ENHANCING THE RECOVERIES AND GRADES OF COBALT FROM NCHANGA AND KONKOLA ORES OF KCM

by

Benjamin Musuku

A dissertation submitted in partial fulfillment of the requirements for the degree of Master of Mineral Sciences in Metallurgy and Mineral processing

The University Of Zambia

July, 2011

DECLARATION OF ORIGINALITY

This is to certify that the work is entirely my own and not of any other person, unless explicitly acknowledged (including citation of published and unpublished sources).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.

....

Benjamin Musuku

June 2011

CERTIFICATE OF APPROVAL

This dissertation of Benjamin Musuku is approved as fulfilling part of the requirements for the award of the degree of Masters of Mineral Sciences in Metallurgy and Mineral Processing by the University of Zambia.

Signatures of Examiners: Date:

1. ....E·H. Jere................   .....27/04/12.............

2. ....

3. ....

ACKNOWLEDGEMENTS

002S3307

To my God, the lover of my soul, who makes things beautiful in His own time, to Him,

be the glory now and forever.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The Nchanga and Konkola ores have substantial amounts of cobalt in the form of Carrollite *(CuCo$_2$S$_4$)* and Cobaltiferous pyrite *((Co,Fe),S$_2$)*. These minerals are found in association with copper minerals such as chalcopyrite *(CuFeS$_2$)*, Bornite *(Cu$_5$FeS$_4$)* and Chalcocite *(Cu$_2$S)*. However, the recoveries of cobalt minerals in both Concentrators are low *(45-50%TCo)*.

In this work, a combination of the electrokinetic, Ultra-Violet spectrometry, X-ray Photoelectron spectrometry, contact angle measurements and micro-flotation techniques were used to characterise the optimal conditions for the improvement of recoveries and grades of cobalt mineral (Carrollite) without adversely affecting the recoveries and grades of copper minerals such as Chalcopyrite.

The studies confirmed that in acidic media (pH 3 – 6), copper ions are easily leached into solution whereas cobalt ions are only leached at high pH values (9 -11) in the alkaline media. The zeta potentials of both Carrollite and chalcopyrite are negative throughout the pH range (3- 11). Charge reversals at pH 7.5 and pH 10.5 are achieved in oxygen saturated solutions for Carrollite mineral. Sodium Isopropyl Xanthate (SIPX) decomposes to xanthic acid at pH 3 whereas at high pH (> pH 6) a substantial amount of Xanthate ions is present due to ionisation of SIPX into metal cation and Xanthate anion. The adsorption of Xanthate ions on Carrollite minerals is rapid in the first 5 minutes of adsorption test work.

A fresh Carrollite mineral sample has the following oxidation states for its elemental constituents; ***Cu (I), Co (III) and S (I &II)***. The Carrollite mineral is fairly stable at pH

3 in water, SIPX and oxygen saturated solution. *$Cu(OH)_2$*, *CuS* and *CuX_2* are formed at high pH values (pH 9 and 11). The formation of hydrophobic species is optimum at pH 9. The maximum contact angles *(33.5^o and 49.8^o)* were achieved at pH 9 both for untreated and treated in SIPX polished sample respectively. This is confirmed in the high recoveries and grades achieved at pH 9 – 10.5. The outcome of the laboratory flotation tests work on the actual cobalt mineral and ores were that pH 9 gave better recoveries for SIPX *(74.7% TCu and 71.8% TCo)* and SIPX: PAX (Potassium Amyl Xanthate) *(74.4% TCu and 78.3% TCo)*as collectors respectively.

These sets of results imply that:

1. the loss of copper/cobalt minerals in aqueous solution is minimal as there is negligible amounts of dissolved metal ions in solution

2. the charge on the mineral surface in solution is influenced by pH and hence gives guidance to the type of collectors that easily adsorb and induce the required effect (activation or depression of the minerals of interest) on the mineral surface

3. the formation and precipitation of metal hydroxide on the mineral surface is detrimental to flotation whereas metal-deficient sulphide rich surfaces, metal sulphide and metal dixanthogen are responsible for flotation.

CHAPTER ONE

1.0 INTRODUCTION

Metallic minerals play an important role in developing the economy of a nation. They are the material resources from which basic metals are derived. Base minerals are used in a broad spectrum of industries such as construction, mechanical, electrical and electronics engineering, shipbuilding, aircraft and automobile manufacturing. Zambia, a country richly endowed with a vast variety of minerals, contributes significantly to the world mining and treatment of copper and cobalt ores. Cobalt is of particular importance due to its specialised use in strategic industries. Cobalt is normally not found native except in meteorites, but occurs as sulphides, arsenides, sulpho-arsenides and oxidised minerals (carbonates, arsenates and complex hydrated oxides) [1].

1.1 General Objective

The general objective of this work is to enhance the recoveries and grades of cobalt from Nchanga and Konkola ores of KCM.

1.2 Specific Objectives

1. Understand surface chemistry of Carrollite through

   a. Spectroscopic studies such as use of X-ray Photo-electron Spectrometry (XPS) to characterise the compounds formed on the surface of the mineral under different conditions, (oxidising, non-oxidising conditions and in the presence of SIPX)

b. Electrokinetic studies which include determination of the zeta potentials through electrophoretic measurements.

c. Determination of contact angles.

2. Understand flotation behaviour using

a. Hallimond tube for collectorless flotation

b. Bench laboratory flotation using a Denver flotation Machine in the presence of normal plant reagents, collectors (SIPX and PAX) and frother (FZK 245).

3. Understand adsorption properties through

a. Determination of concentration of Xanthate using Ultraviolet-Visible (UV-vis)

b. Determination of mono and multi-layer adsorption of SIPX on Carrollite mineral particles.

4. Determine the effect of water through leaching tests by

a. Determination of the amount of cobalt and copper ions that go in aqueous solution at different leaching times.

1.3 Problem Justification

Konkola Copper Mines plc (KCM) is one of the main copper producing companies in Zambia. Its operations are vertically integrated starting with the mining of the ore and ending with production of finished copper in form of copper cathode sheets. The ores which are processed in the Nchanga and Konkola Concentrators are mined from open pit and underground mines. These ores contain oxide and sulphide copper minerals. The oxide minerals mostly from open pit mine include: Malachite ($Cu_2(OH)_2CO_3$), Pseudo-malachite ($Cu_5(PO_4)_2(OH)_4$, Cuprite (Cu_2O), Azurite ($Cu_2(CO_3)_2(OH)_2$ and Chrysocolla ($CuSiO_3nH_2O$). The sulphide minerals which are mostly mined from underground include Chalcopyrite ($CuFeS_2$), Bornite (Cu_5FeS_4) and Chalcocite (Cu_2S).

Table 1.1: Mineralogical Examination of Nchanga and Konkola Ores

Mineral	Nchanga Ore				Konkola Ore			
	Wt%	%TCu	%ASCu	%TCo	Wt%	%TCu	%ASCu	%TCo
Chalcopyrite	0.173	0.06	-	-	0.951	0.328	-	-
Bornite	0.019	0.012	<<0.001	-	1.695	1.073	0.021	-
Chalcocite	1.616	1.29	0.019	-	1.372	1.095	0.016	-
Pyrite	0.302	-	-	0.009	0.006	-	-	0
Carrollite	0.751	0.116	-	0.31	0.06	0.012	-	0.023
Native Copper	-	-	-	-	0.02	0.02	-	-
Malachite	0.871	0.502	0.502	-	0.568	0.327	0.327	-
Pseudomalachite	0.059	0.032	0.032	-	0.121	0.067	0.067	-
Chrysocolla	-	-	-	-	0	0	0	-
Azurite	0.04	0.022	0.022	-	0	0	0	-
Cuprite	0.1	0.089	0.062	-	0.016	0.014	0.009	-
Cupriferous Mica	0.15	0.006	0.002	-	0	0	0	
Wad	0.167	0.012	0.012	0.015	-	-	-	-
Gangue	95.752	-	-	-	95.192	-	-	-
TOTAL	100	2.141	0.65	0.334	100	2.936	0.44	0.023
Assays by: ASD NIBU	-	2.14	0.65	0.33	-	2.94	0.44	0.023

Table 1.1 shows the forms in which copper and cobalt exist. In both the Nchanga and Konkola ores, the sulphides minerals contribute a higher percentage to the total copper as compared to oxide minerals. Mineralogical examinations have revealed that cobalt exists mostly as Carrollite ($CuCo_2S_4$) whereas Cobaltiferous pyrite ($(Co,Fe)S_2$) in trace amounts.

6.0 MTPA CONCENTRATOR & BACK FILLED PLANT FLOWSHEET-KCM, KONKOLA
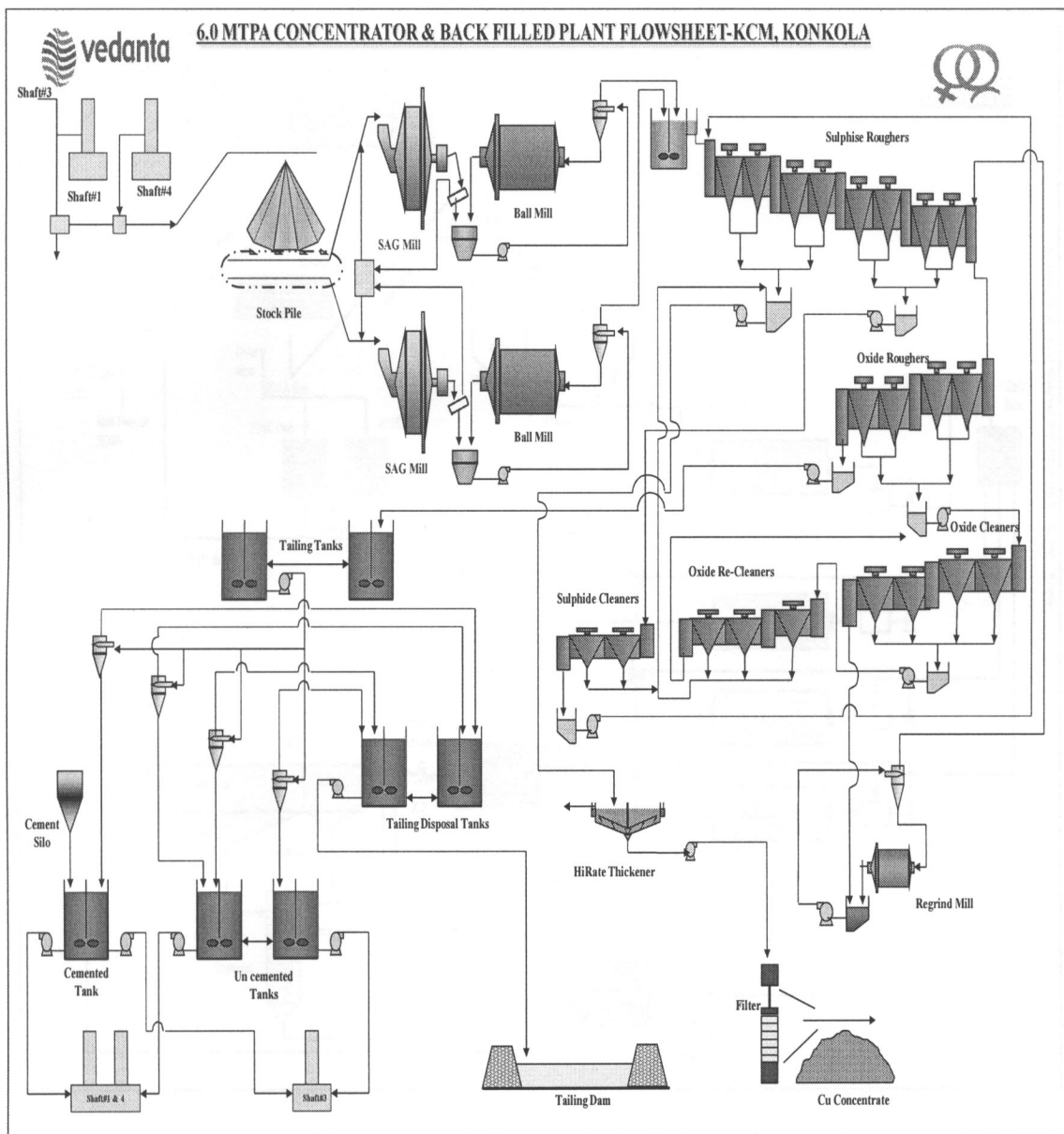
Figure 1.1: Konkola Concentrator flowsheet

Figure 1.1 shows flotation circuit for Konkola contractor that treats copper ores from shaft No. 1 and 3. Figure 1.2 shows the cobalt circuit in Nchanga Concentrator. The Nchanga Concentrator has a cobalt circuit which treats cobalt ore from open pit mine.

COBALT CIRCUIT FLOW (EXISTING)

— Existing circuit
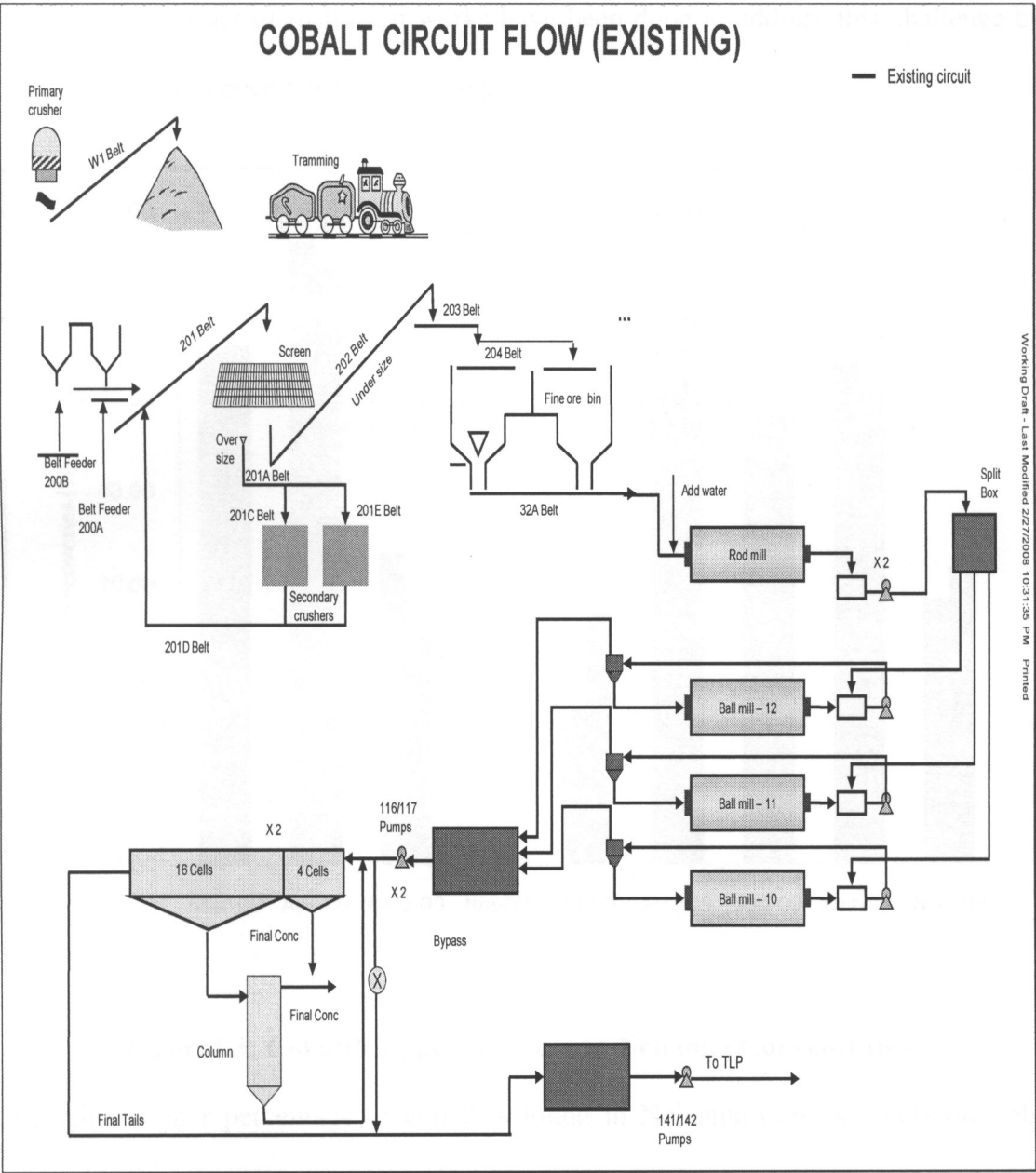
Figure 1.2: Nchanga Cobalt Circuit

However, the recoveries and grades achieved during concentration process are low as shown in Figure 1.3. The current cobalt price (US$ 36,000/tonne) [2] at the London Metal Exchange has prompted KCM to consolidate its efforts in improving the recovery

and grade. A number of insitu-test works have been done to address this challenge but the results have not been very encouraging.
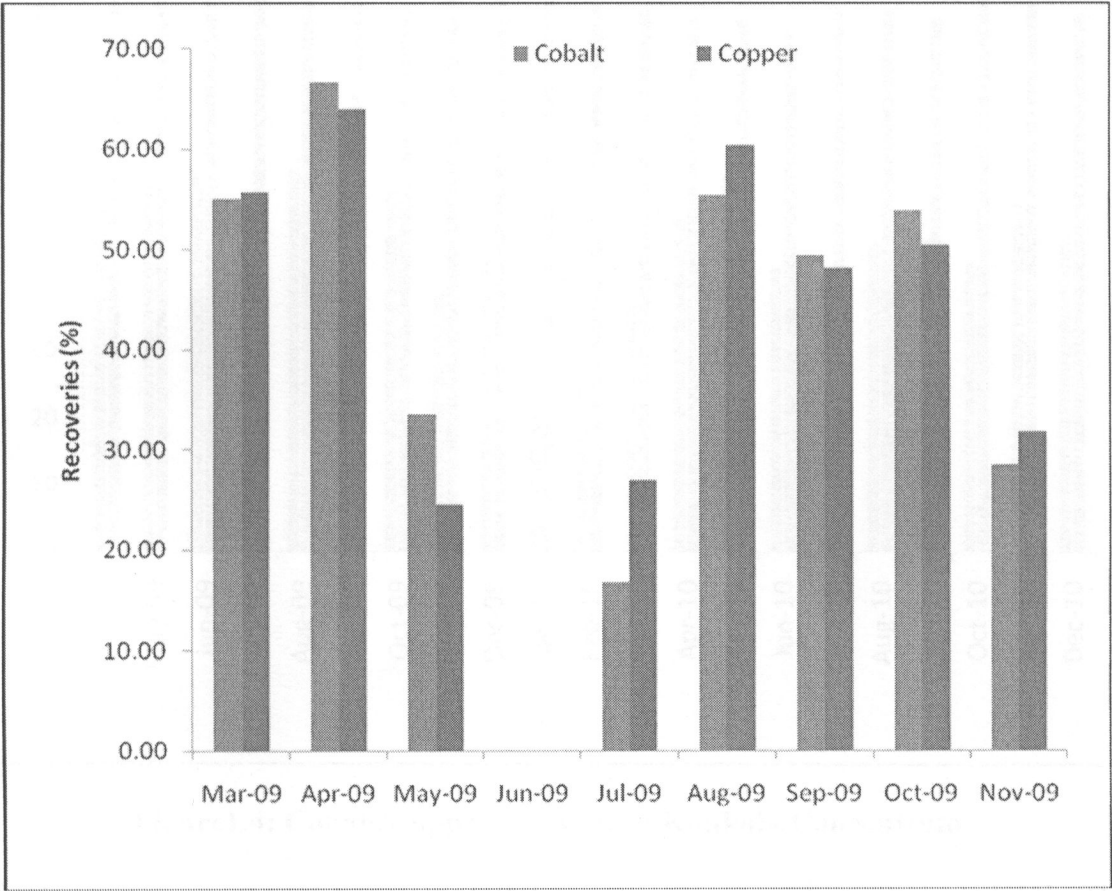
Figure1.3: Cobalt/Copper recovery in Nchanga Concentrator

Although a higher percentage of cobalt is found in Nchanga ores, Konkola ores also have a substantial amount of cobalt as shown in Table 1.1. However, the cobalt mineral in the Konkola ores has not received primary attention until in the recent past due to fact that the Konkola Concentrator is designed to treat copper ores. Figure 1.4 shows that on average about 47% TCo in the Konkola ores reports to the copper concentrates. Therefore, the challenge is to improve the recovery of cobalt without adversely affecting copper recovery.

