalcocite	0.430	0.343	0.005	72:28
Pyrite	0.035	-	-	100:0
Carrollite	TR	-	-	-
Native Copper	0.015	0.015	-	100:0
Malachite	0.610	0.351	0.351	98:2
Pseudomalachite	0.274	0.151	0.151	100:0
Chrysocolla	0.033	0.012	0.012	100:0
Azurite	-	-	-	-
Cuprite	-	-	-	-
Cupriferous Mica	12.000	0.480	0.120	-
Gangue	86.569	-	-	-
TOTAL	100.000	1.370	0.640	-
Assays by: ASD NIBU		1.37	0.64	

Table A1.3: Gangue distribution by weight (%) in SP12 Stockpile.

MINERALS	SP 12	
	%RA	%Wt.
Quartz/Feldspars	52.17	45.17
Carbonates	0.38	0.33
Micas	32.29	27.95
Talc	0.00	0.00
Argillite	7.67	6.64
C/Shale	6.71	5.81
FeOx	0.38	0.33
Tremolite	0.19	0.17
Accessories	0.19	0.17
Total	100.00	86.57

3.3 Mineralogy

3.3.1 SP12 Stockpile

The total copper 1.37% is; 47% ASCu; 53% AICu. The AICu is distributed as: from CuS~48.5%; 49% cupriferous micas and <1% is from native copper.

- The general mineralogy of SP 12 material as given in Table 2(b) and 3 above is micaceous material rich in cupriferous micas which alone account for ~35% and 49% of the TCu and AICu respectively.
- The copper sulphides are scantily distributed. Chalcocite is the main copper sulphide present and is responsible for most of the CuS AICu ~96% and ~46% of the total AICu. Bornite, chalcopyrite and carrollite are minor to trace and contribute insignificantly to the AICu.
- Chalcocite the main copper sulphide is 72% liberated.
- Native copper is present in minor amounts and accounts for 0.05% of the AICu.
- The pyrite content approximately 0.04 Wt% is low.
- The acid soluble copper is mainly from malachite with pseudomalachite and cupriferous micas contributing lesser amounts. The contribution from chrysocolla is negligible.
- The gangue minerals are mainly in form of quartz-feldspar, lesser micas, minor as argillite and carbonaceous shale. Carbonates and the other constituents are negligible, see Table A3

3.4 Flotation tests spreadsheets.

Table A1-4: Release curve computation (30gpt SIPX).

Milling time (min)	Sample Fraction	Weight of fraction (g)	%Cu in fraction	%ASCu	%AlCu	Weight of copper in fraction (g)	Cumulative % Recovery	Unit Weight	Feed Grade (%Cu)
2	Concentrate 1	26.16	3.41	0.72	2.69	0.89	1.3	38	1.16
	Concentrate 2	8.52	2.07	0.74	0.77	0.18	1.6	50	
	Concentrate 3	11.7	1.51	0.97	1.1	0.18	1.8	68	
	Concentrate 4	101.95	1.15	0.52	0.63	1.17	3.5	216	
	Tails	5761.55	1.15	0.47	0.7	66.26	100.0	8606	
4	Concentrate 1	34.6	3.98	0.66	3.32	1.38	2.1	53	1.1
	Concentrate 2	14.06	1.67	0.77	0.9	0.23	2.5	75	
	Concentrate 3	13.43	1.3	0.65	0.65	0.17	2.7	95	
	Concentrate 4	114.23	1.15	0.42	0.7	1.31	4.8	271	
	Tails	5740.24	1.08	0.38	0.7	61.99	100.0	9089	
8	Concentrate 1	37.4	4.16	0.62	3.54	1.56	2.5	60	1.05
	Concentrate 2	12.44	1.33	0.78	0.55	0.17	2.8	80	
	Concentrate 3	14.65	1.55	1.01	0.54	0.23	3.1	104	
	Concentrate 4	143.17	1.03	0.61	0.61	1.47	5.5	334	
	Tails	5703.38	1.03	0.61	0.42	58.74	100.0	9508	
16	Concentrate 1	36.09	5.08	0.21	4.87	1.83	2.2	43	1.42
	Concentrate 2	9.08	1.79	1	0.79	0.16	2.4	53	
	Concentrate 3	12.66	1.88	0.61	1.22	0.24	2.6	68	
	Concentrate 4	132.49	1.35	0.64	0.71	1.79	4.8	225	
	Tails	5744.26	1.4	0.53	0.87	68.52	100.0	7009	

Table A1-5: Release curve computation (SIPX@50gpt).