7
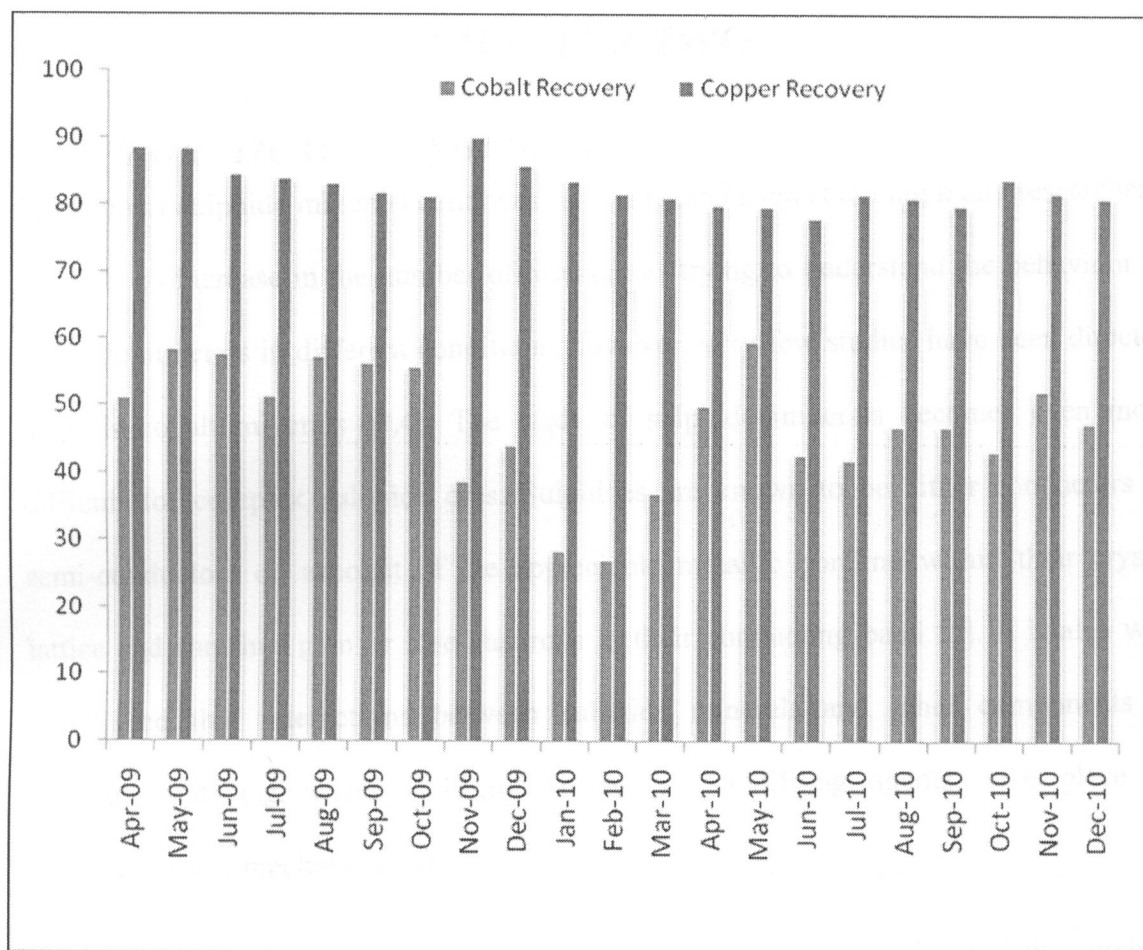
Figure1.4: Cobalt/Copper recovery in Konkola Concentrator

Similar works on the Nchanga and Baluba Ores were earlier conducted [3]. The emphasis of this work was on characterisation of the mineral surface to effect the separation of cobalt from copper minerals using flotation. This research work focuses on improving/promoting the cobalt minerals in the copper concentrate. In this study, Chalcopyrite and Carrollite minerals from Konkola and Nchanga mines were subjected to electrokinetic experiments under different conditions. In an effort to address the low recoveries of cobalt minerals in the two Concentrators, this research work was formulated to understand the electrokinetic properties of Carrollite and chalcopyrite mineral.

8

CHAPTER TWO

2.0 THEORETICAL BACKGROUND

Flotation of sulphide minerals continues to be a heated subject among many researchers. There is an increase in the number of researchers trying to understand the behaviour of sulphide minerals in different conditions, however, very few studies have been directed towards cobalt minerals [3,4]. The study of sulphide minerals becomes even more difficult for complex sulphide ores. Sulphides are known to be either conductors or semi-conductors on account of the appreciable metallic bonding within their crystal lattice and can thus gain or lose electrons in their conducting band [5]. It is also well established that interactions between sulphide minerals and other components of flotation pulp e.g. water, collector species or modifying agents, take place by electrochemical mechanism [5].

The reactions involving electron transfer between dissolved species and the sulphide mineral surfaces across the double layer may occur leading to chemical and physical changes of the interacting species. These reactions generally involve anodic oxidation of the mineral surface coupled with the cathodic reduction of oxygen. Of all the common sulphides minerals, chalcopyrite has received the most attention in terms of understanding its behaviour under different conditions [3,6]. In almost all the research work on the floatability of chalcopyrite it is clear that the mineral has a tendency of floating even without the addition of a collector or with starvation amounts of collector. This has been demonstrated in the works of many researchers [3,7]. In all of these

9

studies an oxidising environment with high pulp potential seemingly contributed to the collectorless flotation of chalcopyrite [3,5,6,7].

The nature of the mixed reactions, reduction and oxidation reaction, taking place on the surface of the mineral and in media surrounding the mineral makes it clear that electrochemical techniques are indispensable in the quest to study the surface reactions on the sulphide minerals. Particles in aqueous solutions acquire an electrical charge; this charge plays an important role in determining the properties and behaviour of the mineral and may be monitored through electrokinetic measurements. Electrokinetic studies have shown that the charge on the surface of the mineral changes with pH and the environment in which the mineral is prepared [8]. The emphasis in most of these studies has been on the purity of the mineral, contaminations always alter the behaviour of pure mineral. While the zeta potentials may not be exactly the same for the same mineral from different sources, the electrokinetic properties show a similar trend.

2.1 Mineral Solution – Interface Chemistry

Mineral processing begins with comminution (crushing and grinding) prior to any chemical treatment. Comminution is an indispensable process to liberate the valuable mineral particles from the gangue so that the ore can be subjected to recovery of valuable minerals. The liberated valuable minerals are separated from the gangue using recovery techniques such as flotation. The galvanic interactions in wet grinding of sulphide ores and flotation which involve interactions of thiol collectors with sulphide minerals all involve oxidation- reduction reactions.

2.1.1 Galvanic Interaction

The interaction between two sulphide minerals resulting from their electrochemical reactivities is called galvanic. Such interactions occur whenever two or more sulphide minerals (or a sulphide mineral/grinding media) are in contact. The electrochemical reactivity is indicated by the rest potential of the sulphide mineral, ie the higher the rest potential, the nobler it is and the less active in a thermodynamic sense. When two sulphide minerals are in contact with each other, a galvanic cell is established in which the mineral with higher rest potential draws electrons from the one with lower rest potential thus undergoing a cathodic reaction [9].

The cathodic reaction can be represented by:

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \tag{1}$$

While the anodic oxidation of the sulphide mineral with a lower rest potential is given by:

$$MeS \rightleftharpoons Me^{2+} + S + 2e^- \tag{2}$$

The overall reaction being :

$$2MeS + O_2 + 2H_2O \rightleftharpoons 2Me^{2+} + 2S + 4OH^- \tag{3}$$

The higher the difference in rest potentials of two sulphide minerals, the higher is the rate of oxidation (dissolution) of the sulphide with the lower rest potential [9]. The rest potential of some sulphide minerals are given in Table 2.1.

Table 2.1: Rest potentials of some sulphide minerals at pH 4.

Mineral	Rest Potential (V vs. SHE)
Pyrite	0.66
Chalcopyrite	0.56
Carrollite	0.45
Bornite	0.42

The rest potentials vary depending upon the type of solution, the pH, the nature of impurities in the mineral and the purity of the electrolyte.

2.1.2 Grinding

The grinding environment in the mill, i.e. reducing or non-reducing, influences the flotation behaviour [10,11]. Several reactions which occur during grinding such as dissolution of oxidized species, release of metal ions into the pulp solution, precipitation, preferential adsorption of the reaction products and ions onto mineral surfaces, etc are the result of the mineral-mineral, mineral – reagent, mineral grinding media interactions in the milling environment [9]. Conventional mill (ferruginous grinding) has a reducing environment which may be attributed to the following reactions:

$$Fe^{2+} + 2e^- \Leftrightarrow Fe \qquad (E_0 = -0.440V) \qquad (4)$$

$$Fe(OH)_2 + 2H^+ + 2e^- \Leftrightarrow Fe + 2H_2O \qquad (E_0 = -0.047V) \qquad (5)$$

$$Fe_3O_4 + 8H^+ + 8e^- \Leftrightarrow 3Fe + 4H_2O \qquad (E_0 = -0.084V) \qquad (6)$$

12

However, in autogenous mill the environment is non-reducing and generally a higher potential is expected. Sulphide minerals react as follows in an oxidizing environment:

$$MeS \Leftrightarrow Me^{2+} + S^{2-} \tag{7}$$

$$2S^{2-} + 3H_2O \Leftrightarrow S_2O_3^{2-} + 6H^+ + 8e^- \tag{8}$$

$$S_2O_3^{2-} + 5H_2O \Leftrightarrow 2SO_4^{2-} + 10H^+ + 8e- \tag{9}$$

2.1.3 Effect of Grinding on Flotation

The effect of grinding on the floatability of some sulphide minerals has been studied in terms of galvanic interactions [12,13]. The conclusion from both of these research works is that sulphide mineral – grinding media interactions lead to oxy-hydroxide coatings on noble minerals, thereby affecting their floatability. This comes about as a result of Iron in the steel ball undergoing anodic reaction thereby giving out electrons which are subsequently picked up in cathodic reaction of oxygen giving oxy-hydroxide as the main product.

$$Fe \Leftrightarrow Fe^{2+} + 2e^- \quad \text{(anodic reaction)} \tag{10}$$

$$O_2 + 2H_2O + 4e^- \Leftrightarrow 4OH^- \quad \text{(cathodic reaction)} \tag{11}$$

$$Fe^{2+} + 2OH^- \Leftrightarrow Fe(OH)_2 \quad \text{(precipitation)} \tag{12}$$

The oxy-hydroxide reacts with iron ions to give iron hydroxide as shown in equation 12. With the change in pH from acidic to alkalinity, the iron hydroxide precipitates thereby covering the surfaces of valuable minerals and consequently inhibiting flotation [13]. Multi-electrode galvanic cells are formed in multi-minerals system. For example, in wet grinding of chalcopyrite – Carrollite – Bornite, the noblest is chalcopyrite and will act as cathode while grinding media as anode [9]. The other sulphides develop an intermediate cathodic or anodic behaviour with respect to each other depending on their rest potentials, relative position with respect to main cathode and main anode and the polarisation characteristics of the electrodes [14].

The simultaneous presence of a collector during grinding appears to minimise the galvanic interactions by prior adsorption on the mineral surface [9]. However, in the case of Xanthate as a collector, the corrosion rate of steel balls increases, i.e. the metastable ferric Xanthate formed as a result of Xanthate – grinding media interaction decomposes into dixanthogen and Fe^{2+} ions, thereby enabling the freshly formed ball surfaces to react further with Xanthate. Another factor that would lead to higher ball rate corrosion would be the number of sulphide minerals present in the ores. This is due to the fact that sulphide minerals are cathodic to the grinding media; an increase in the sulphide minerals implies a larger cathodic surface which may consequently lead to enhanced iron dissolution from the grinding media [9].

2.2.0 Charged Interface

Most substances acquire a surface electric charge when brought into contact with a polar (e.g. aqueous) medium, possible charging mechanisms being ionisation, ion preferential

adsorption and dissolution [3]. The acquired surface charge influences the distribution of nearby ions in the polar medium [15]. Counter ions, which are opposite ions, are attracted towards the charged surface, while co-ions are distributed away from the surface into the polar medium. According to Brownian motion theory, in the absence of external forces all suspended particles, regardless of their size, have the same average translational kinetic energy [15]. The motion of individual particles is continually changing direction as a result of random collisions with molecules of medium, other particles and the walls of the containing vessel. Each particle pursues a complicated and irregular zig-zag path. When the particles are large enough for observation, this random motion is referred to as Brownian motion. The counter charges may consist of simply a diffuse atmosphere of counter ions or it may take the form of a compact layer of bound charges and a diffuse layer. The set up of the surface, compact and diffuse layer charges together constitute the so called Electric Double Layer (edl) as shown in Figure 2.1.
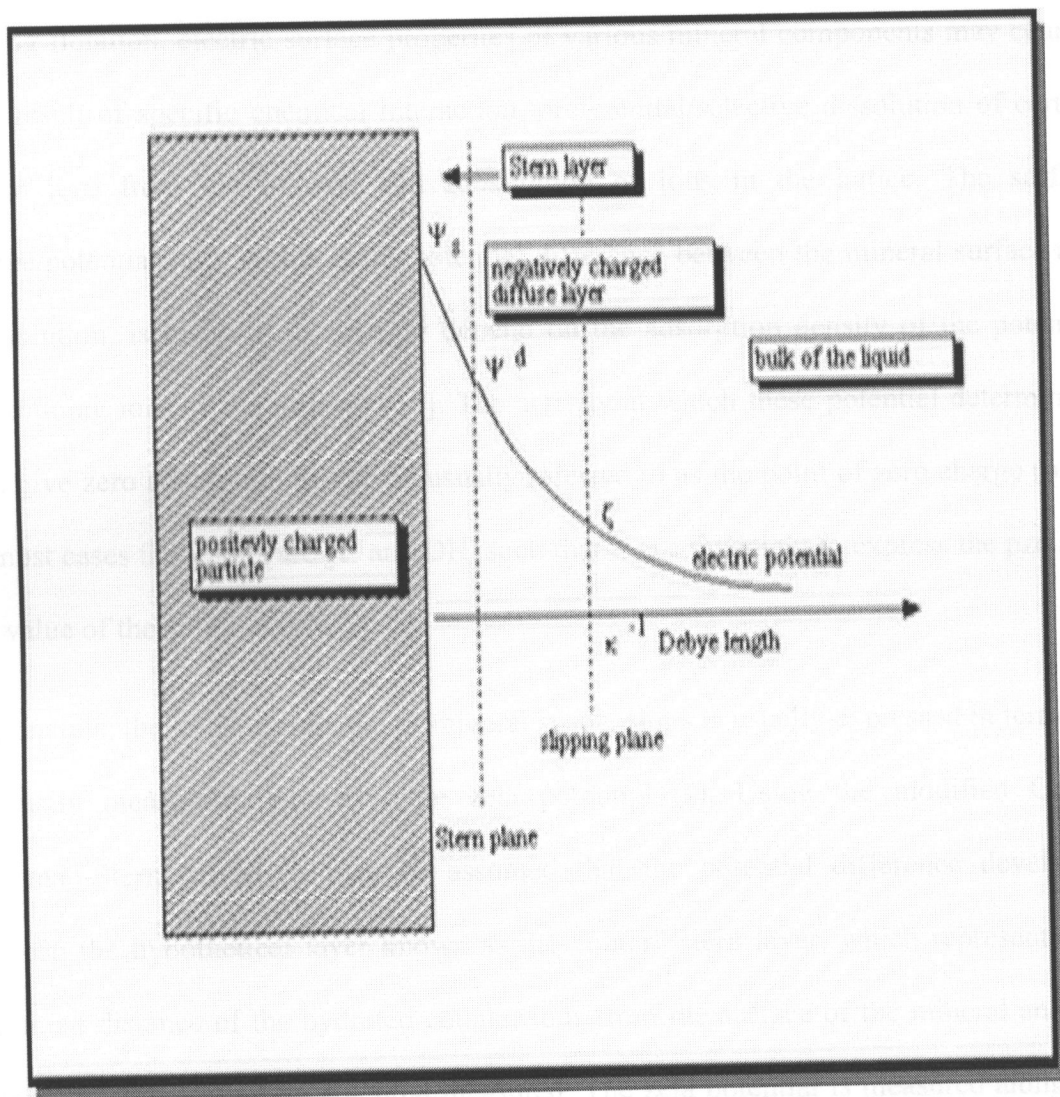
Figure 2.1: Electric Double layer

Most minerals acquire a positive surface charge when in contact with aqueous solution. The stern layer consists of counter ions accumulated on the charged surface to maintain electro-neutrality of the mineral surface. The excess charge on the surface leads to the diffuse layer towards the bulk of the solution having equal but oppositely charged ions. The slipping plane demarcates the bulk solution and stationery layer (consisting of stern and diffuse layer).

During flotation, electric surface properties of various mineral components may change as a result of specific chemical interaction, preferential/selective dissolution of certain lattice ions from the mineral and substitution of ions in the lattice. The surface charge/potential (ψ_0), which is the potential difference between the mineral surface and the solution, is believed to strongly depend on the adsorption density of the potential determining ions of the mineral [15]. The activity at which these potential determining ions give zero adsorption density is usually referred to as the point of zero charge (pzc). In most cases these ions are H^+ and OH^- such that it is convenient to express the pzc as a pH value of the solution (pH_{pzc}).

In principle, the surface potential of mineral suspensions is usually expressed in terms of an easily measurable property, the zeta potential (ζ). Using the modified Guoy-Chapman-Stern Model, it may be assumed that the potential difference developed between the hypothetical layer known as the "outer" stern layer, which represents the minimum distance of the hydrated counter ions from the surface of the mineral and the solution results in the zeta potential measured. The zeta potential is measured along the slipping plane as shown in Figure 2.1. This potential may be measured by four basic techniques i.e. electrophoresis, electro-osmosis, streaming potential and sedimentation potential described below depending on the material involved [16]. The most applicable ones in mineral processing are electrophoresis and streaming potential.

Table 2.2: Techniques for zeta potential (ζ) measurements

Name	Principle involved
Electrophoresis	Invoves the movement of charged colloidal particles with respect to a stationery electrolyte due to an applied potential gradient.
Streaming potential	Deals with the electrical potentials generated as a result of the flow of an electrolyte through a stationery bed (porous) of charged solid particles.
Electroosmosis	Refers to the movement of charged solid particles through a capillary or capillaries due to an applied potential.
Sedimentation potential	Describes the potential generated by a dispersion of charged colloidal particles settling due to gravitational pull.

The information obtained from zeta potential measurements may play a very determining role in arriving at suitable separation models for various systems. In mineral processing this information helps to:

1. Arrive at a possible explanation of the adsorption mechanism for various reagents on the mineral of interest;

2. Select appropriate mineral processing reagents for various environments; and

3. Characterise the activation and depression mechanism by various reagents

2.2.1 Electrophoresis

Electrophoresis is the motion of dispersed particles relative to a fluid under the influence of a spatially uniform electric field. It is ultimately caused by the presence of a charged interface between the particle surface and the surrounding fluid. The term electrophoresis refers to the motion of a charged particle when an electric field is applied [3]. When the velocity of the particle is measured, by timing over a known distance, it is

18

possible to calculate the electrical potential at the surface of shear between the particle and the surrounding medium and from this the electric charge contained within the surface of shear [15]. When the particle is in a relative charge free medium, such as air or a low dielectric constant liquid, it becomes convenient to calculate the charge directly. Careful consideration must be given to whether the charge is an equilibrium property of the particle or whether it is an accidental property determined by the history of the particle and what it happens to have collided with [15]. However in aqueous solution (or in liquids of all but the lowest dielectric constant) the surface potential and charge of a particle is a reproducible quantity that gives valuable information both on the way the particle can interact with other particles or surfaces and on the nature of the particle surface. The dispersed particles have an electric surface charge, on which an external electric field exerts an electrostatic coulomb force. According to the double layer theory, all surface charges in fluids are screened by a diffuse layer of ions, which has the same absolute charge but opposite sign with respect to that of the surface charge [15]. The electric field also exerts a force on the ions in the diffuse layer which has direction opposite to that acting on the surface charge. This latter force is not actually applied to the particle, but to the ions in the diffuse layer located at some distance from the particle surface, and part of it is transferred all the way to the particle surface through viscous stress. This part of the force is also called electrophoretic retardation force.

Considering the hydrodynamics friction on the moving particles due to the viscosity of the dispersant, in the case of low Reynolds number (Re) and moderate electric field

strength, the velocity of a dispersed particle is simply proportional to the applied field, which leaves the electrophoretic mobility defined as:

$$\mu_e = \frac{v}{E}.$$ (13)

Where

- E is electric field strength *(v/m)*

- v is velocity of dispersed particles *(m/s)*

- μ_e is electrophoretic mobility *(m²/sv)*

The most well known and widely used theory of electrophoresis was developed in 1903 by Smoluchowski and related the electrophoretic mobility to zeta potential as follows:

$$\mu_e = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta},$$ (14)

where

- ε_r is the dielectric constant of the dispersion medium

- ε_0 is the permittivity of free space ($C^2\,N^{-1}\,m^{-2}$), η is dynamic viscosity of the dispersion medium (Pa s)

- ζ is zeta potential (i.e., the electrokinetic potential of the slipping plane in the double layer)

The Smoluchowski theory is very powerful because it works for dispersed particles of any shape at any concentration. Unfortunately, it has limitations on its validity. It

20

follows, for instance, from the fact that it does not include Debye length κ^{-1}. However, Debye length must be important for electrophoresis. Increasing thickness of the electric double layer (DL) leads to removing point of retardation force further from the particle surface. The thicker DL, the smaller retardation force must be.

Detailed theoretical analysis proved that the Smoluchowski theory is valid only for sufficiently thin DL, when particle radius a is much greater than the Debye length [15] $(a\kappa \gg 1)$. This model of "thin Double Layer" offers tremendous simplifications not only for electrophoresis theory but for many other electrokinetic theories. This model is valid for most aqueous systems because the Debye length is only a few nanometres there. It breaks only for nano-colloids in solution with ionic strength close to water.

The Smoluchowski theory also neglects contribution of surface conductivity. This is expressed in modern theory as condition of small Dukhin number (Du) [15] (Du < < 1). In the effort of expanding the range of validity of electrophoretic theories, the opposite asymptotic case was considered, when Debye length is larger than particle radius: (κa < 1). Under this condition of a "thick Double Layer", Huckel predicted the following relation for electrophoretic mobility:

$$\mu_e = \frac{2\varepsilon_r \varepsilon_0 \zeta}{3\eta}.$$ (15)

This model can be useful for some nano-particles and non-polar fluids, where Debye length is much larger than in the usual cases.

There are several analytical theories that incorporate surface conductivity and eliminate the restriction of a small Dukhin number, pioneered by Overbeek and Booth. Modern, rigorous theories valid for any Zeta potential and often any κa stem mostly from Dukhin-Semenikhin theory. In the thin Double Layer limit, these theories confirm the numerical solution to the problem provided by O'Brien and White [15].

Recent molecular dynamics simulations nonetheless suggest that a surface charge is not always required for electrophoresis to occur, and that even neutral particles can migrate in an electric field due to the molecular structure of water at the interface [15].

2.2.2 Adsorption of Xanthates

The misplacement of valuable minerals to the wrong product is a common problem in flotation. This may be caused by inadequate liberation, mechanical entrainment or flotation process due to the properties inherent in the mineral or induced by contaminant species. One source of contamination in processing sulphide ores is the release of metal ions from one mineral by anodic oxidation, often enhanced by galvanic interaction, which then migrate to other mineral surfaces. Contamination of the mineral surface arising from metal ion transfer may change the floatability of minerals and affect selectivity. Metal ions may be present on the surface as "hydroxides" [35], which render the sulphide minerals hydrophilic and decrease floatability. In other situations, metal ion species may induce interaction with xanthate and enhance floatability. Cu ions are often considered to play this role. Xanthates are widely used in flotation of the sulphide minerals. Xanthates are the reaction products of carbon disulphide, an alcohol and an alkali [37]. Commercial xanthates rarely have a purity of more than 90% [16], and they

22

contain an oxidation product (dixanthogen), polysulphides and other sulphur compounds formed by side reactions in small quantities [36]. There is also xanthic acid that is a decomposition product of xanthate ion. Hydrolysis of the xanthate ion is [16]:

$$K^+ + ROCS_2^- + H_2O \Leftrightarrow K^+ + OH^- + ROCS_2H \tag{16}$$
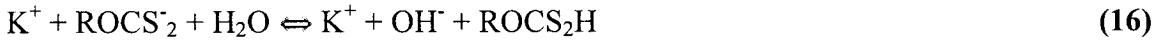
The sole effect of pH is to control the degree of dissociation of xanthic acid. The equilibrium expression for xanthic acid is:

$$Ka = \frac{[H^+][X^-]}{[HX]} \tag{17}$$

where $[X^-]$ is concentration of xanthate ions, $[H^+]$ is concentration of hydrogen ions, $[XH]$ is concentration of xanthic acid and Ka is the dissociation constant [37]. In the presence of oxygen, xanthate is oxidized to dixanthogen according to the reaction below [37,16]:

$$\tag{18}$$
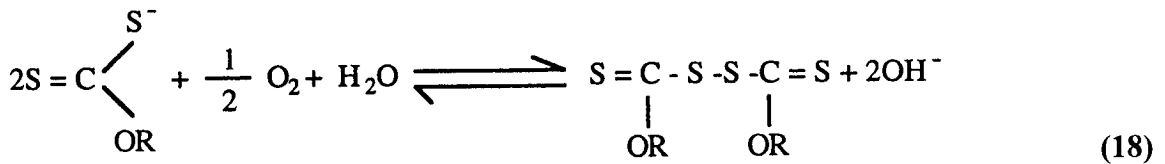
Xanthogen is not stable in dilute aqueous solutions; rapid decomposition occurs in the range of pH < 4 and >9 [39]. The dixanthogen is reverted to xanthate in alkaline solutions [16,39,40].

2.2.3 Langmuir Equation

The Langmuir equation (also known as the Langmuir isotherm, Langmuir adsorption equation or Hill-Langmuir equation) relates the coverage or adsorption of molecules on

a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature. The equation was developed by Irving Langmuir in 1916 [40]. The equation is stated in a simplified form as:

$$\frac{P}{V} = \frac{1}{aV_m} + \frac{P}{V_m}$$ (19)

A plot of $\frac{P}{V}$ against P will result in a straight line from which V_m can be obtained as reciprocal of the slope.

Where

- V is volume of gas adsorbed at pressure P
- V_m is monolayer capacity
- a is affinity constant.

The constant α is the Langmuir adsorption constant and increases with an increase in the binding energy of adsorption and with a decrease in temperature. Whenever a gas is in contact with a solid there will be an equilibrium established between the molecules in the gas phase and the corresponding adsorbed species (molecules or atoms) which are bound to the surface of the solid.

As with all chemical equilibria, the position of equilibrium will depend upon a number of factors :

1. The relative stabilities of the adsorbed and gas phase species involved

2. The temperature of the system (both the gas and surface, although these are normally the same)

3. The pressure of the gas above the surface

In general, factors (2) and (3) exert opposite effects on the concentration of adsorbed species - that is to say that the *surface coverage* may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.
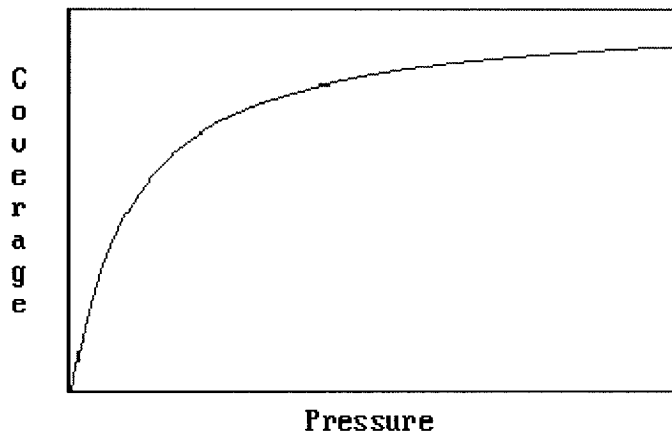
In the case of Xanthate adsorption on the mineral surface, a mono-layer is achieved with respect to time. There is no further adsorption for some time until a critical point has been reached where a layer (double / multi-layer) is formed on top of a monolayer. In the flotation process, the monolayer is usually sufficient to effect the desired properties on the mineral surface. Multi-layers are detrimental in inducing hydrophobicity on the mineral surface and are a waste of reagents. Multi-layer adsorption is explained by the BET equation.

2.2.4 BET Theory

Molecules often do form multilayers, that is, some are adsorbed on already adsorbed molecules and the Langmuir isotherm may not be valid. In 1938 Brunauer, Emmett, and Teller developed a model isotherm that takes that possibility into account [40]. Their theory is called the BET theory, whose mathematical formulation is as follows:

$$\frac{P}{V\left(P_o - P\right)} = \frac{P}{P_o}\left[\frac{1}{V\,c} + \frac{(C-1)}{Vm}\right] \tag{20}$$

A straight line is obtained when $\dfrac{P}{V\left(P_o - P\right)}$ is plotted against $\dfrac{P}{P_o}$ with $\dfrac{1}{V_m c}$ as the intercept, from which V_m can be calculated.

Where

- P_o is the vapour pressure of the liquefied gas

- V is the volume of adsorbed adsorbate at standard temperature and pressure (dm^3)

- V_m is the volume of the amount of adsorbate required to form a monolayer at standard temperature and pressure (dm^3)

- c is the affinity constant

The key assumption used in deriving the BET equation is that the successive heats of adsorption for all layers except the first are equal to the heat of condensation of the adsorbate.

2.3.0 Surface Characterisation

2.3.1 Photoelectron Spectroscopy

The principle of photoelectron spectroscopy utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons. This helps to study the composition and electronic state of the surface region of a sample. The techniques for analysing surface species can be subdivided into two according to the source of exciting radiation:

i.   *X-ray Photoelectron Spectrometry*

- Using soft X-rays with a photon of $200 - 2000eV$ to examine core electrons.

ii. *Ultraviolet Photoelectron*

- Using vacuum UV radiation with photo energy of $10 - 45eV$ to examine valence levels.

In understanding the behaviour of minerals in different conditions it is imperative to characterise the species formed on the mineral surface as these formed species have an effect on flotation. There are various techniques used to characterise surfaces [3]. X-ray Photo-electron Spectroscopy (XPS) is the most widely used technique which has been used by a number of researchers [3,4,33].

2.3.2 X-Ray Photoelectron Spectroscopy

Photoelectron spectroscopy is based upon ejection of an electron using a single photon. The energy of a photon of all types of electromagnetic radiation is given by the Einstein relation :

$$E = h\nu \tag{21}$$

where

h – Planck's constant (6.62×10^{-34} J s)

ν - frequency of the radiation (Hz)

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy).

In XPS the photon is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a core electron. However, in Ultraviolet Photoelectron Spectrometry (UPS) the photon interacts with valence levels of the molecule or solid, leading to ionisation by removal of one of these valence electrons.

The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyser and a photoelectron spectrum can thus be recorded [34].

The process of photo-ionization can be considered in several ways : one way is to look at the overall process as follows :

28

$$A + h\nu \rightarrow A^+ + e^-$$
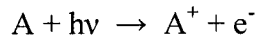
Conservation of energy then requires that :

$$E(A) + h\nu = E(A^+) + E(e\text{-})$$

The electron's energy is present solely as kinetic energy (KE) this can be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - (E(A^+) - E(A))$$

The difference in energy between the ionised and neutral atoms is called binding energy (BE) of the elctron- this then leads to the following equation:

$$KE = h\nu - BE$$

An alternative approach is to consider a one-electron model along the lines of the following pictorial representation.
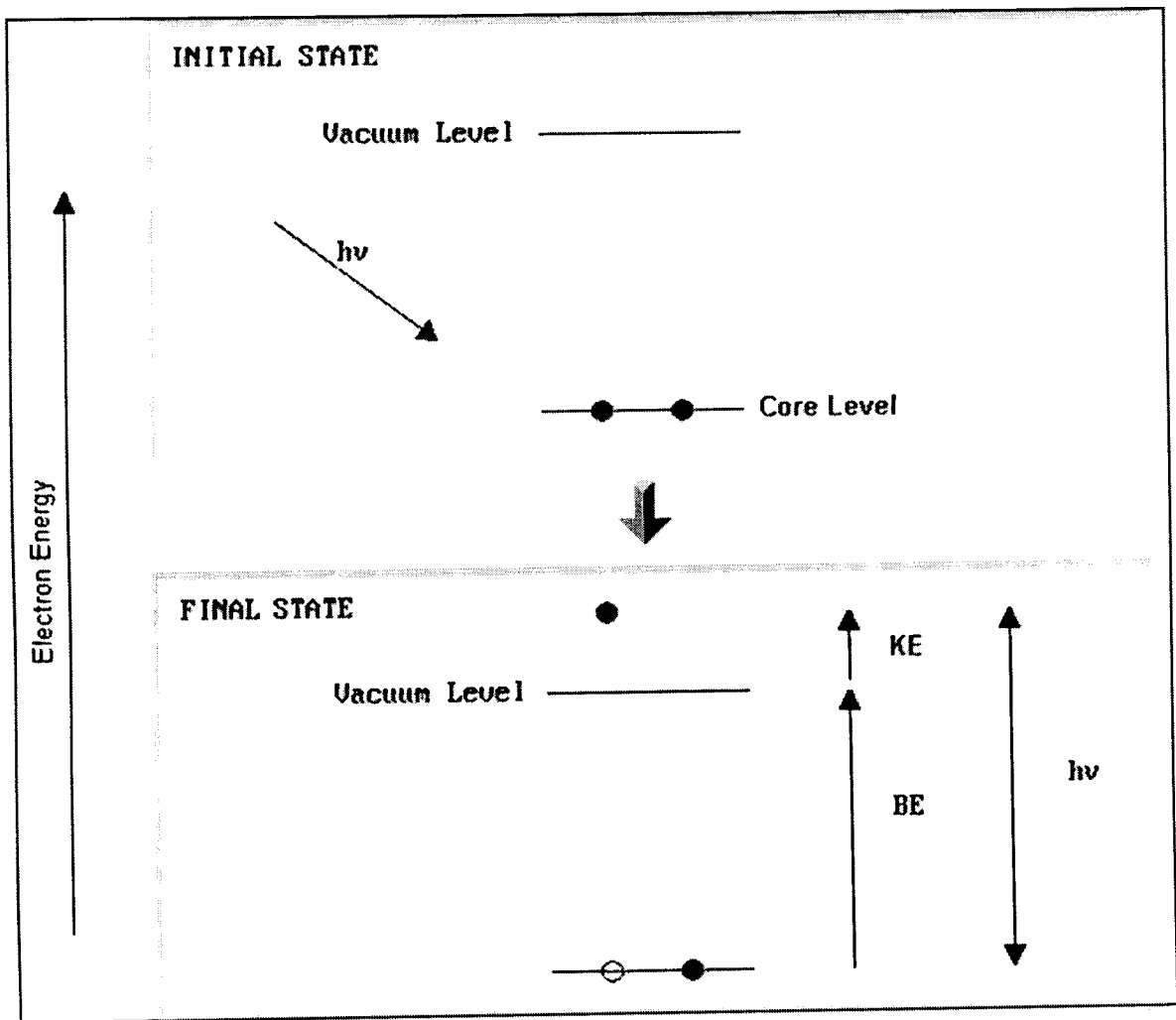
The BE is now taken to be a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level.

NOTE - the binding energies (BE) of energy levels in solids are conventionally measured with respect to the Fermi-level of the solid, rather than the vacuum level. This involves a small correction to the equation given above in order to account for the work function (φ) of the solid.

$$E_b = h\nu - E_k - \varnothing \qquad (22)$$

Where

E_b is core-electron binding energy

$h\nu$ is energy of the exciting radiation

E_k is Kinetic energy

Ø is spectrometer work function, a constant for a given analyser.
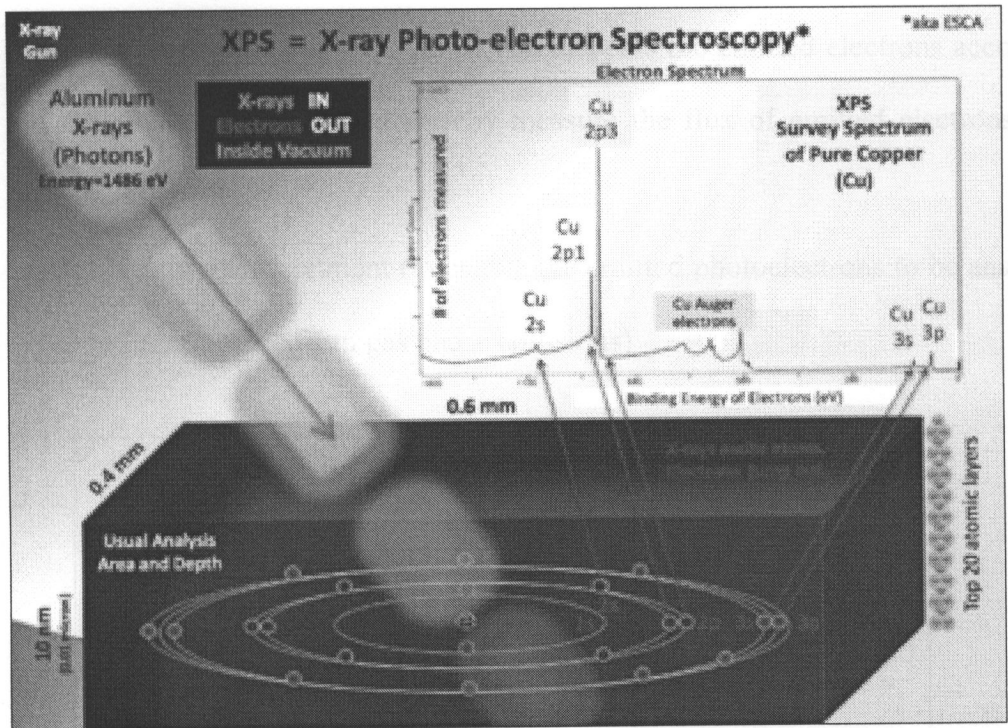
Figure 2.2: Surface characterization using XPS

Binding energies define a specific atom. The energy of the ejected electron E_k is characteristic of the atom involved and its chemical environment. Although the incident X-ray photon may penetrate and excite photoelectrons to a depth of several hundred nanometres, only the photoelectrons from the outermost layers have any chance to

escape from the material environment and eventually be measured. The sample size is a microgram or less whereas the sampling area is approximately $1 cm^2$ [17].

Experimental Details

The basic requirements for a photoemission experiment (XPS and UPS) are:

1. a source of fixed-energy radiation (an x-ray source for XPS or, typically, a He discharge lamp for UPS)

2. an electron energy analyser (which can disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy)

3. a high vacuum environment (to enable the emitted photoelectrons to be analysed without interference from gas phase collisions)
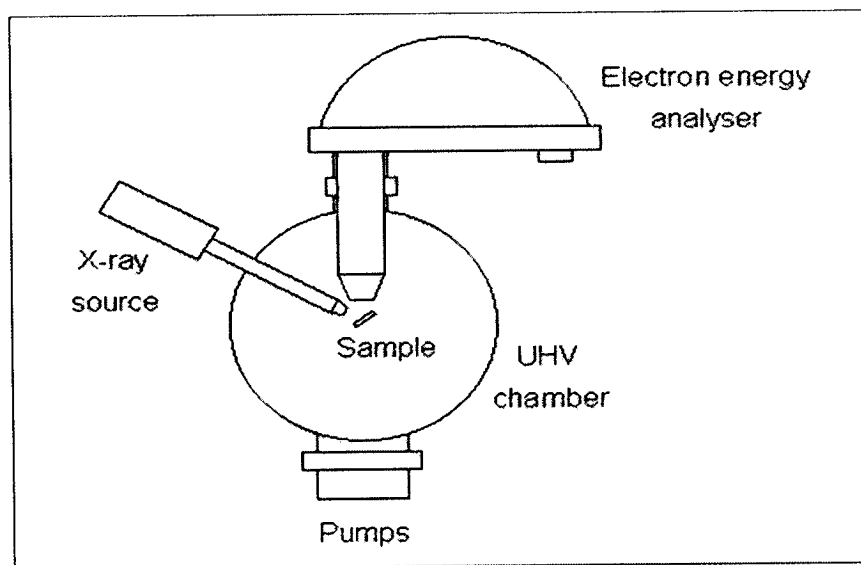
Figure 2.3 Schematic Representation of XPS

There are many different designs of electron energy analyser but the preferred option for photoemission experiments is a concentric hemispherical analyser (CHA) which uses an electric field between two hemispherical surfaces to disperse the electrons according to their kinetic energies [34].

2.3.3 Chemical Shift

For each and every element, there will be a characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies.

The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study - furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region. Thus, the technique provides a *quantitative analysis of the surface composition* and is sometimes known by the alternative acronym , ESCA (Electron Spectroscopy for Chemical Analysis).

The most commonly employed x-ray sources are those giving rise to:

Mg K$_\alpha$ radiation : $h\nu$ = 1253.6 eV and **Al K$_\alpha$** radiation : $h\nu$ = 1486.6 eV

The emitted photoelectrons will therefore have kinetic energies in the range of 0 - 1250 eV and 0 - 1480 eV respectively.

The binding energies of core electrons are affected by the valence electrons and therefore by the chemical environment of the atom. When the atomic arrangement

33

surrounding the atom that ejects a photoelectron is changed, it alters the local (quantum) charge environment at the atomic site. This change, in turn, is reflected as a variation in the binding energy of all the electron of that atom. Thus, not only the valence electrons but also the binding energies of the core electrons experience a characteristic shift. In simplicity, the shifts of the photoelectron lines in an ESCA spectrum reflect the increase in binding energy as oxidation state of the atom becomes more positive.

2.4.0 Contact Angles

The contact angles are a very common measure of the hydrophobicity of a solid surface and are an important parameter in wet processing of minerals such as in froth flotation. The hydrophilic/hydrophobic balance at the surface of the mineral can be evaluated in terms of the contact angle developed between three phases: liquid, solid, and gas [18]. Hence, a variety of contact angles has been defined to address different situations and some of these are outlined below.

2.4.1 The Young Equation

The relationship between surface tension and contact angle was first recognised by Young [18].
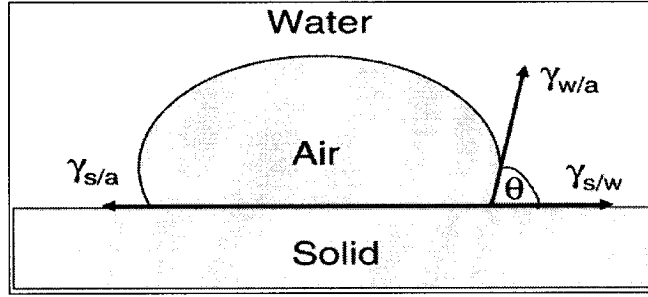
Figure 2.4: Contact angle between bubble and mineral solid surface in an aqueous medium.

In principle, the contact angle of an air bubble on a solid surface in aqueous solution is determined by the mechanical equilibrium under the action of three interfacial tensions:

- $\gamma_{s/a}$ solid–air surface tension

- $\gamma_{s/l}$ solid–liquid interfacial tension

- $\gamma_{l/a}$ liquid–air surface tension.

The contact angle determined by balancing the surface tension forces is known as Young's contact angle, θ_Y, and the relationship describing the balance of surface forces is known as Young's equation [18] as given in equation 23.

$$\gamma_{s/a} = \gamma_{s/l} + \gamma_{l/a} \cos\theta \tag{23}$$

The validity of Young's equation assumes that the solid surface is smooth, flat, homogenous, inert, insoluble, nonreactive, non-porous, and of non-deformable quality.

A surface, which meets all the requirements of the Young equation, is referred to as an ideal surface. However, most practical surfaces are not-ideal and the measurable contact

angle values on such surfaces are referred to as the apparent contact angles, θapp [18].

As a consequence, this value is not unique but falls into a more or less wide interval between the advancing (largest) and the receding contact angle (smallest). The difference between them is called contact angle hysteresis. It can be quite large, as much as 50° for water on mineral surfaces [19]. The three main contributing factors relating to not-ideal surfaces are: contamination of either the liquid or the solid surface, surface roughness, and surface immobility on a macromolecular scale.

2.5.0 Flotation

It is generally recognized that most sulphide minerals are readily floated though the reasons may differ considerably. Some sulphide minerals can be floated without collectors whereas others require a small quantity of a collector (starvation amounts). Flotation of various minerals may be classified in four categories depending on the type of minerals involved. In the case of sulphide minerals, three forms may be identified [3].

- Collectorless flotation

- Selective flotation in which micro-bubble maybe assumed to attach on specific mineral surfaces in the presence of both collector and frother.

- Differential/segregation flotation in which a bulk concentrate is first obtained in the roughing circuit and then specific minerals are differentially/preferentially floated in a subsequent stage.

2.5.1 Collectorless Flotation

Molybdenite is one of the few sulphide minerals which are naturally floatable. The basis for native floatability rests on the assumption that sulphide lattice ions are expected to be weakly hydrated and do not interact strongly with water molecules [20]. Sulphide

minerals react with oxygen and water. The charge transfer mechanism between sulphur and oxygen leads to various oxidation states of sulphur. Extremely low levels of oxygen in the order of 10^{-20} atm can establish an oxidizing potential (E_h). One of the significant findings of electrochemical research on sulphide minerals is the recognition that under certain conditions sulphides will be oxidized to elemental sulphur. Under certain conditions the sulphur reacts with sulphides to form poly-sulphide species or metal deficient sulphides as shown in equation 24.

$$(x-1)S + S^{2-} \Leftrightarrow S_x^{2-} \tag{24}$$

Polysulphides and metal deficient sulphides are usually formed at pH > 8 while elemental sulphur is dominant at pH < 6 [21]. When these species are formed they render the mineral surface hydrophobic and hence a basis for collectorless flotation. This, however, should be distinguished from inherent floatability exhibited by a few sulphide minerals such as molybdenite, which is due to the composition and structure which makes them inherently hydrophobic [22].