Milling time (min)	Sample Fraction	Weight of fraction (g)	%Cu in fraction	%ASCu	%AICu	Weight of copper in fraction (g)	Cumulative % Recovery	Unit Weight	Feed Grade (%Cu)
2	Concentrate 1	24.84	4.19	0.8	3.39	1.04	1.4	33	1.26
	Concentrate 2	10.95	1.87	0.78	1.09	0.20	1.7	48	
	Concentrate 3	10.57	2.35	0.93	1.42	0.25	2.0	62	
	Concentrate 4	90.34	1.39	0.48	0.91	1.26	3.7	183	
	Tails	5786.01	1.24	0.52	0.72	71.75	100.0	7950	
4	Concentrate 1	29.04	4.06	0.67	3.39	1.18	1.8	44	1.11
	Concentrate 2	10.62	1.7	0.88	0.82	0.18	2.1	61	
	Concentrate 3	7.82	2.1	0.85	1.25	0.16	2.3	72	
	Concentrate 4	117.69	1.1	0.45	0.65	1.29	4.3	252	
	Tails	5750.74	1.09	0.47	0.62	62.68	100.0	9032	
8	Concentrate 1	30.38	4.98	0.79	4.19	1.51	2.3	47	1.08
	Concentrate 2	13.9	1.65	1.08	0.57	0.23	2.7	69	
	Concentrate 3	13.21	1.55	0.78	0.77	0.20	3.0	89	
	Concentrate 4	192.33	1.05	0.46	0.59	2.02	6.1	387	
	Tails	5711.05	1.06	0.44	0.62	60.54	100.0	9241	
16	Concentrate 1	32.42	4.51	0.38	4.13	1.46	2.3	51	1.08
	Concentrate 2	7.95	1.7	1.2	0.5	0.14	2.5	63	
	Concentrate 3	13.63	1.52	0.89	0.63	0.21	2.8	84	
	Concentrate 4	140.9	1.09	0.63	0.46	1.54	5.2	305	
	Tails	5715.2	1.06	0.57	0.49	60.58	100.0	9246	

Table A1-6: Release curve computation (SIPX@70gpt).

Size Distribution	Sample Fraction	Weight of fraction (g)	%Cu in fraction	%ASCu	%AICu	Weight of copper in fraction (g)	Cumulative % Recovery	Unit Weight	Feed Grade (%Cu)
50% passing 75µm	Concentrate 1	27.3	3.4	0.73	3.33	0.93	1.4	41	1.13
	Concentrate 2	10.42	1.98	0.85	0.91	0.21	1.7	57	
	Concentrate 3	13.11	1.67	0.96	0.69	0.22	2.0	77	
	Concentrate 4	102.66	1.09	0.46	0.55	1.12	3.7	232	
	Tails	5694.67	1.12	0.45	0.54	63.78	100.0	8827	
60% passing 75µm	Concentrate 1	25.9	5.68	1.15	4.53	1.47	2.3	40	1.09
	Concentrate 2	12.14	2.23	1.39	0.84	0.27	2.7	59	
	Concentrate 3	12.09	2.2	1.27	0.93	0.27	3.1	78	
	Concentrate 4	134.28	1.17	0.54	0.63	1.57	5.6	286	
	Tails	5738.82	1.06	0.62	0.44	60.83	100.0	9196	
70% passing 75µm	Concentrate 1	14.14	12.6	0.79	11.81	1.78	3.9	31	0.77
	Concentrate 2	9.94	2.82	1.04	1.78	0.28	4.5	53	
	Concentrate 3	8.8	1.44	0.82	0.62	0.13	4.8	72	
	Concentrate 4	160.38	0.91	0.37	0.54	1.46	8.0	424	
	Tails	5745.61	0.73	0.36	0.37	41.94	100	13026	
80% passing 75µm	Concentrate 1	17.24	15.9	0.4	15.5	2.74	5.1	32	0.89
	Concentrate 2	10.19	3.22	1.14	2.08	0.33	5.7	51	
	Concentrate 3	6.72	2.01	1.12	0.89	0.14	6.0	64	
	Concentrate 4	198.59	0.97	0.44	0.53	1.93	9.6	436	
	Tails	5747.17	0.84	0.28	0.56	48.28	100	11197	