2.5.2 Oxidation of Sulphide Minerals

Oxidation of sulphide mineral surfaces is an important phenomenon, especially in the flotation process where it affects the attachment of collectors and may reduce the recovery and grade of valuable minerals. The occurrence of various reactions and their kinetics are strongly influenced by the potential difference across the mineral-solution interface [23]. Thus the floatability of sulphide minerals excluding those which are believed to be naturally hydrophobic is greatly influenced by the degree of oxidation of the mineral surface. The presence of oxygen plays a pivotal role in ensuring that surfaces are adequately oxidized to aid flotation of the valuable minerals [24,25].

37

Several kinds of electrochemical reactions involving sulphide minerals, dissolved oxygen and flotation reagents may occur depending on various thermodynamic conditions prevailing [3]. The most common ones are:

i.   Cathodic reduction of oxygen which may proceed through an intermediate reaction involving H_2O_2

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \tag{25}$$

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \tag{26}$$

To give the overall reaction

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \tag{27}$$

ii.   Anodic oxidation of collector through an adsorption phase

$$X^- \rightleftharpoons X_{ADS} + e^- \tag{28}$$

$$X_{ADS} + X^- \rightleftharpoons 2X_{ADS} + e^- \tag{29}$$

To give an overall reaction

$$2X^- \rightleftharpoons X_2 + 2e^- \tag{30}$$

Or

$$MS + 2X^- \rightleftharpoons MX_2 + S + 2e^- \tag{31}$$
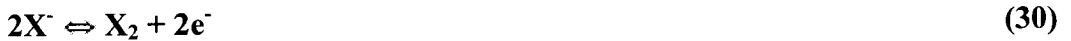
iii. Sulphide mineral oxidation and formation of Polysulphides:

$$MS + 2H_2O \Rightarrow M(OH)_2 + S + 2H^+ + 2e^- \tag{32}$$

38

$$xS + yH2O \Leftrightarrow SxO_y^{2-} + 2yH^+ + (2y\text{-}2)e^- \tag{33}$$

Equation 27 is the most important cathodic reaction and suggests that the presence of oxygen in sulphide systems is a pre-requisite for flotation to occur as was earlier postulated by other researchers [26].

It is generally postulated that, the initial oxidation of simple sulphide minerals in acidic solutions may correspond to a reaction of the type [23]:

$$M_zS \Leftrightarrow zMn^+ + S + zne^- \tag{34}$$

With its equivalent in neutral or alkaline solution as

$$M_zS + znH_2O \Leftrightarrow zM(OH)n + S + znH^+ + zne^- \tag{35}$$

Oxidation leading to sulphur like products is usually considered to be critical in rendering some sulphide minerals such as chalcopyrite [6] and galena [7] naturally floatable (self induced floatable). However, oxidation leading to further oxidation products deteriorates this self induced floatability property. It implies that the nature of oxidation product is very critical more especially if they are soluble [3].

$$xS + yH2O \Leftrightarrow SxO_y^{2-} + 2yH^+ + (2y-2)e^- \tag{33}$$

Equation 27 is the most important cathodic reaction and suggests that the presence of oxygen in sulphide systems is a pre-requisite for flotation to occur as was earlier postulated by other researchers [26].

It is generally postulated that, the initial oxidation of simple sulphide minerals in acidic solutions may correspond to a reaction of the type [23]:

$$M_zS \Leftrightarrow zMn^+ + S + zne^- \tag{34}$$

With its equivalent in neutral or alkaline solution as

$$M_zS + znH_2O \Leftrightarrow zM(OH)n + S + znH^+ + zne^- \tag{35}$$

Oxidation leading to sulphur like products is usually considered to be critical in rendering some sulphide minerals such as chalcopyrite [6] and galena [7] naturally floatable (self induced floatable). However, oxidation leading to further oxidation products deteriorates this self induced floatability property. It implies that the nature of oxidation product is very critical more especially if they are soluble [3].

CHAPTER THREE

3.0 Sampling

3.1.0 Sample

A Sample is a part of a sampling unit or a sample space selected such that a measured value for the part is an unbiased estimate for the sampling unit or sample space [27]. The importance of obtaining representative samples in the field and retaining their integrity throughout their analytical procedures is fundamental to the generation of meaningful data. The sampling of bulk material is well documented in literature but concise definitions, uniform symbols and common rules remain elusive targets [27].

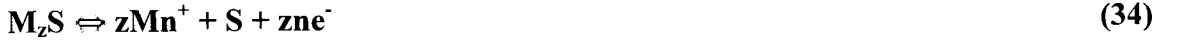Generally, sampling is the process of selecting a part of a whole such that a measured value for the part is an unbiased estimate of the whole. In mineral processing a whole is referred to as a sampling unit such as a mass of mill feed, dewatered concentrate or bullion, or a volume of cyclone overflow or tailings slurry. The validity of the sampling process is based on the following;

3.1.1 Accuracy

A generic term that implies closeness of agreement between the measured value or central value of a set (arithmetic mean or weighed average) and the unknown true value of a stochastic variable [27].

This definition implies that accuracy is an abstract concept. On the other hand, the absence of accuracy can be measured in terms of bias or systematic error. Therefore, sample measurements which are not biased are said to be accurate by definition.

3.1.2 Bias

This is a statistically significant difference between a single measured value or central value of a set, and an unbiased estimate of the unknown value of the stochastic variable [27]. Sampling in mineral processing essentially goes with testing for biasness and unbiasness.

3.1.3 Precision

A generic term that refers to the magnitude of randomly distributed variations (random variation) in the measurement procedure applied to estimate the central value of the stochastic variable of interest [27].

To achieve a sample that has minimal errors and hence representative of the whole (lot) it is necessary to observe the salient features of the Theory of Sampling (ToS).

3.2.0. Theory of Sampling

The practice of sampling remains to be one of the most important exercises in achieving results that are representative of the field of study. In the mining industry a sample that is biased and does not represent the characteristics of the lot would cost the company millions of dollars, this is also true in other industries.

The theory of sampling explains how the errors can be eliminated or minimized so as to come up with the sample that is so close in characteristics to the bulk material. Different types of errors may be caused by material characterisation, sampling protocol and the sampling equipment used and handling. In addressing errors under the theory of sampling, one needs to know the difference between an error and uncertainty.

Error is the difference between an observed or calculated value and a true value; variation in measurements, calculations, or observation of a quantity due to mistakes or uncontrollable factors [27].

Uncertainty is the lack of sureness about someone or something; something that is not known beyond doubt [27].

The following are some of sampling errors [28];

1. **Accidental errors**: these arise from special circumstances and cannot be predicted. These can be dealt with only if they are observed to be occurring.

2. **Average errors**: this is arithmetic mean of a series of samplings (plus or minus).

3. **Systematic errors**: this is a series of samplings which is always wrong in the same way, and thus it produces a cumulative error.

4. **Observation errors**: this is due to misreading a signal or measuring index, or faulty recording.

5. **Personal errors**: this may be random and may cancel out in a carefully observed series.

3.2.1 Material Characterisation

In reality there is no material that is homogeneous. All materials carry a certain level of heterogeneity that becomes a source of errors during sampling process. Such typical amount of heterogeneity is called structural property. If we limit our analysis to zero-dimensional movable lots, two kinds of heterogeneity are identified:

Constitution Heterogeneity of the lot, it consists of typical differences between individual fragments, and mixing has no effect on these differences [27].

Distribution Heterogeneity of the lot, it consists of typical differences between groups of fragments (.i.e. increments), mixing has an effect on these differences. These are the sources of *Fundamental Errors (FE)* and *Group and Segregation Errors (GSE)* respectively. These errors can be minimized by reducing the size of fragments in the lot and mixing thoroughly. This gives every fragment an equal chance of being part of a sample during sampling.

3.2.2 Equipment and Handling

The errors that may come from equipment used in sampling and the way of handling the material can be eliminated if caution is applied in the selection and use of type of sampling equipment and care in material handling. There are three errors that can come from equipment and handling:

Increment Delineation Error, this is caused when the geometry of the outlined increment is not completely recovered. This type of error can be eliminated.

Increment Extraction Error, caused when the material extracted does not coincide with the delineated increment. This can be eliminated.

Increment Preparation Error, this comes from all sources of non-stochastic variation after extraction of the material. This error can be eliminated.

3.2.3 Process and Procedure

The process and procedure of sampling should be as flawless as possible. There are two types of errors that come from this:

43

Increment Weighing Error, this may come from the individual weights of the increment and can be eliminated.

Continuous Selection Error, this comes from random, time and cyclic fluctuation and can be eliminated.These are the main sources of errors in sampling [27].

3.3.0 Estimating Sampling Errors

The salient features in sample preparations which include reduction in particle size and distribution heterogeneity, are designed to minimize fundamental errors and group and segregation errors. The relationship between the fundamental error, sample size and particle size is shown in Gy's formula as follows [29].

$$S^2 = \frac{C*d^3}{m} \tag{36}$$

Where:

S^2 is Relative Variance of contaminant concentration due to fundamental errors

S is Relative standard deviation of contaminant concentration due to fundamental errors

C is Sampling constant for the material to be sampled (gcm^{-3})

d is Diameter of the largest particle (cm)

m is Sample mass (g)

The term S is used to obtain the measure of confidence in the results of sampling procedure. The relative standard deviation of a normal distribution curve representing random assay-frequency data for a large number of samples taken from the ore is S and

the relative variance is S^2. The sampling constant C is specific to the material being sampled, taking into account the mineral content, and its degree of liberation [29].

$$C = fglm \tag{37}$$

Where:

f= Shape factor which is normally taken as 0.5 except for Gold ores.

l=Liberation factor.

m=Mineralogical composition factor.

g=Factor dependant on the particle size range

There are three main sources of error in sampling, material characterisation, sampling protocol and sampling equipment. Errors from sampling protocol and sampling equipment can be minimized by being accurate in all the measurements and procedures and choosing the correct sampling equipment. Material characterisation constitutes of Fundamental Errors (FE) and Group and Segregation Errors (GSE). The Fundamental and Group and Segregation Errors can be minimized by reducing the particle size and mixing the material thoroughly. These errors are determined by the Gy formula.

CHAPTER FOUR

4.0 EXPERIMENTAL METHODS

4.1.0 Materials and Sample Preparations

Hand-picked natural almost pure samples of Carrollite and Chalcopyrite were obtained from the Nchanga and Konkola ores of KCM and elemental composition were determined using X-ray Fluorescence (XRF) whose results are shown in Table 4.1. Sodium Isopropyl Xanthate (SIPX) and Potassium Amyl Xanthate (PAX) of about 84% purity were used as collectors, Potassium hydroxide (KOH) and Nitric acid (HNO$_3$) were used to regulate the pH and FZK 245 was used as frother. Pure water was used in the measurements of advancing contact angle. Leaching, electrokinetics, adsorption, micro-flotation, contact angles, XPS and bench scale flotation were conducted at 25 ± 1^0C. Ore Sample for bench scale flotation was sampled on a moving conveyor belt using a one meter cutter at 30 minutes time interval for 48 hours. All experiments were done at *Kyushu University, Department of Earth Resource Engineering, Laboratory of Mineral Processing and Recycling, Faculty of Engineering, Japan* except for leaching experiments which were done at the University of Zambia and bench scale flotation tests on Nchanga ores which were done in Nchanga Metallurgical laboratory.

Table 4.1: Elemental analysis of Carrollite and Chalcopyrite

XRF Results (Metal %)							
Mineral	Cu	Co	S	Si	Al	K	Ni	Fe
Carrollite	15.60	47.50	35.20	0.18	0.05	0.02	0.22	1.26
Chalcopyrite	38.20	**	30.00	**	**	**	**	31.80

*** means below detection*

The samples were crushed with a porcelain mortar and sieved in a grove plastic to obtain -105µm to +78µm of size fraction for flotation and adsorption experiments and -38µm fractions for electrokinetic experiments.

Figure 4.1: Groove plastic with sieves and porcelain mortal for crushing mineral samples in nitrogen environment.

4.2.0 Leaching Experiments

To determine the amount of copper and cobalt ions lost in solution, leaching experiment using tap water as a solvent were conducted. 100g of Carrollite grains from the Nchanga and Konkola ores were pulverized in the University of Zambia Metallurgical laboratory. 1g of pulverized Carrollite sample was weighed and dissolved in 100ml of water at pH 6, 7.5 and 9. This was performed in triplicates and at different leaching times. The sample was filtered for each specific leaching time and analysed for copper and cobalt content in the filtrate using Atomic Absorption Spectrometry (AAS).

Table 4.2: Leaching times at different pH values

pH	Leaching Time (Minutes)			
6.0	2	4	6	8
7.5	2	4	6	8
9.0	2	4	6	8

4.3.0 Zeta Potential Experiments

Figure 4.2: Electrophoresis Machine ZEECOM ZC-2000

-38µm Carrollite and Chalcopyrite samples were suspended separately in 80ml of $10^{-3}M$

Potassium Chloride (KCl) at specific pH values and conditioned for 10, 30 and 60

minutes. After conditioning at the required pH values, the zeta potentials were measured

using the electrophoretic machine equipped with a video camera. Pellets of SIPX were

used as a collector with a mineral suspension of 6.25g/l. A total reading of 50

electrophoretic mobilities were recorded at first stationery level (0.15mm from the front

rectangular cell wall) and converted to zeta potential using the ZEECOM ZC-

2000system (kyowa Interface Science Co., Ltd) as shown in Figure 4.2.

4.4.0 Adsorption Experiments

Adsorption experiments were performed by preparing 80 ml of aqueous SIPX solutions of 2.53×10^{-5} and 2.02×10^{-4}M. The pH of the solution was maintained in the range (3–11) by adding KOH or HNO_3. To these solutions, 0.5 g of -105μm to +78μm particle size of Carrollite mineral was added and shaken in a temperature-controlled water bath for 5, 15, 30 and 60 minutes. The suspensions were then filtered and filtrate, before and after, were tested for Xanthate concentration using UV (UV- 60 A SHIMADZU, Japan) at 301 nm. The amount of Xanthate ions adsorbed was calculated from the difference between the initial and final concentration of the solutions as shown in equation 38.

$$X_{ad} = X_i - X_f \tag{38}$$

Where

- X_{ad} is amount of Xanthate adsorbed on the mineral surface (ppm)

- X_i is initial Xanthate concentration in solution (ppm)

- X_f is final Xanthate concentration in solution (ppm)

4.5.0 Micro-Flotation

Microflotation tests were carried out in a Hallimond tube at different pH values. For each mineral, a sample of +75μm to -106μm fraction was prepared in a 10^{-3} M KCl solution at different pH (3-11). The solution was conditioned for 10 minutes with and without SIPX before flotation at a constant stirrer rotational speed. During flotation nitrogen gas was used for aeration and the float was collected after 1minute of flotation. The tailings and float were dried and weighed. This procedure was applied to both

minerals. The recoveries were calculated based on the percentage weight of material

floated of total weight of the sample (tailings + float).

$$R(\%) = \frac{C \cdot 100}{(C - T)}$$

(39)

Where

- R is recovery (%)

- C is weight of floated material (g)

- T is weight of Tailings (g)

Flotation tests on the actual cobalt ores were also done at bench scale at Nchanga

metallurgical laboratory using a laboratory flowsheet as follows:

Reagent	gpt	Vol (cc)	Wt (g) of Dry Reagt.	Reagent	gpt	Vol (cc)	Wt (g) of Dry Reagt.
SIPX	0	0.00	0.000	SIPX	0	0.00	0.000
Modifier	0	0.00	0.000	Modifier	0	0.00	0.000
Frother	0	0.000	0.000	Frother	0	0.000	0.000

Feed → 3min Conditioning → 6min Float → 3min Conditioning → 4min Float → Tails

6min Float → Con 1

4min Float → Con 2
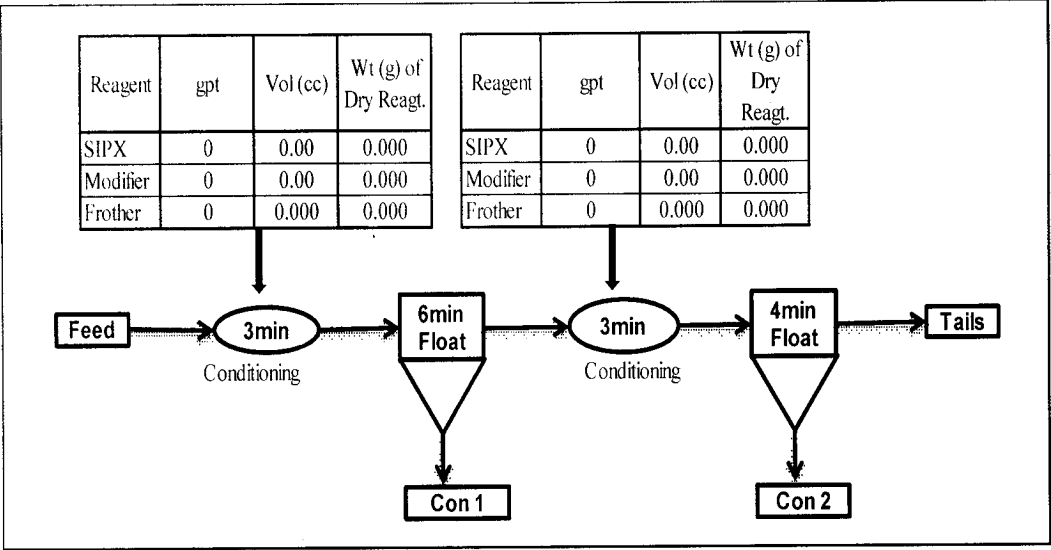
Figure 4.3: Laboratory flotation flowsheet

$$R(\%) = \frac{F(f) * 100}{[F(f) + T(t)]} \qquad\qquad \textbf{(40)}$$

Where

- **R** is recovery (%)

- **f** is the grade of valuable floated mineral in the material (%)

- **F** is weight floated material (g)

- **t** the grade of valuable un-floated mineral in the material (%)

- **T** is weight of un-floated material (g)

4.6.0 Contact Angles

A 2mm Carrollite sample was mounted in epoxy and allowed to solidify. A formed briquette was polished using polishing disc covered with different types of cloth roughness (3000 to 1μm) and using lubricant solution and diamond paste as lubricant. A mirror-like surface was then taken for contact angle measurements after pre-treatment for 10 minutes in acidic and alkaline media (pH 3- 11) using Drop Master Machine. The angles which were measured in this research work were advancing contact angles.
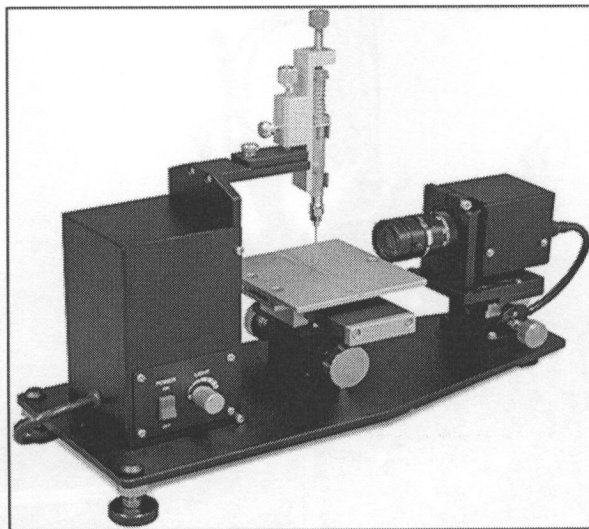
Figure 4.4: Drop master machine for contact angle measurements.

4.7.0 Surface Characterisation Experiments

0.5g of Carrollite samples of -38μm particle size were suspended in 10^{-3}M KCl solution separately and conditioned for 1hour in 100ml Erlenmeyer flask in three different environments; without any additive, with oxygen being bubbled using a glass frit for producing small oxygen bubble with magnetic stirring and in the presence of SIPX at pH 3, 9 and 11.

After 1hour the mineral particles were separated by membrane filtration. Dissolved ions of Cu, Co and S concentrations were determined by ICP-AES, Seiko Vista, Japan. Solid residues were dried overnight for analysis with XPS (PHI 5800 ESCA) as shown in Figure 4.5. The collected data were analysed with Casa XPS software (Ver. 2.3.12).
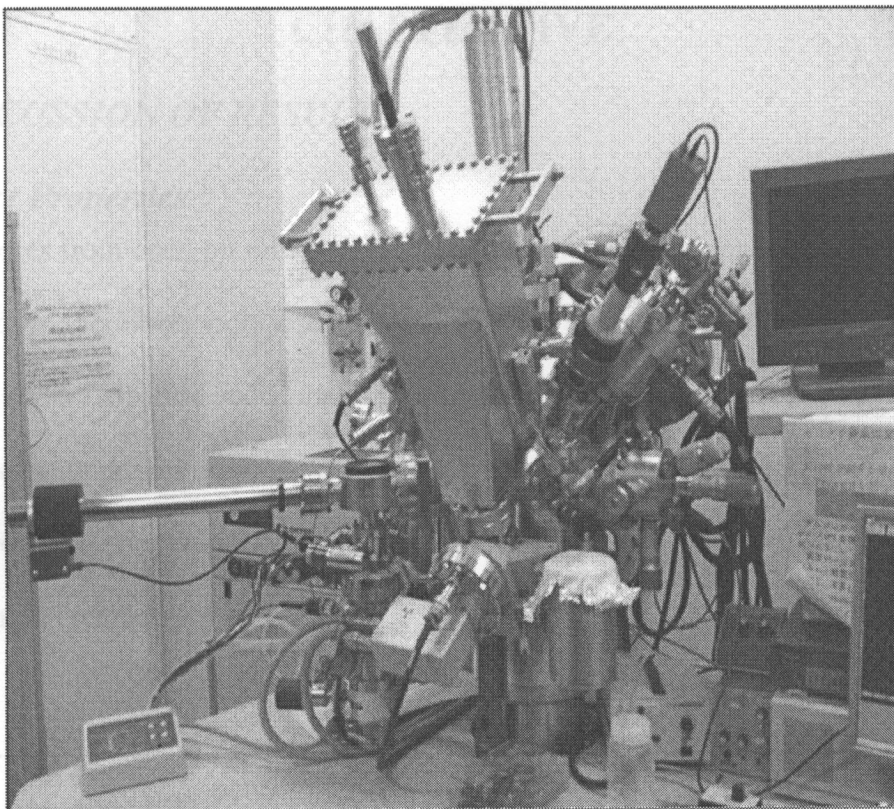
Figure 4.5:X-ray Photoelectron Spectrometer (XPS)PHI 5800 ESCA

CHAPTER FIVE

5.0 DISCUSSION OF RESULTS

5.1.0 Ore Properties

Nchanga ores from open pit mines have a relatively high cobalt content compared to the Konkola ores ,therefore, more attention was directed towards Nchanga ores. Most of the cobalt exists as Carrollite and Cobaltiferous pyrite. However, the cobalt minerals usually co-exist with copper minerals (Chalcopyrite, Chalcocite and Bornite). Open pit ores (cobalt ores) is harder than Konkola ores and as thus it consumes more energy during comminution (see Table 5.1).

Table 5.1: Ore properties

	NCHANGA ORE (OPEN PIT)	KONKOLA ORE(1 & 3 SHAFT)
SPECIFIC GRAVITY	2.65	2.7
BULK DENSITY	*	*
AVG %TCu / ASCu	2.14/0.65	3.00/0.5
AVG %TCo / ASCo	0.344/0.015	0.04/0.004
WORK INDEX (kWh/tonne)	14.84	11.24

means not done

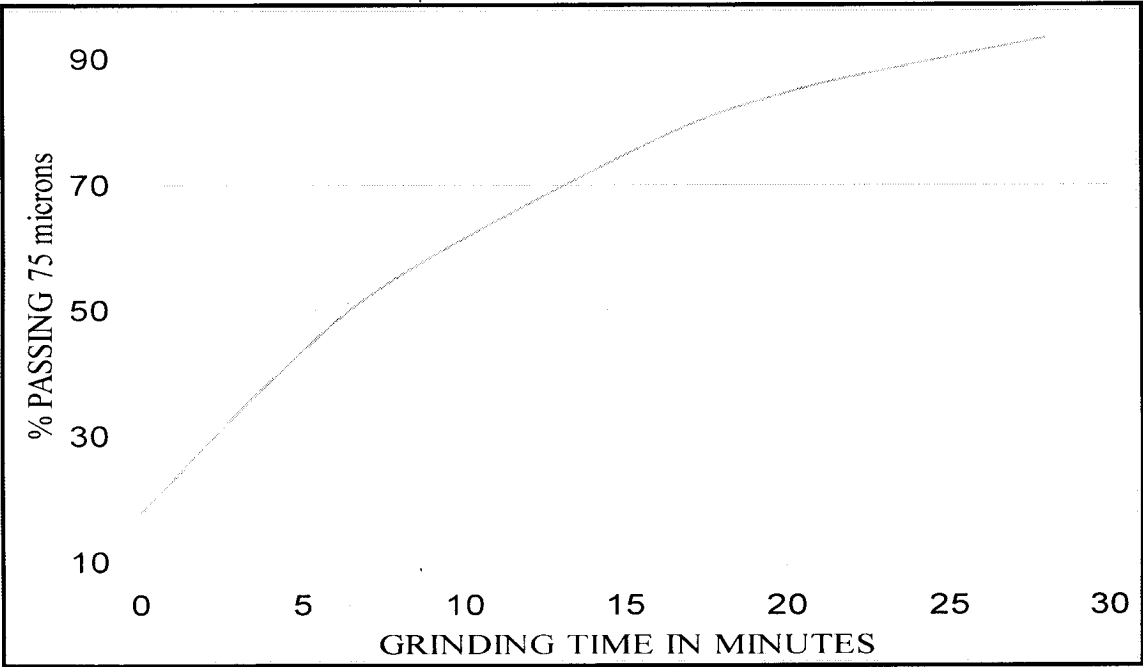To fully liberate the minerals, an optimum mesh of grind was determined as shown in Figure 5.1.

Figure 5.1: Graph of % Passing 75μmVs Grinding time (min.) for Cobalt ore

The results were fairly reproducible for each set of experiments as shown in Table 5.2

Table 5.2 Statistical analysis of Grinding test Results and liberation of minerals

Grinding tests Using 75microns mesh										
Time	Test 1 (%) Passing	Test 2 (%) Passing	Test 3 (%) Passing	Test 4 (%) Passing	Test 5 (%) Passing	Average	Standard Deviation	Coefficient Of Variation.	Free	Locked
0	17.5	17.3	17.4	17.9	17.9	17.6	0.3	1.8	40	50
4	38.6	38.0	39.3	37.7	39.4	38.6	2.3	6.0	55	45
8	55.7	55.3	55.4	55.2	56.4	55.6	0.9	1.7	75	25
12	70.0	69.7	70.2	70.1	69.9	70.0	0.1	0.2	98	2
16	76.6	78.1	78.2	77.0	76.1	77.2	3.4	4.4	98	2
20	83.9	84.2	84.3	84.3	86.3	84.6	3.7	4.4	99	1
24	88.9	89.2	89.5	88.8	89.6	89.2	0.5	0.6	100	0
28	90.8	94.3	93.4	94.0	93.5	93.2	7.7	8.3	100	0

At 12minutes the cobalt minerals were fully liberated (98% free) from the gangue minerals at about 70% passing 75microns. There was no significant difference beyond this grinding time in terms of liberation of cobalt and copper minerals. This means that

12 minutes was the optimum grinding time and all flotation experiments were to be done at this optimum grinding time. However, some of the Carrollite mineral was still associated with copper minerals. The implication is that the cobalt mineral would either be recovered or lost together with the copper minerals. If the cobalt-copper mineral association is more than the individual liberated minerals, recovery and grade of individual minerals would be compromised. This would be a challenging situation in the case of producing separate cobalt and copper concentrate using segregation or differential flotation. However, the challenge in this work is to improve the recoveries of both copper and cobalt minerals using bulk flotation. Therefore, the existence of associated minerals does not pose a challenge at all as regards to this work.

Table 5.3: Liberation of minerals in the ores at optimum grinding time

Mineral	Nchanga Ore					Konkola Ore				
	Wt%	%TCu	%ASCu	%TCo	F:L	Wt%	%TCu	%ASCu	%TCo	F:L
Chalcopyrite	0.173	0.06	**	**	98 : 2	0.951	0.328	**	**	99 : 1
Bornite	0.019	0.012	<<0.001	**	97 : 3	1.695	1.073	0.021	**	99 : 1
Chalcocite	1.616	1.29	0.019	**	98 : 2	1.372	1.095	0.016	**	99 : 1
Pyrite	0.302	**	**	0.009	98 : 2	0.006	**	**	0	98 : 2
Carrollite	0.751	0.116	*	0.31	99 : 1	0.06	0.012	**	0.023	99 : 1
Native Copper	**	**	**	**	**	0.02	0.02	**	**	**
Malachite	0.871	0.502	0.502	**	100 : 0	0.568	0.327	0.327	**	100 : 0
Pseudo-malachite	0.059	0.032	0.032	**	100 : 0	0.121	0.067	0.067	**	100 : 0
Chrysocolla	**	**	**	**	99 : 1	0	0	0	**	100 : 0
Azurite	0.04	0.022	0.022	**	99 : 1	0	0	0	**	100 : 0
Cuprite	0.1	0.089	0.062	**	99 : 1	0.016	0.014	0.009	**	99 : 1
Cupriferous Mica	0.15	0.006	0.002	**	98 : 2	0	0	0	**	98 : 2
Wad	0.167	0.012	0.012	0.015	99 : 1	**	**	**	**	99 : 1
Gangue	95.752	**	**	**		95.192	**	**	**	
TOTAL	100	2.141	0.65	0.334		100	2.936	0.44	0.023	
	**	2.14	0.65	0.344		**	2.94	0.44	0.04	

** *means below detection*

5.2.0 Leaching In Aqueous Solution

5.2.1 Nchanga Ore

The dissolution of copper into the water was relatively higher whereas cobalt recorded insignificant amounts as shown in Figure 5.2. This implies that in acidic media copper bearing minerals underwent an oxidation reaction [5] in which there was electron transfer from the minerals to oxygen in the water and dissolution of copper ions into solution.
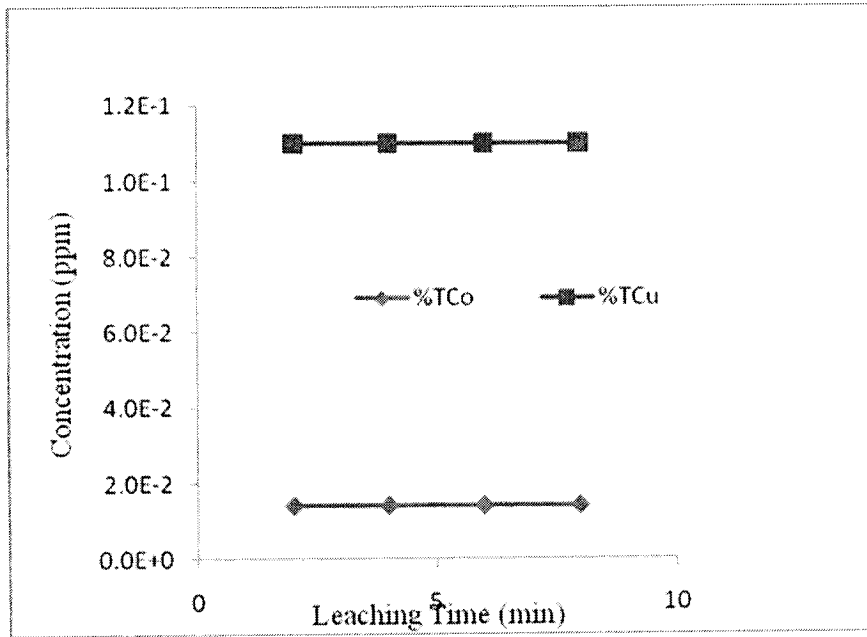
Figure 5.2: Leaching at pH 6.0 at different leaching times

This can be attributed to behaviour of most sulphide minerals which display instability in acidic media. On the other hand, Carrollite, which is the principle source of cobalt showed stability in acidic media. This is confirmed in the works of other researchers [3] who have demonstrated the stability of Carrollite mineral in acidic media.
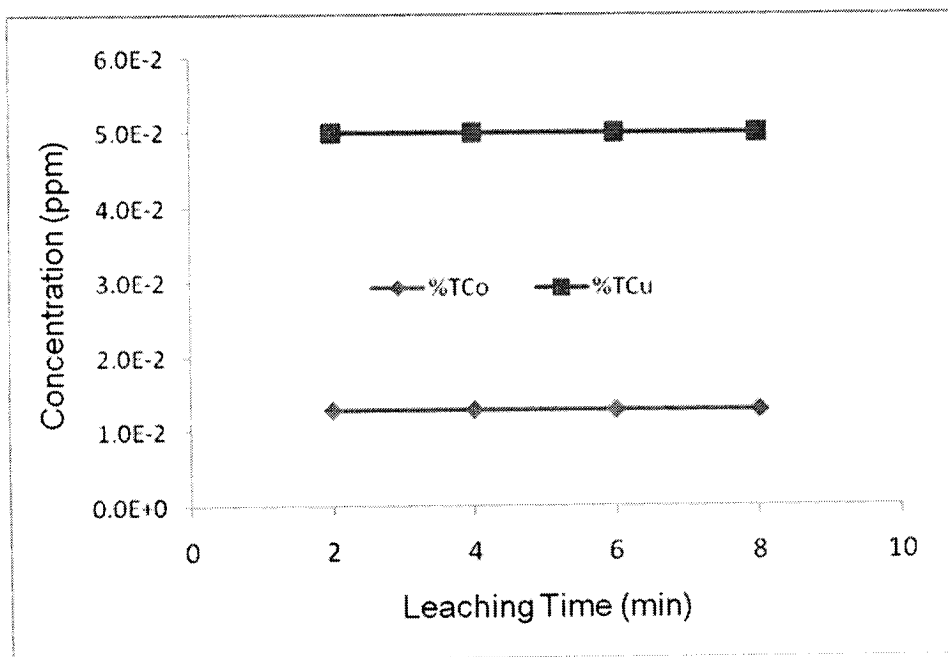
$$MS \Leftrightarrow M_{1-x}S + xM^{n+} + xne^-$$ (41)

Figure 5.3: Leaching at pH 7.5 at different leaching times

Figure 5.3 shows a similar trend to Figure 5.2, however, there was a noticeable change in the amount of copper in solution. The amount of copper ions at pH 7.5 was almost half of that at pH 6. The reduction of copper ions in solution can be attributed to the formation and precipitation of copper hydroxide. It is well documented that copper hydroxide begins to precipitate at pH 5 [3,30], the precipitation is even more pronounced in alkaline media. Equation 42 depicts a general behaviour of sulphide mineral in alkaline media.
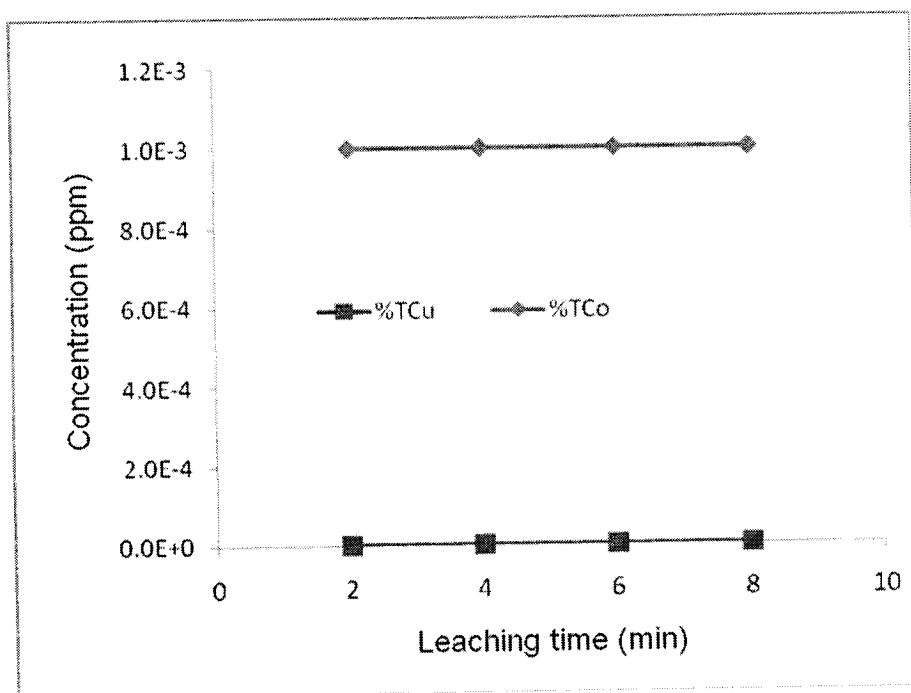
$$MS + xnH_2O \Leftrightarrow M_{1-x}S + M(OH)_n + xnH^+ + xne^- \tag{42}$$
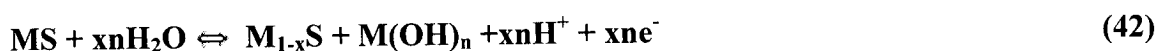
Figure 5.4: Leaching at pH 9.0 at different leaching times

At pH 9 the copper ions in solution was below detection whereas the cobalt ions registered an increase. The possible explanation to the reduction of copper ions in solution is that at this pH almost all the copper ions have reacted and formed copper hydroxide which subsequently precipitated at high pH. However, alkaline media seemed to have favoured the dissolution of cobalt ions. This behaviour implies that the Carrollite mineral underwent oxidation reaction, in which electron transfer occurred and unlocked some of the cobalt ions from Carrollite lattice structure. It can, therefore, be deduced that at pH 9 most of the cobalt ions were still in solution whereas copper ions had precipitated. This behaviour was the same for Konkola ores as shown in Figures 5.5, 5.6 and 5.7. The dissolution of copper ions was relatively more at pH 6 and 7.5 compared to cobalt ions. however, at pH 9 the dissolution of cobalt ions in solution was higher than copper ions.
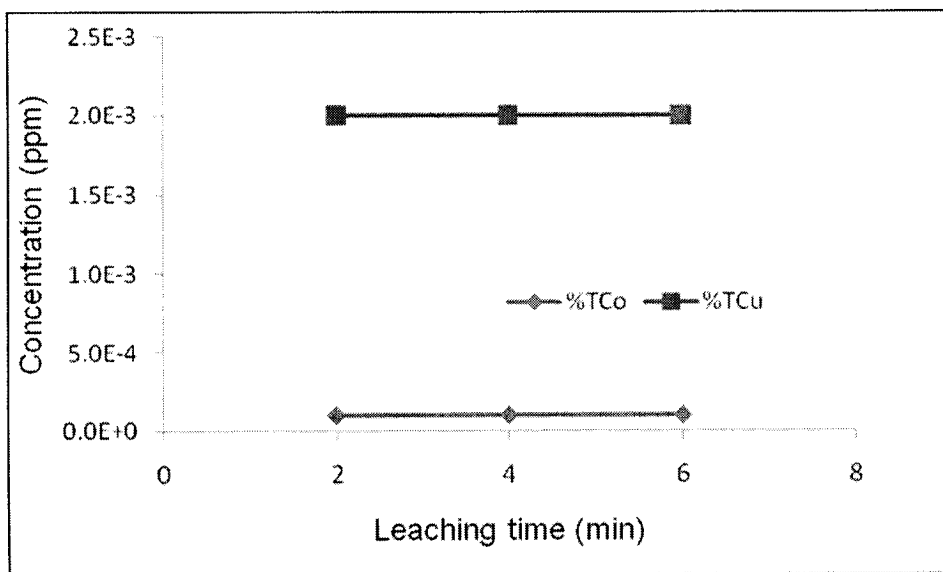
Figure 5.5: Leaching at pH 6.0 at different leaching times for Konkola ores
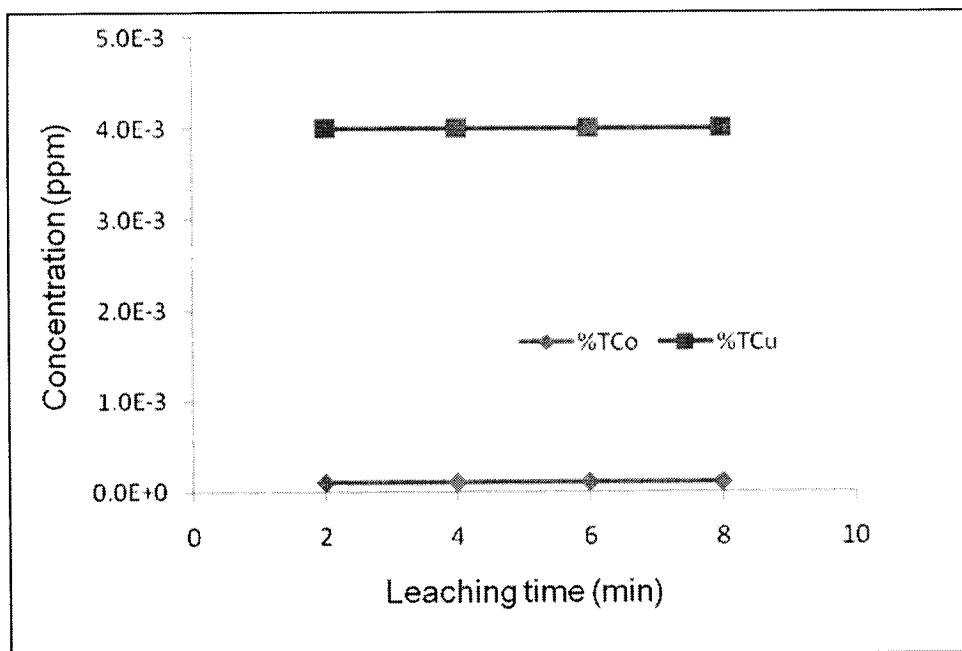

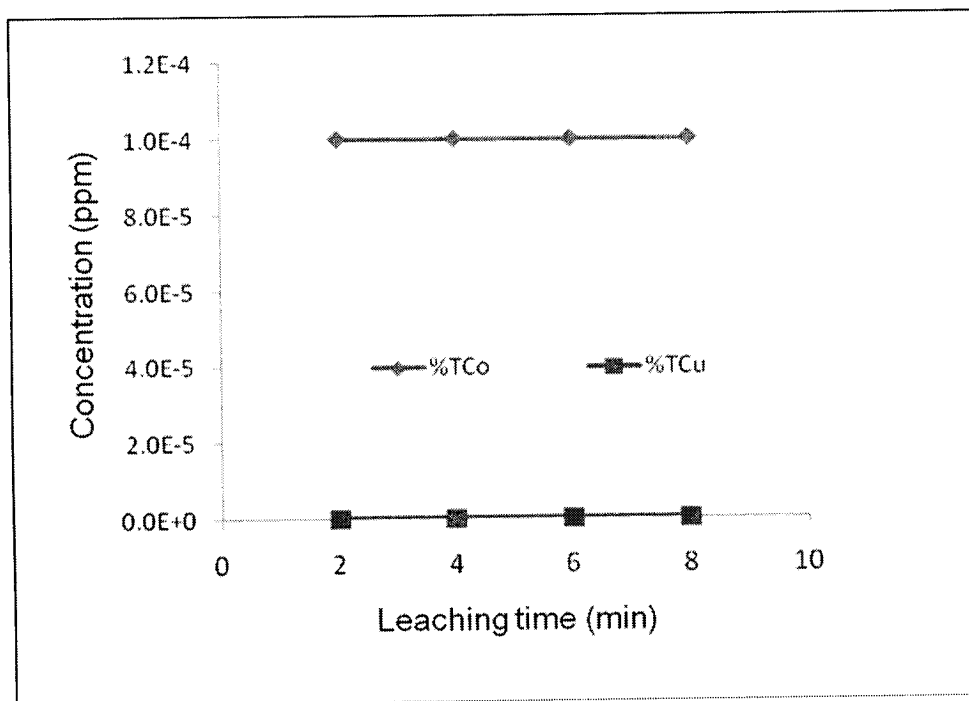**Figure 5.6: Leaching at pH 7.5 at different leaching times for Konkola ores**