Table A1-7: Release curve computation (SIPX@50gpt with NAHS@200gpt)

Sample grinding time (minutes)	Sample Fraction	Weight of fraction (g)	%Cu in fraction	%ASCu	%AlCu	Weight of copper in fraction (g)	Cumulative % Recovery	Unit Weight	Feed Grade (%Cu)
2	Concentrate 1	10.3	10.84	1.1	9.74	1.12	2.3	22	0.81
	Concentrate 2	12.4	6.48	4.97	1.33	0.80	4.0	47	
	Concentrate 3	8.95	2.19	0.86	1.51	0.20	4.4	66	
	Concentrate 4	69.28	1.28	0.65	0.63	0.89	6.3	211	
	Tails	5829.85	0.77	0.32	0.45	44.89	100	12383	
4	Concentrate 1	11.93	23.5	1.44	22.06	2.80	5.0	21	0.94
	Concentrate 2	6.33	16.4	8.92	7.48	1.04	6.9	33	
	Concentrate 3	5.39	2.77	1.1	1.67	0.15	7.1	42	
	Concentrate 4	73.51	1.33	0.77	0.56	0.98	8.9	174	
	Tails	5861.07	0.87	0.3	0.57	50.99	100	10647	
8	Concentrate 1	12.04	16.98	0.36	16.62	2.04	4.3	25	0.8
	Concentrate 2	4.08	15.9	14.8	1.1	0.65	5.6	34	
	Concentrate 3	4.07	1.97	0.93	1.04	0.08	5.8	42	
	Concentrate 4	80.5	1.32	0.81	0.51	1.06	8.0	211	
	Tails	5858.86	0.75	0.33	0.42	43.94	100	12474	
16	Concentrate 1	8.94	28	26.2	1.8	2.50	5.1	18	0.82
	Concentrate 2	18.11	16.1	0.16	15.94	2.92	11.1	55	
	Concentrate 3	3.21	2.22	1.51	0.71	0.07	11.2	62	
	Concentrate 4	81.11	1.15	0.79	0.36	0.93	13.1	228	
	Tails	5814.84	0.73	0.28	0.45	42.45	100	12126	

Table A1-8: Release curve computation (SIPX@50gpt with NaHS@300gpt)

Sample grinding time (minutes)	Sample Fraction	Weight of fraction (g)	%Cu in fraction	%ASCu	%AlCu	Weight of copper in fraction (g)	Cumulative % Recovery	Unit Weight	Feed Grade (%Cu)
2	Concentrate 1	6.78	20.6	16.6	4	1.40	3.0	15	0.78
	Concentrate 2	13.02	12.4	1.3	11.1	1.61	6.6	43	
	Concentrate 3	5.36	2.34	1.01	1.33	0.13	6.8	55	
	Concentrate 4	64.2	1.21	0.63	0.58	0.78	8.5	195	
	Tails	5820.33	0.72	0.26	0.46	41.91	100	12898	
4	Concentrate 1	8.69	21.75	18.3	3.45	1.89	4.5	21	0.7
	Concentrate 2	15.63	15.05	1.58	13.47	2.35	10.1	58	
	Concentrate 3	4.13	3.13	1.46	1.67	0.13	10.4	68	
	Concentrate 4	54.06	1.14	0.78	0.36	0.62	11.8	196	
	Tails	5897.26	0.63	0.29	0.34	37.15	100	14190	
8	Concentrate 1	9.01	27.1	18.8	8.3	2.44	5.7	21	0.71
	Concentrate 2	18.41	11.65	1.35	10.3	2.14	10.8	65	
	Concentrate 3	3.31	2.52	1.89	0.63	0.08	11.0	72	
	Concentrate 4	75.84	1.08	0.57	0.51	0.82	12.9	251	
	Tails	5870.81	0.63	0.37	0.26	36.99	100	14073	
16	Concentrate 1	12.2	17.3	13.97	3.33	2.11	4.5	26	0.78
	Concentrate 2	15.37	13.5	0.17	13.33	2.07	8.9	59	
	Concentrate 3	6.68	1.48	0.83	0.65	0.10	9.1	73	
	Concentrate 4	134.17	0.97	0.56	0.41	1.30	11.9	359	
	Tails	5818.36	0.71	0.23	0.48	41.31	100	12766	