Figure 5.7: Leaching at pH 9.0 at different leaching times for Konkola ores
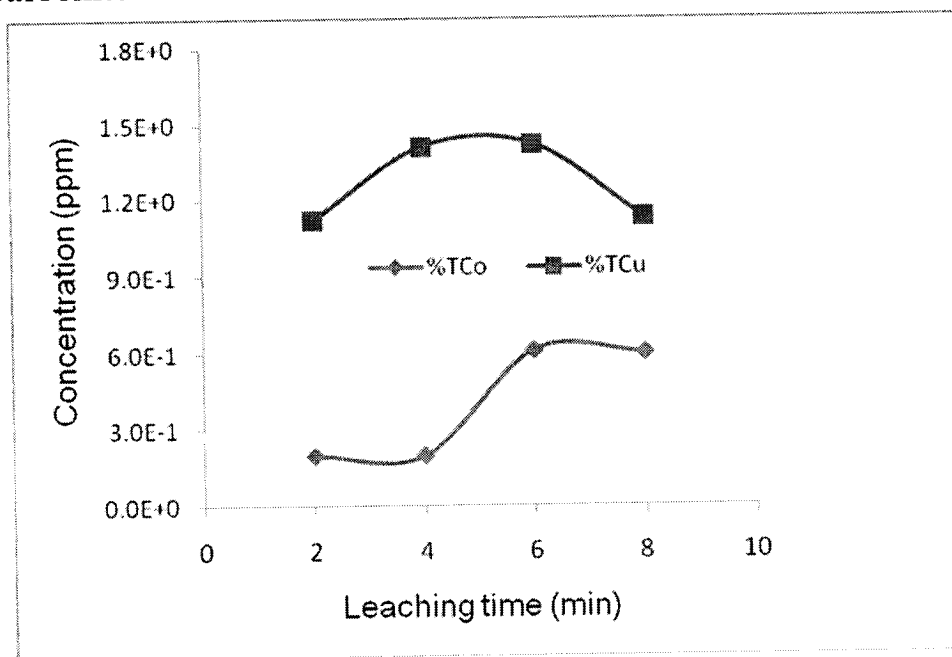
5.2.2 Carrollite Mineral

Figure 5.8: Leaching of Carrollite at pH 6.0 at different leaching times

Carrollite mineral can be represented as a double sulphide $CuS.Co_2S_3$ as proposed by other researchers [3,4]. From Figure 5.8 it can be deduced that the first 4 minutes of leaching at pH 6 had more effect on the copper in Carrollite mineral, as they were more copper ions in solution as compared to cobalt ions (Co:Cu was 1:7). This implies that at this pH the copper was unstable and as thus dissolved as shown in eq. 43.

$$CuS \rightleftharpoons Cu^{2+} + S + 2e^- \tag{43}$$

On the other hand Co_2S_3 part of Carrollite mineral showed stability in acidic media as they were insignificant amount of cobalt ions in the first 4 minutes. However, after 4minutes cobalt ions increased while the copper ions reduced up to Co:Cu ratio of 1:2. The reduction of copper ions in solution with time can be attributed to the fact that the increase in copper ions increased the formation of copper hydroxides which, depending on concentrations and other factors, began to precipitate. On the other hand cobalt ions concentration remained constant after first 6 minutes. This implies that at pH 6 leaching time has significant effect on copper ions than cobalt ions.
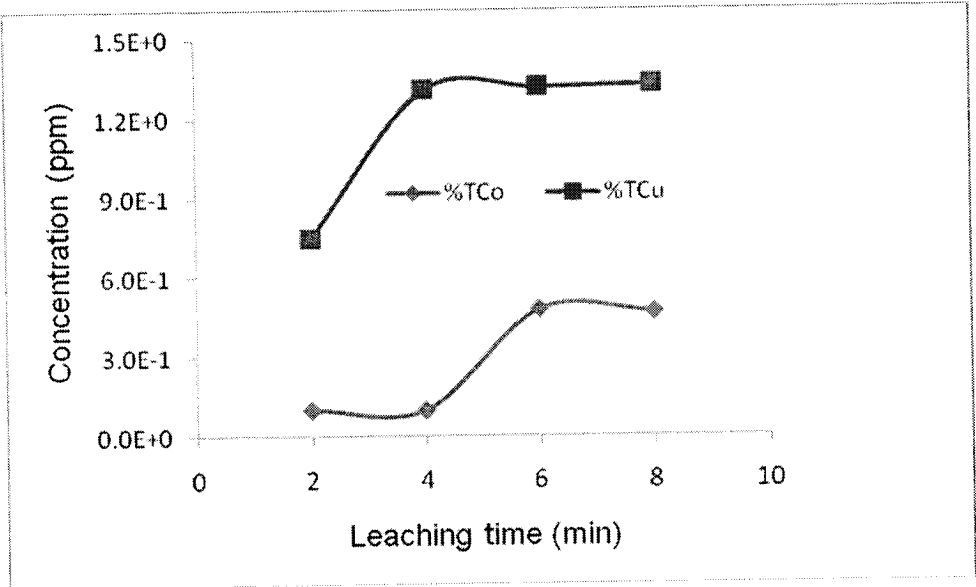

Figure 5.9: Leaching of Carrollite at pH 7.5 at different leaching times

63

Figure 5.9 had a similar trend to Figure 5.8, however, the amounts of both copper and cobalt ions reduced slightly. This is an expected trend as pH moves from acidic to alkaline, the formation of metal hydroxides is increased [3].
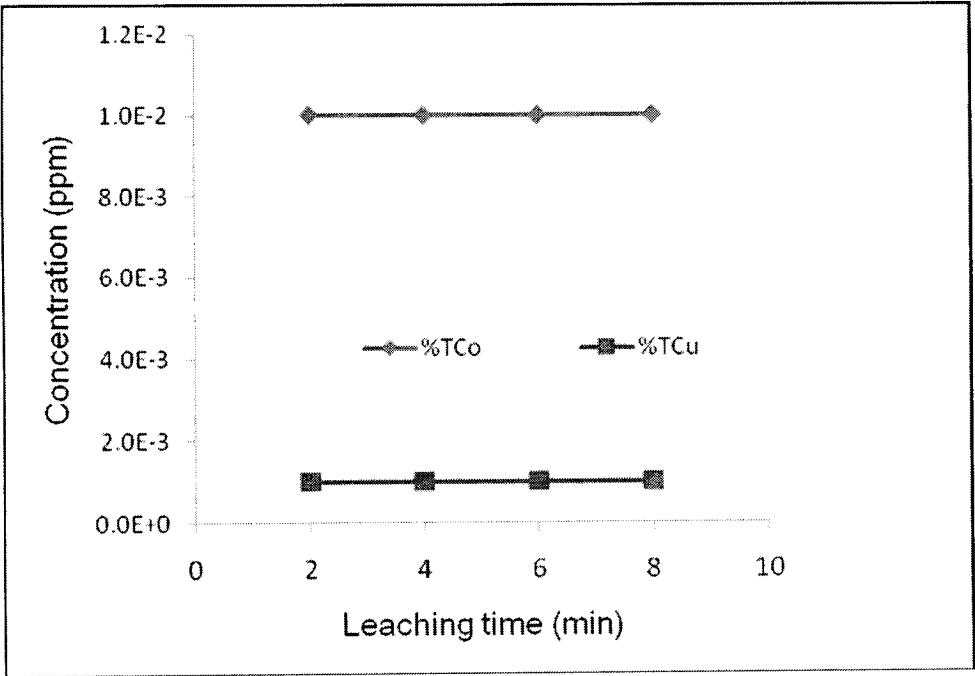
Figure 5.10: Leaching of Carrollite at pH 9.0 at different leaching times

Figure 5.10 showed a significant difference from pH 6 and 7.5 in terms of amounts of metal ions in solution and the general trend of concentration with time. The concentration of copper ions reduced by over a thousand times whereas cobalt ions by about 20 times. The high jump in copper concentration can be attributed to almost complete formation and precipitation of copper hydroxides. Although the cobalt ions reduced by 20 times, the overall concentration compared to copper ions was more than at pH 6 and 7.5 (Co:Cu, 10:1). It can be deduced that not all cobalt ions in solution formed metal hydroxides and precipitated at pH 9. This agrees very well with what was reported elsewhere [3].

5.3.0 Zeta Potentials

5.3.1 Zeta Potential of Carrollite
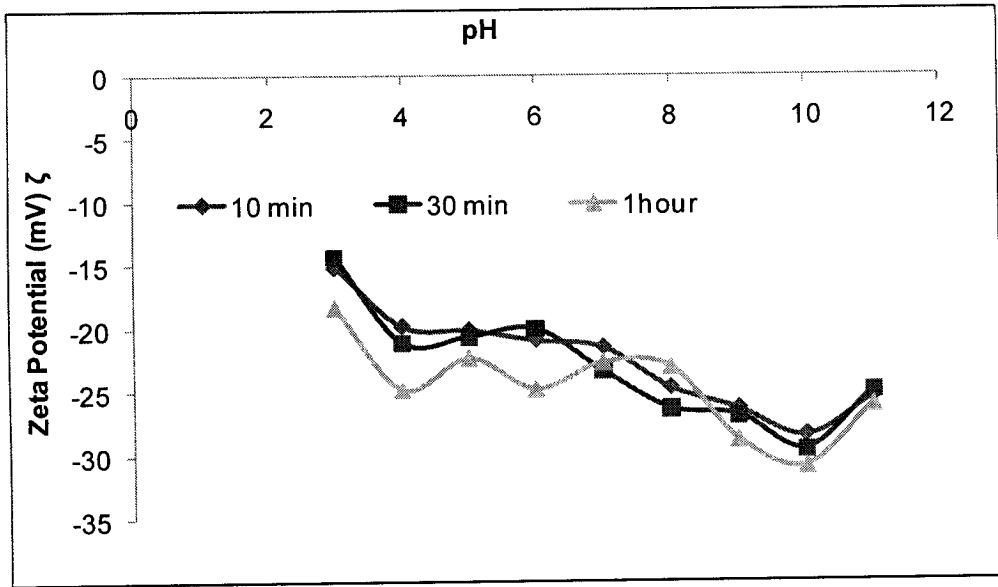

Figure 5.11: Zeta potentials of Carrollite in water

The zeta potentials of Carrollite in ordinary water were negative throughout the pH range as shown in Figure 5.11. Conditioning for 10 and 30 minutes did not give significant difference whereas 60 minutes condition time showed high negativity. From this, it may be implied that the reaction governing this behaviour was the same. However, the extent seemed to vary with condition time. From the general trend of the change in the zeta potentials with pH observed for elemental sulphur or non-oxidised sulphide minerals [8], one may logically conclude that, the sulphide mineral surface may be covered with sulphur bearing species which can become charged by reacting with protons in a similar manner to metal oxides. In the acidic media, the copper ions from the Carrollite lattice structure went into solution. This is demonstrated in the leaching experiments which showed relatively higher copper ions concentration than cobalt ions. This behaviour is believed to be due to the presence of oxygen in water [3,30]. The

oxygen accepts electron from the copper ions thereby undergoing a cathodic reduction reaction as shown in equation 44.

$$O_2 + 2H_2O + 4e^- \Leftrightarrow 4OH^- \qquad (44)$$

The cathodic reaction causes the sulphide mineral to have a deficiency in metal ions and hence electrically unbalanced. As the metal ions go in solution, the overall surface charge is dominated by a negative charge which gives the mineral surface its negative charge. The oxy-hydroxide formed from cathodic reaction of oxygen coats the metal-deficient sulphide rich mineral surface at higher pH values hence giving it a more negative charge. As pH increases from acidic to alkalinity, the copper ions react with the oxy-hydroxide to form copper hydroxide [3]. This is demonstrated in Figure 5.11 in which the 3 curves almost flattens out between pH 4 and 8. As the pH increased beyond 8, the negativity increased up to pH 11. This was a result of dissolution of cobalt ions into solution and cathodic reaction of oxygen (eq. 44) hence formation of oxy hydroxides which are negatively charged. The reactions may be represented by the following equations:

$$CuCo_2S_4 \Leftrightarrow Cu^{2+} + 2CoS_2 + 2e^- \qquad (45)$$

CoS_2 is very unstable, therefore, it dissociates through the following step [3]:

Dissolution of cobaltous ions to form a cobalt deficient sulphur rich surface rather than elemental sulphur

$$CoS_2 \Leftrightarrow xCo^{2+} + Co_{1-x}S_2 + 2xe^- \qquad (46)$$

The oxidation of cobaltous ions to cobaltic ion at higher oxidation potential and pH

$$Co^{2+} \rightleftharpoons Co^{3+} + e^{-} \tag{47}$$

The hydrolysis of cobaltous hydroxide species whose concentration are largely dependent on solution pH;

$$Co^{2+} + H_2O \rightleftharpoons Co(OH)^{+} + H^{+} \tag{48}$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(OH)_{2(aq)} + 2H^{+} \tag{49}$$

$$Co^{2+} + 3H_2O \rightleftharpoons Co(OH)_3^{-} + 3H^{+} \tag{50}$$
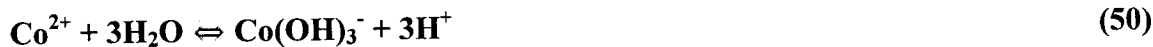
Finally the formation

$$Co(OH)_{2(aq)} \rightleftharpoons Co(OH)_{2(s)} \tag{51}$$
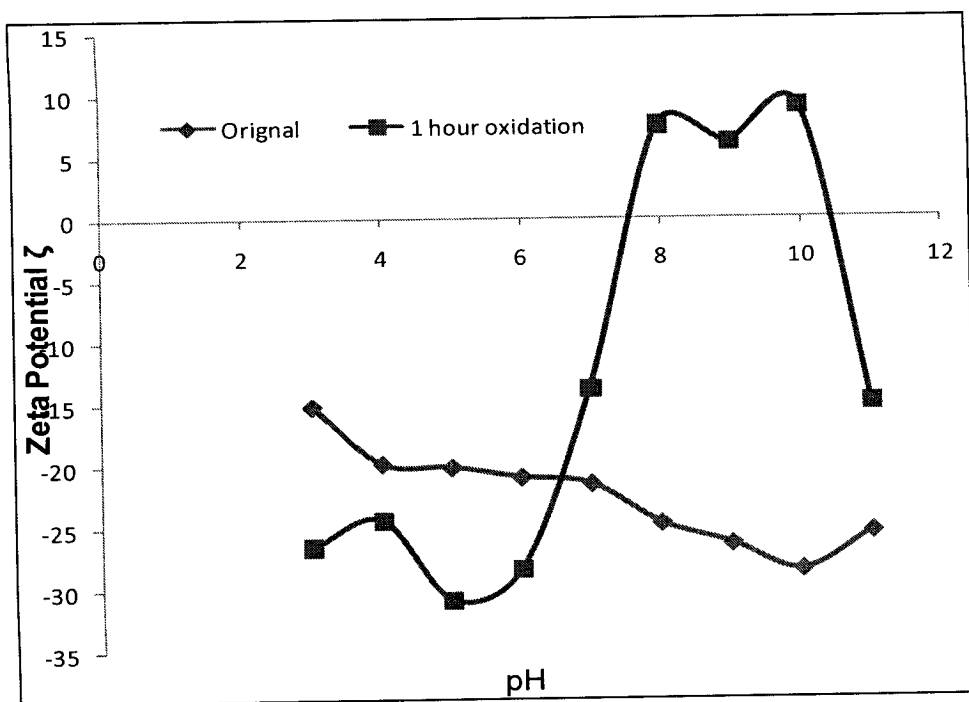

Figure 5.12: Zeta potentials of Carrollite in oxygen saturated solution

The zeta potential after oxidation was more negative between pH 3 and 7 as shown in Figure 5.12. This can be attributed to the presence of oxygen in solution. This implies that cathodic reaction of oxygen was enhanced and as thus the amount of oxy-hydroxide

formed and coated was more than the original scenario. This demonstrates the role of oxygen in determining zeta potentials of minerals. At higher pH, they were two charge reversals at pH 7.5 and 10.5. The initial charge reversal can be attributed to the precipitation of copper hydroxide on the mineral surface. It is well documented that copper hydroxide precipitates at pH higher than 5 [30].   The dissolution of cobalt ions into solution leaves behind a positively charged metal deficient sulphide rich surface as some of the metal ions which are positively charged cover the mineral surface. As the pH increased, the cobalt ions formed cobalt hydroxides (eq. 47-51) and consequently reduced the positive zeta potential, causing a second charge reversal at pH 10.5. Figure 5.10 demonstrates that the ionic species found in solution at lower pH are copper ions whereas at higher pH cobalt ions are present. This implies that most of cobalt ions can only go in solution around pH 9 and its hydroxides are formed at higher pH. From Figure 5.10 it can be deduced that copper ions play a pivotal role in determining zeta potential in acidic media whereas cobalt does so in alkaline media [3].

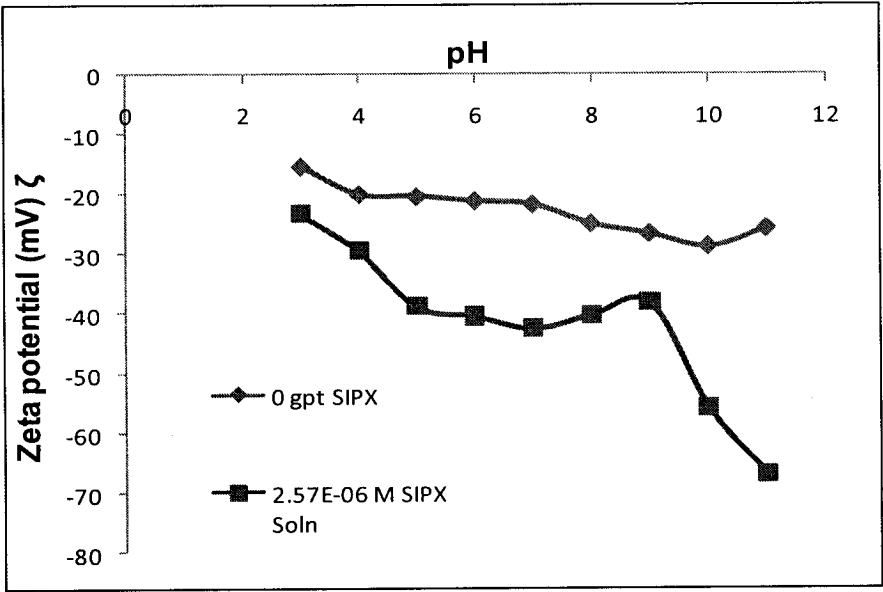## 5.3.2 Zeta Potential of Carrollite in SIPX Solution

Figure 5.13: Zeta potentials of Carrollite in SIPX saturated solution

When SIPX goes in solutions, depending on the pH, Xanthate ions are formed [20]. These anions are believed to coat the mineral surface throughout pH range hence increasing the negative charge on the mineral surface as shown in Figure 5.13. Therefore, the negative zeta potential can be attributed to the presence of Xanthate anions on the mineral surface.
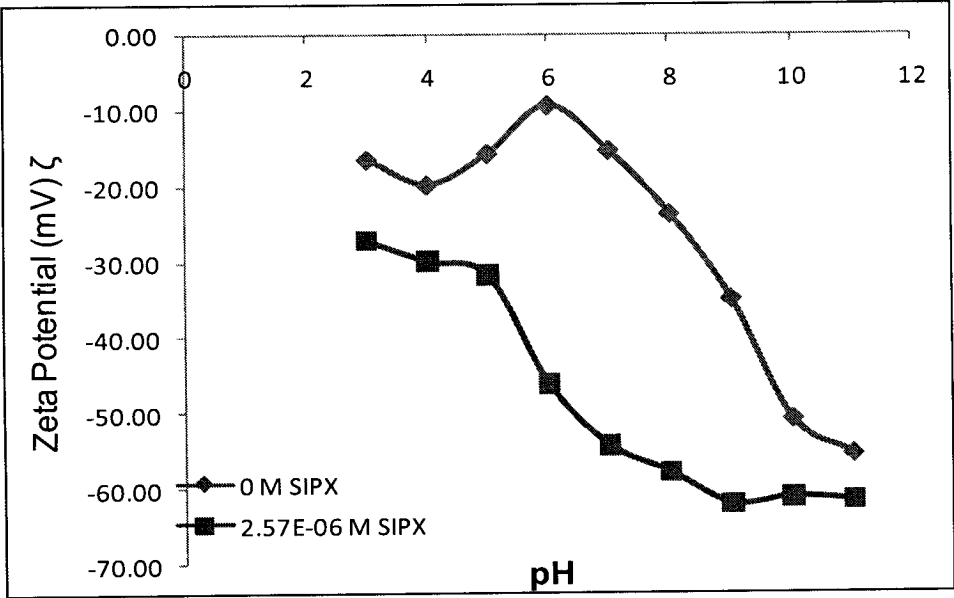
5.3.3 Zeta potential of Chalcopyrite

Figure 5.14: Zeta potentials of chalcopyrite

A number of studies have been done on chalcopyrite and important conclusions drawn [3,8,30]. What has been a general view of most researchers is that, chalcopyrite maintains a negatively charged surface throughout pH range as demonstrated in Figure 5.14 and the negativity is enhanced in the presence of Xanthate species. In oxidising environment there is a charge reversal at somewhere around pH 4.5 [3,8].
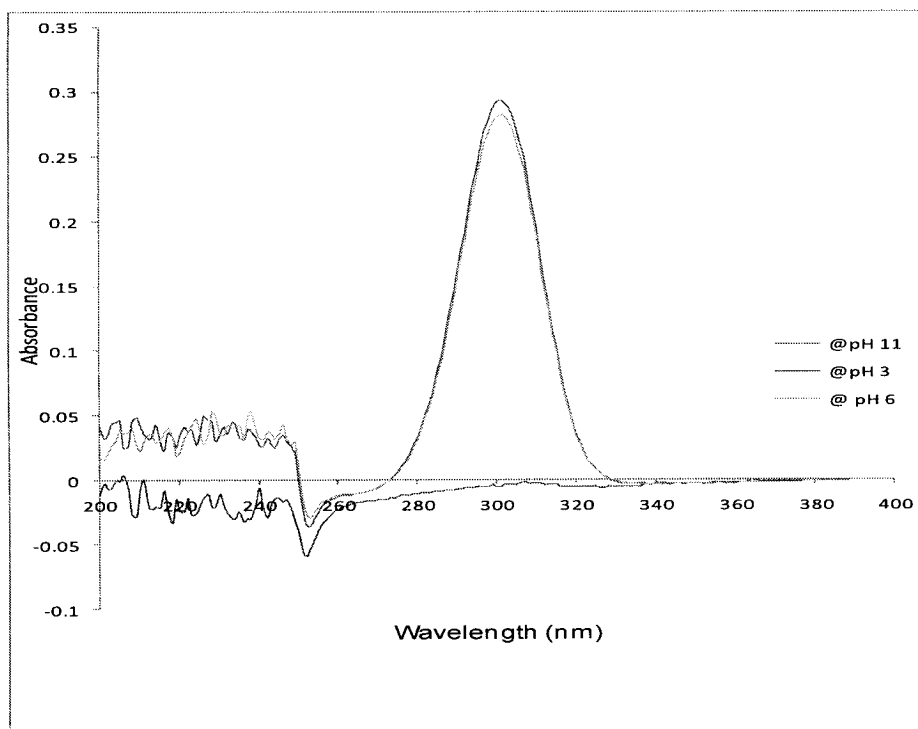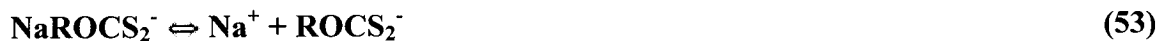
5.4.0 Adsorption of Xanthate

Figure 5.15: UV – Visible Spectra for Xanthate

The wavelength for Xanthate ions is 301nm [31]. From Figure 5.15, the amount of Xanthate ions at pH 3 is negligible whereas at pH 6 and 11 have substantial amount respectively. The negligible amount at pH 3 can be attributed to the decomposition of SIPX as shown in eq. 52.

$$Na^+ + ROCS_2^- + H_2O \rightleftharpoons Na^+ + OH^- + ROCS_2H \quad \text{(Xanthic acid)} \quad \text{(52)}$$

The results agree very well with what other researchers have concluded [31,35]. This implies that around pH 3 eq. 52 will be the most probable reaction. However, as pH increases from acidic to alkaline, the amount of Xanthate ions increases. This implies that at higher pH SIPX ionises to metal ion and Xanthate ion as shown in eq. 53.

$$NaROCS_2^- \rightleftharpoons Na^+ + ROCS_2^- \quad \text{(53)}$$

71

It can, therefore, be deduced that at pH 6 – 11 a substantial amount of Xanthate ions are present. This conclusion helped in drawing up a pattern for the adsorption of Xanthate ions on mineral surface.
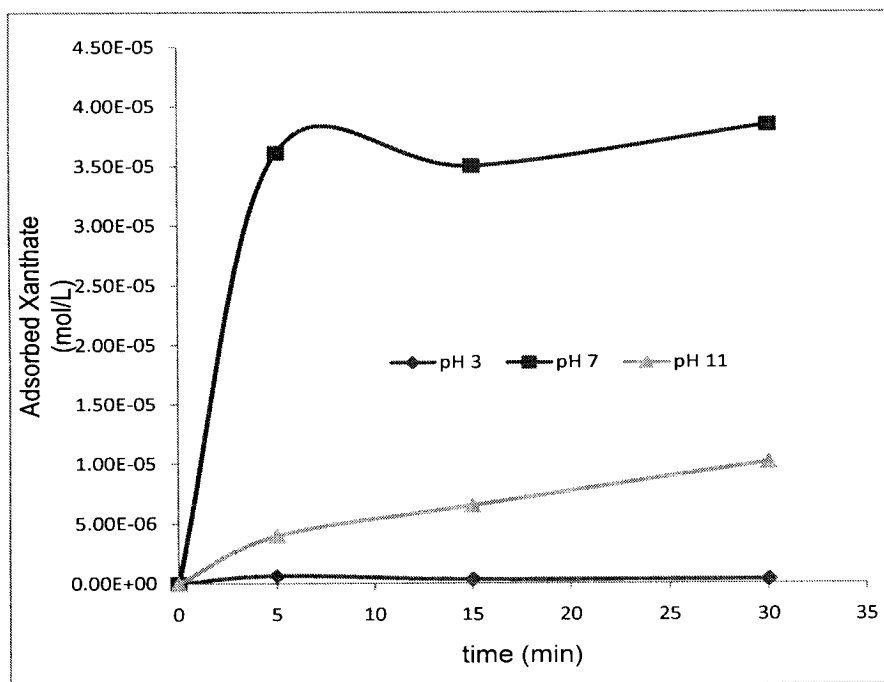

Figure 5.16: Adsorption of Xanthate ions on Carrollite mineral

Adsorption of Xanthate ions was maximum at pH 7 whereas pH 3 was the lowest as shown in Figure 5.16. The low adsorption of Xanthate ions at pH 3 can be attributed to the decomposition of Xanthate to form xanthic acid [31]. However, at pH 7 the presence of Xanthate ions in solution is substantial as shown in Figure 5.15. The copper and cobalt ions are relatively abundant at this pH as shown in Figure 5.17 and thus a reaction between Xanthate ions and metal ions take place to form metal xanthates.
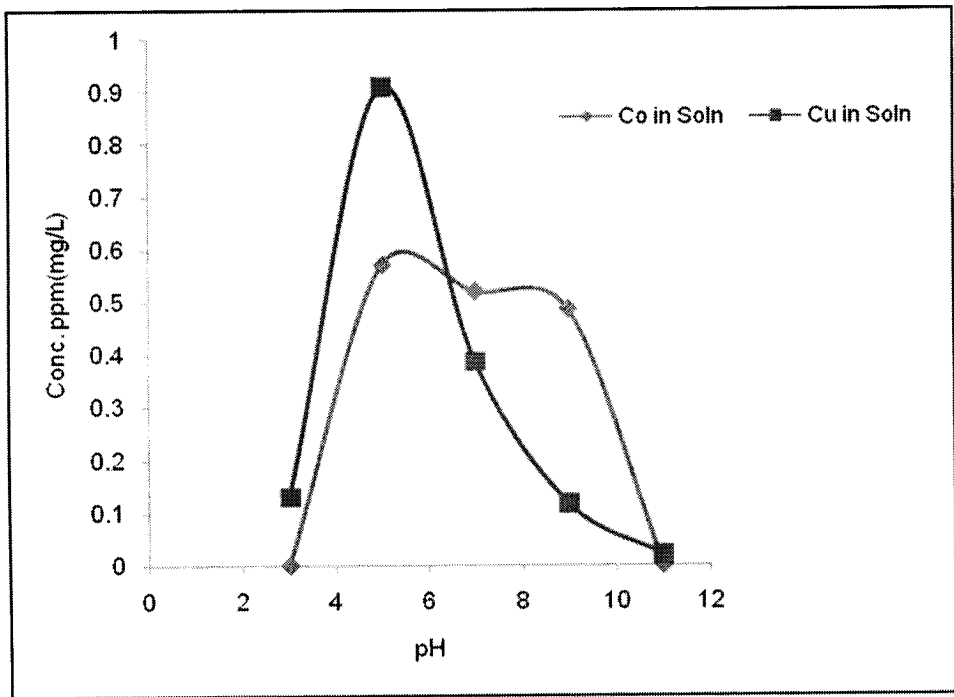
Figure 5.17: Dissolution of Copper and Cobalt ions

$$Cu^{2+} + 2X^- \rightleftharpoons CuX_2 \qquad\qquad (54)$$

$$Co^{2+} + 2X^- \rightleftharpoons CoX_2 \qquad\qquad (55)$$

The rate of adsorption of Xanthate ions varies with time range as shown in Table 5.4 and figure 5.18. The first 5 minutes recorded high adsorption rate as compared to remaining time intervals. This implies that during this period (0 – 5 minutes), a monolayer of Xanthate ions adsorbed on the mineral surface.

Table 5.4: Adsorption rate of Xanthate ions on Carrollite mineral

Time Range (min)	0 - 5	5 - 15	15 - 30	30 - 60
Rate of Adsorption(ppm/min)	5.3287E-06	4.4144E-07	9.14393E-07	5.78067E-08

73

This is demonstrated in Figure 5.16 in which the amount of adsorption at 5 and 15 minutes was almost the same, implying that after a monolayer has been achieved, there was little adsorption. However, between 15 and 30 minutes, there was a substantial amount of adsorbed Xanthate ions. This is indicative of a second layer of Xanthate ion adsorption. Beyond 30 minutes there was little adsorption. This implies that the first 5 minutes is the most critical time in which most of adsorption (60% of total amount adsorbed) takes place.
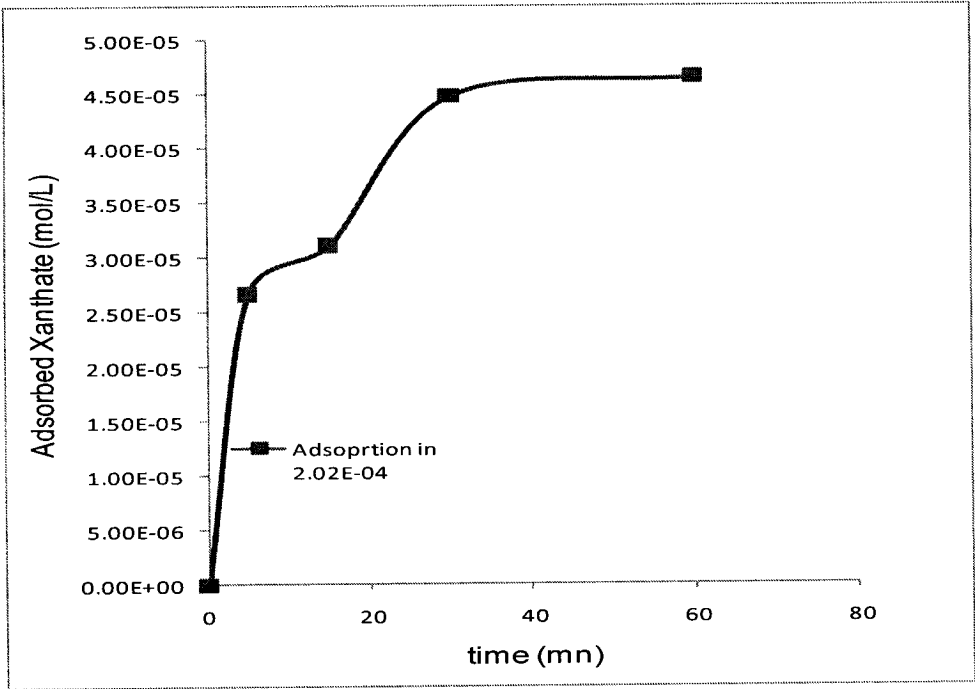

Figure 5.18: Adsorption of Xanthate on Carrollite mineral.

5.5.0 Surface Characterisation
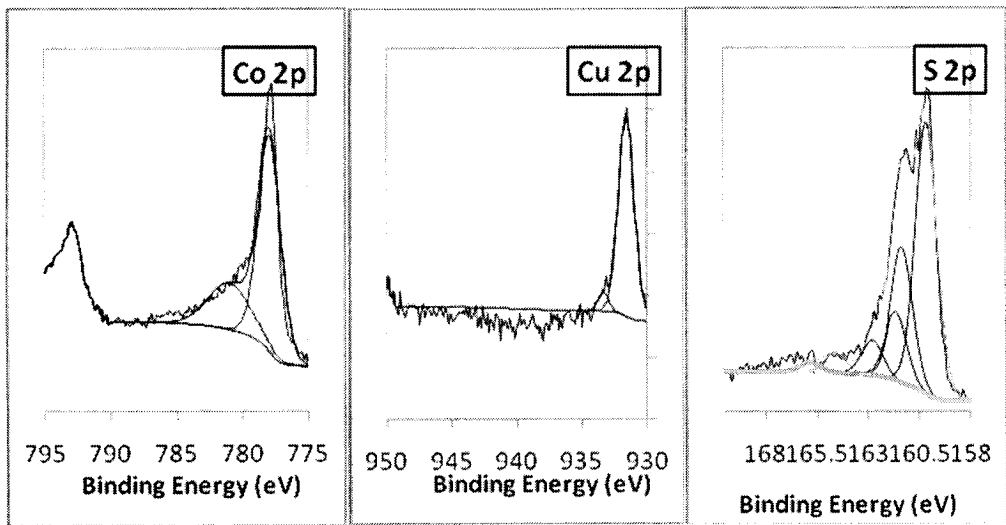
5.5.1 Fresh Sample

Figure 5.19: Cu 2p, Co 2p and S 2p Spectra for untreated Carrollite sample

The binding energy (BE) in this study for Cu $2p_{3/2}$ peak was observed to be 932.3 eV which is characteristic of Cu (I) [30]. This is within the agreeable range as found elsewhere [30]. Other researchers [3,4] determined the Cu $2p_{3/2}$ binding energy for Carrollite to be 932.6 eV and 932.5 eV respectively for Cu (I). The 778 eV BE found in this work is characteristic of Co (III). Other researchers have found binding energy values which are within an agreeable range. Table 5.5 shows some of the works from different researchers. The results from the Table below for Co binding energy are found to be characteristic of Co (III). The peak separation between $2p_{3/2}$ and $2p_{1/2}$ was found to be 15.0 eV, this agrees very well with the findings from other works [3,4].

Table 5.5: Co $2p_{3/2}$ and S $2p_{3/2}$ BE (eV) for Carrollite from different works

| Material	Source	Co$2p_{3/2}$ BE (eV)	$2p_{3/2}$ - $2p_{1/2}$	S $2p_{3/2}$ BE (eV)	Reference
CuCo$_2$S$_4$	Baluba,	~ 779	15	161.7	[1]
CuCo$_2$S$_4$	Katanga	779	15	161.2	[17]
CuCo$_2$S$_4$	Nchanga	778	15	161.4	This work

The 161.4 eV binding energy for S $2p_{3/2}$, as observed in this work can be assigned to S (II) [4]. The second peak at BE 161.7 eV can be assigned to S (I). Therefore, the oxidation state of Carrollite was found to be in the form $\boldsymbol{Cu^I Co^{III} S^{-II} S^{-I}}$.

5.5.2 Treatment with Water SIPX and Oxygen

Figure 5.20 shows effect of water, SIPX and Oxygen at different pH values on the surface of the mineral. Carrollite was observed to be fairly stable at pH 3 in water, SIPX and Oxygen. This agrees very well with the amount of metal ions in solution as shown in Figure 5.17. At pH 9, there was an increase in intensity at BE 933.8 eV, with the peak being more pronounced in oxygen environment. This was assigned to Cu (II) [4]. The Cu is believed to be oxidized from Cu (I) to Cu (II).

$$Cu^+ \Leftrightarrow Cu^{2+} + e^- \tag{56}$$

Therefore, the most probable products to be formed at this pH would be $CuO/Cu(OH)_2/CuS$. Work done earlier [3] has concluded using cyclic voltammetry experiments that CuS is formed on the surface of Carrollite mineral in alkaline media;

$$CuS.Co_2S_3 + 4H_2O \Leftrightarrow CuS + 2Co(OH)_2 + 3S + 4H^+ + 4e^- \tag{57}$$
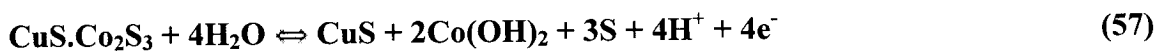
CuO and $Cu(OH)_2$ was ruled out due to the fact that beyond pH 7 the two compounds are unstable and this was confirmed by XRD experiments and E_h – pH digram [3]. At pH 11 the peak for 933.8 eV, characteristic of Cu (II) was more pronounced.
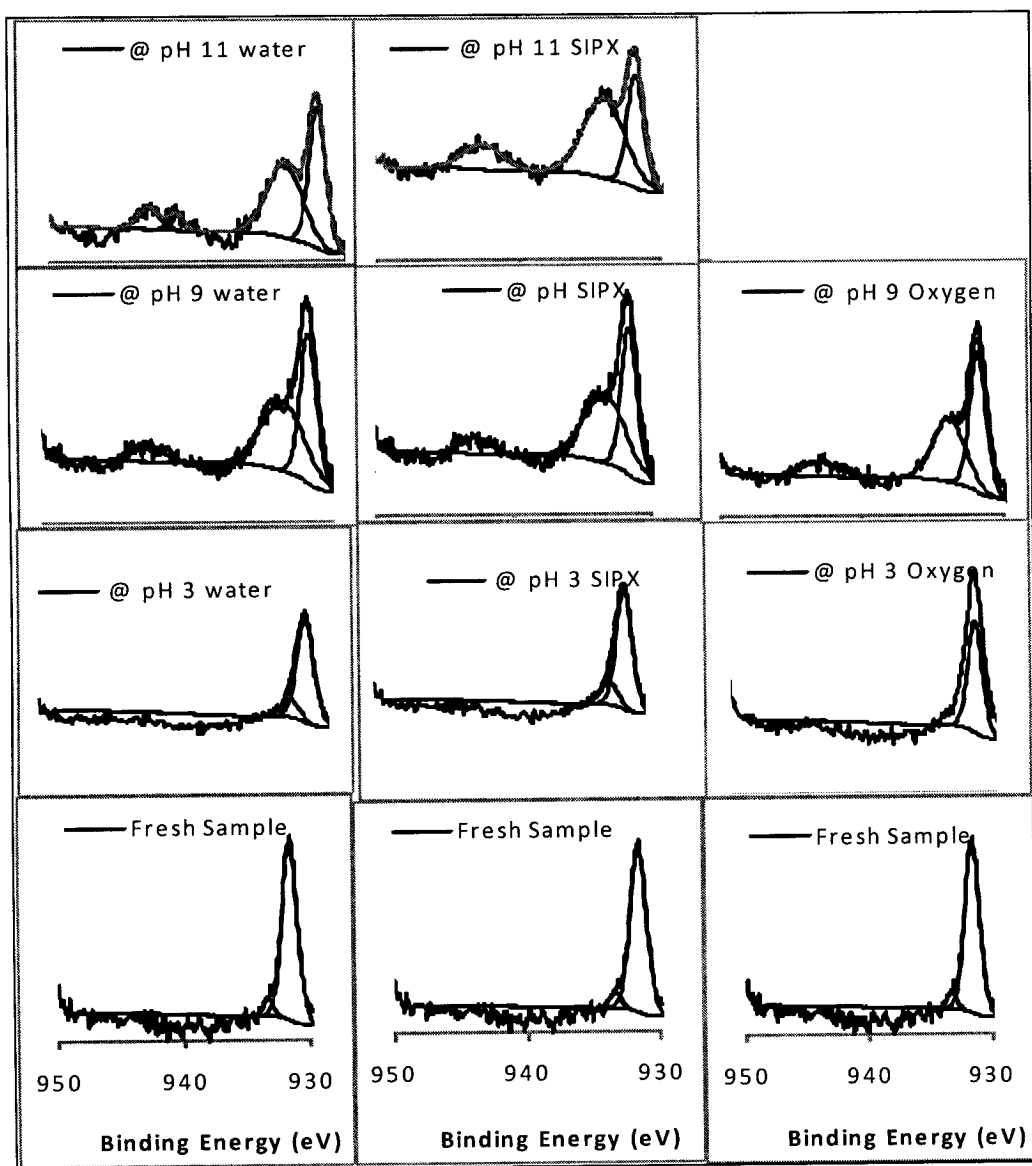
Figure 5.20: Cu 2p Spectra for Carrollite in water, SIPX and Oxygen

Co $2p_{3/2}$ is shown in Figure 5.21 before and after treatment with water, SIPX and in oxygen at pH 3, 9 and 11. The Co spectra do not seem to be affected at pH 3. This is in conformity with the amount of Co ions that went in solution at pH 3 as shown in Figure 5.17. A slight change on mineral surface is observed at pH 11. The binding energy of 781.0 eV slightly increased compared to original sample. This BE is characteristic of Co(II). This implies that in alkaline media, Co (III) is reduced to Co (II). The expected

77

product at this pH is Co(OH)$_2$. This assumption is confirmed by the findings of other researchers [3].
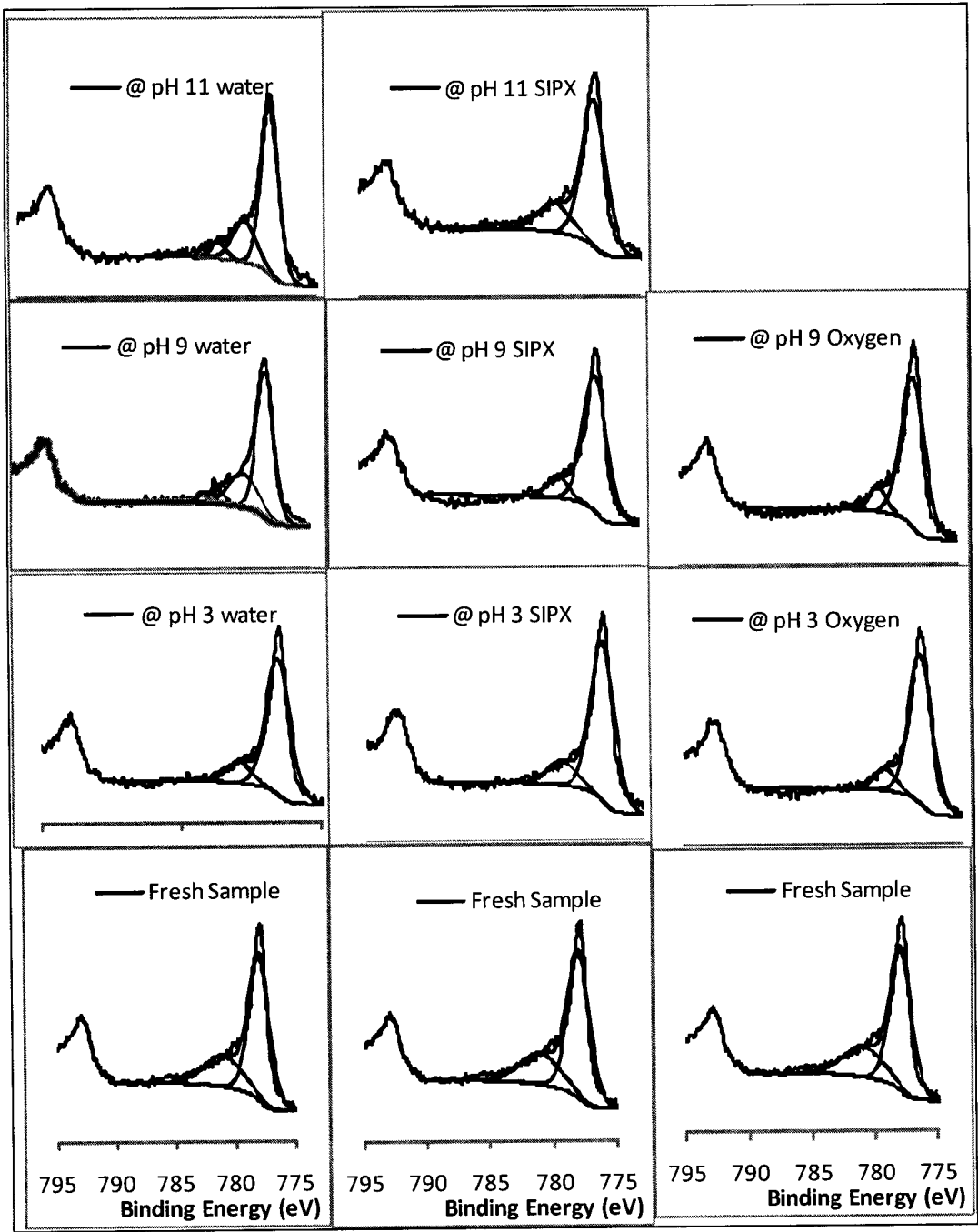
Figure 5.21 Co 2p Spectra for Carrollite in water, SIPX and Oxygen

Figure 5.22 S 2p Spectra for Carrollite in water, SIPX and Oxygen

The S 2p XPS spectra in Figure 5.22 confirm the presence of metal hydroxide, metal-deficient sulphide, polysulphide and elemental sulphur on the cobalt mineral. BE 163.0 and 164.2 eV confirm the presence of metal-deficient sulphide and poly sulphide respectively [3]. These products are more pronounced at pH 9 and disappear at pH 11.

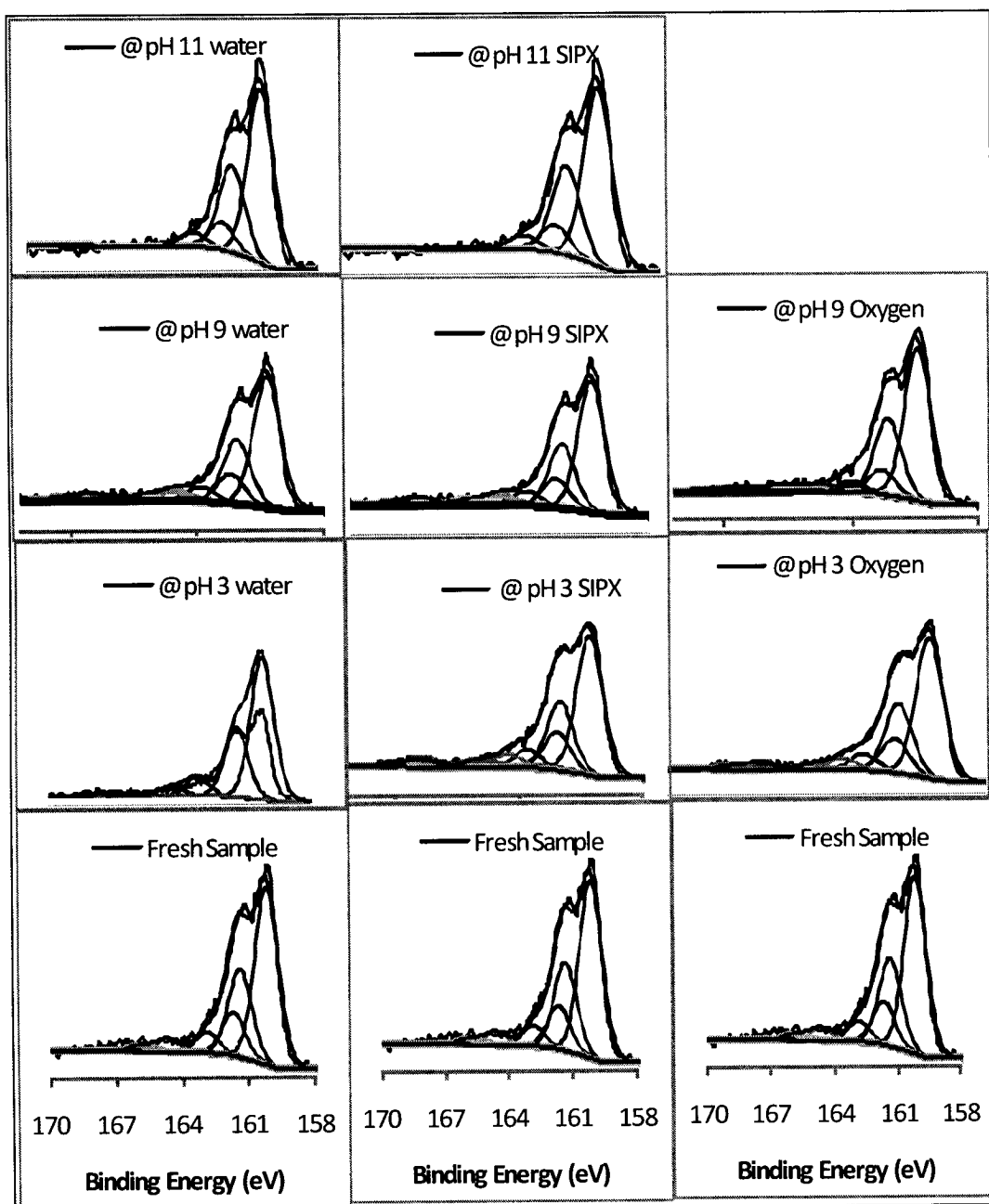The peak at BE 161.4 eV increases with pH which confirms the formation Cu (II) products.

5.6.0 Contact Angles

The contact angle is an important parameter; it is a common measure of the hydrophobicity of a solid surface. Advancing angles were measured and results are shown in Figure 5.23.
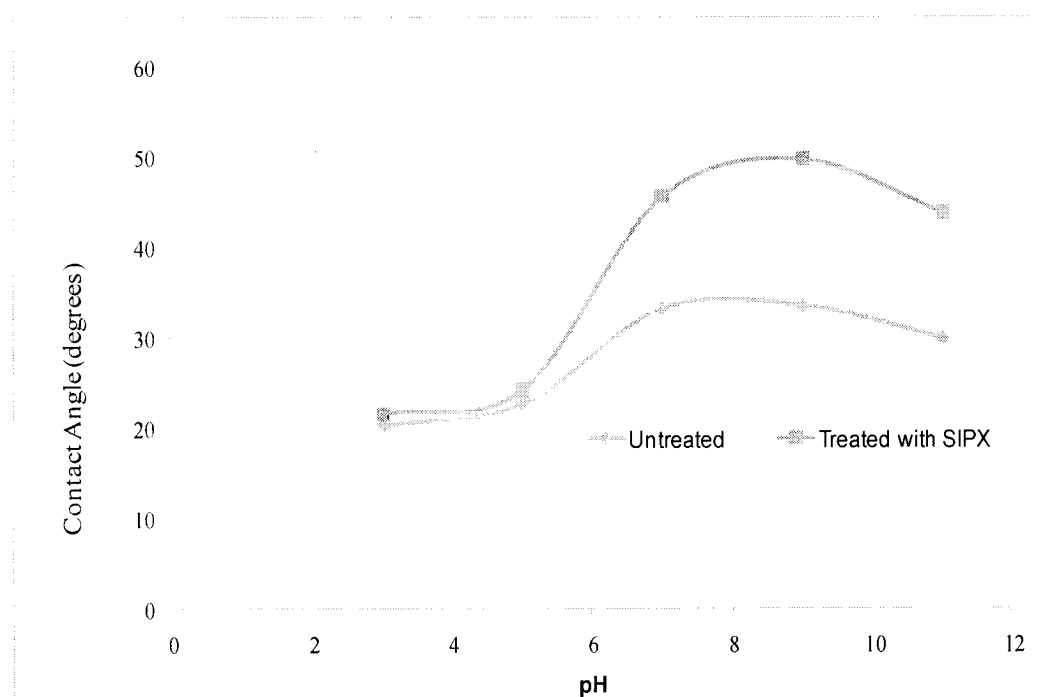
Figure 5.23: Advancing contact angles on Carrollite as function of pH

Both graphs for treated and untreated showed a similar trend, contact angles increasing with the increase in pH as shown in Figure 5.23. This implies that compounds responsible for hydrophobicity of a mineral surface were present. XPS results showed that at pH 9 there was evidence of metal deficient sulphide, *CuS* and poly sulphide on the surface of the mineral. Beyond pH 9 metal hydroxides were observed on the mineral surface. Therefore, from these results, it can be deduced that metal deficient sulphide,

CuX, *CuS* and poly sulphide were responsible for rendering the mineral surface hydrophobic while the decrease in contact angle beyond pH 9 can be attributed to the hydrophilic metal hydroxides on the mineral surface.

5.7.0 Flotation

The recovery of minerals floated under batchwise conditions may be described by a first-order rate equation assuming that the mineral quantity transferred to the froth is a direct fuction of it's concentration when most parameters are maintained constant (type of mineral, pulp density, pH, reagent addition, aeration, etc.) as follows

$$R_{(t)} = R_o(1-e^{-kt}) \tag{58}$$

Where

$R_{(t)}$ is the recovery of a specific mineral at time t

R_o is the maximum recovery of specific mineral at time $t = \infty$

K is the first order rate constant for each mineral.

5.7.1 Microflotation of Carrollite Mineral Using Hallimond tube
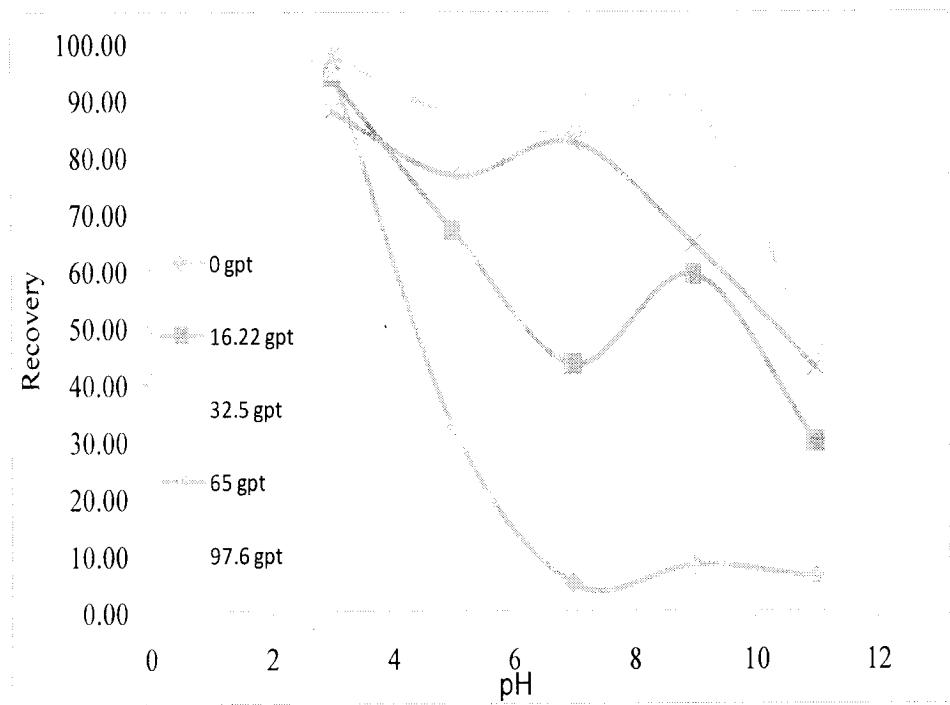
Figure 5.24: Hallimond tube flotation of Chalcopyrite mineral

Collectorless flotation of Carrollite showed very poor results except for pH 3 as shown in Figure 5.24. Addition of collector (SIPX) improved the recovery throughout all pH range. The increase in recovery between pH 7-10 can be attributed to the metal deficient sulphide and elemental sulphur as shown by XPS results. The recovery reduces beyond pH 10, which agrees with the presence of hydrophilic $Co(OH)_2$ on the mineral surface.

Figure 5.25: Recovery of Carrollite mineral at pH 7-10

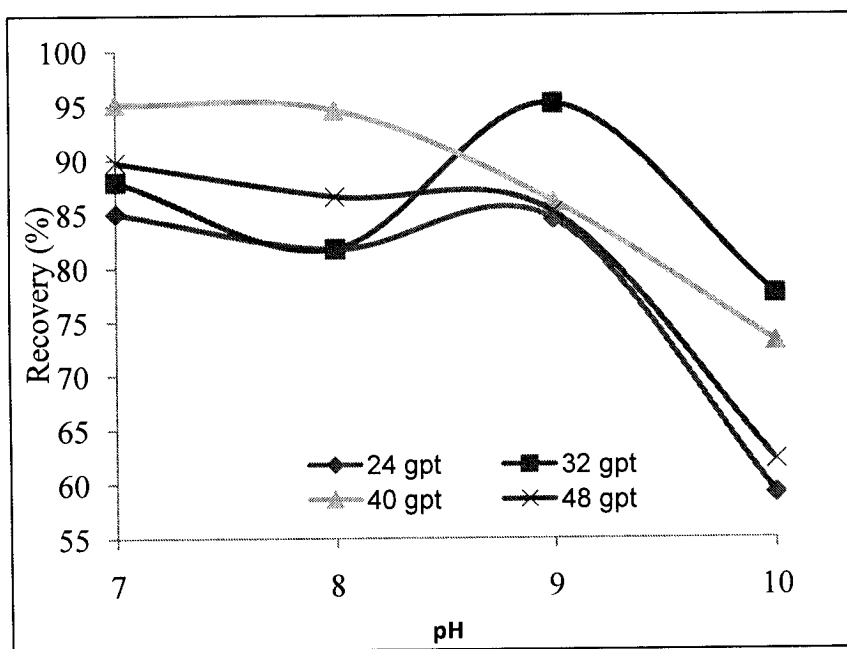Maximum recovery (95.21%) was achieved at pH 9 with 32gpt SIPX dosage as shown in Figure 5.25. This confirms the findings of earlier work elsewhere [3]. Other dosages showed steady drop in recovery with increase in pH.

The low recoveries can be attributed to the amount of adsorption of Xanthate ions on the mineral surface. In the case of low dosage (24gpt) the amount of Xanthate ions attaching on the mineral surface to induce hydrophobicity can be thought of as insufficient. However, the trend at pH 9 is similar to 32gpt, and it can be deduced from this that probably pH 9 is the optimum pH for the formation of species on the mineral surface responsible for hydrophobicity. Formation of dixanthogen, which is responsible for hydrophobicity, is favoured at about pH 9 as revealed by UV-Vis experiments on SIPX. However, at higher dosage (40 and 48gpt), it can be assumed that multilayer of the collector is adsorbed on the mineral surface. This situation re-orients the collector molecules, thus depressing the mineral.

83

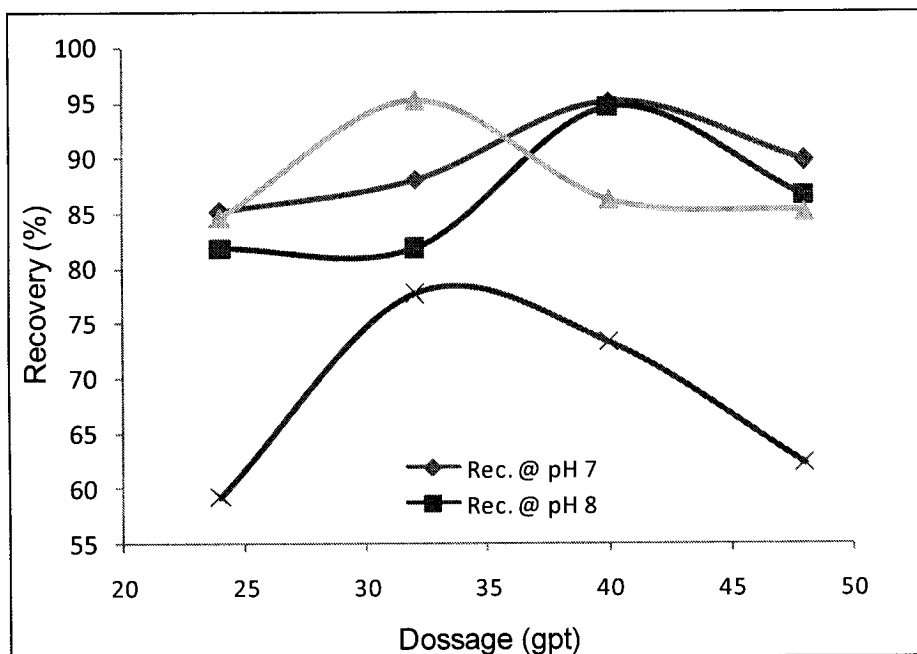**Figure 5.26: Recovery at different conditioning pH**

The recovery was maximum at conditioning pH 9 as shown in Figure 5.26. This may be attributed to the presence of xanthate ions which would probably form metal dixanthogen at pH 9 as compared to other pH values, thereby inducing hydrophobicity and subsequently improving the recoveries. 32gpt was the optimum dosage as established earlier on.

5.7.2 Microflotation of Chalcopyrite Mineral
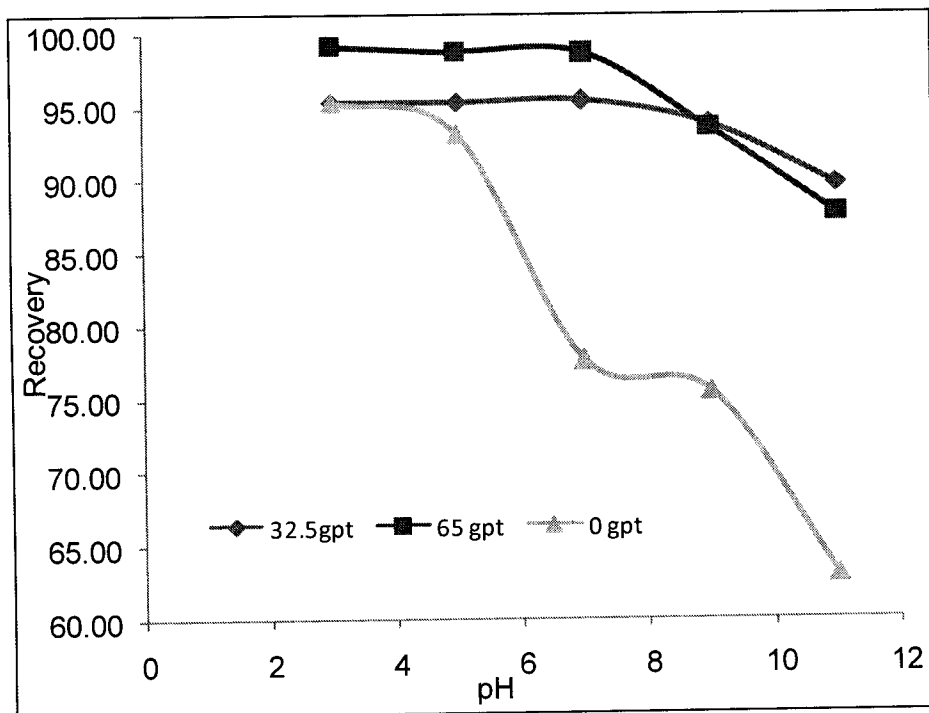
Figure 5.27: Hallimond tube flotation of Carrollite Mineral

Chalcopyrite mineral is among sulphide minerals that have received a lot of research attention [3,8,23,24]. The recoveries for collectorless flotation were above 90% from pH 3 – 5 as shown in Figure 5.27. This behaviour can be attributed to the presence of sulphur element or metal deficient sulphide on the mineral surface as confirmed by other researchers [3,8,24]. The reduction in recovery after pH 5 is attributed to the formation and precipitation of copper hydroxide [3]. These species have been tested and found to be hydrophobic species [20,22]. The addition of SIPX improved the recovery throughout pH range with 65gpt giving best recoveries.

5.7.3 Bench Scale Flotation of Nchanga Ores Using Denver Cell

Table 5.6: Statistical Analysis of Flotation Results

pH	Test 1	Test 2	Test 3	Test 4	Test 5	Average	Standard Deviation	Coefficient Of Variation.
Copper Recovery Using SIPX								
8.22	65.3	65.2	64.9	66.0	64.4	65.2	1.4	2.1
9.42	58.0	58.4	60.2	59.3	57.6	58.7	4.4	7.5
10.44	74.7	74.7	74.5	74.2	75.5	74.7	1.0	1.3
Cobalt Recovery Using SIPX								
8.22	68.5	68.3	68.5	67.8	69.3	68.5	1.3	1.8
9.42	67.8	67.2	67.9	67.4	67.0	67.4	0.6	1.0
10.44	72.3	71.9	70.9	70.8	72.9	71.8	3.2	4.5
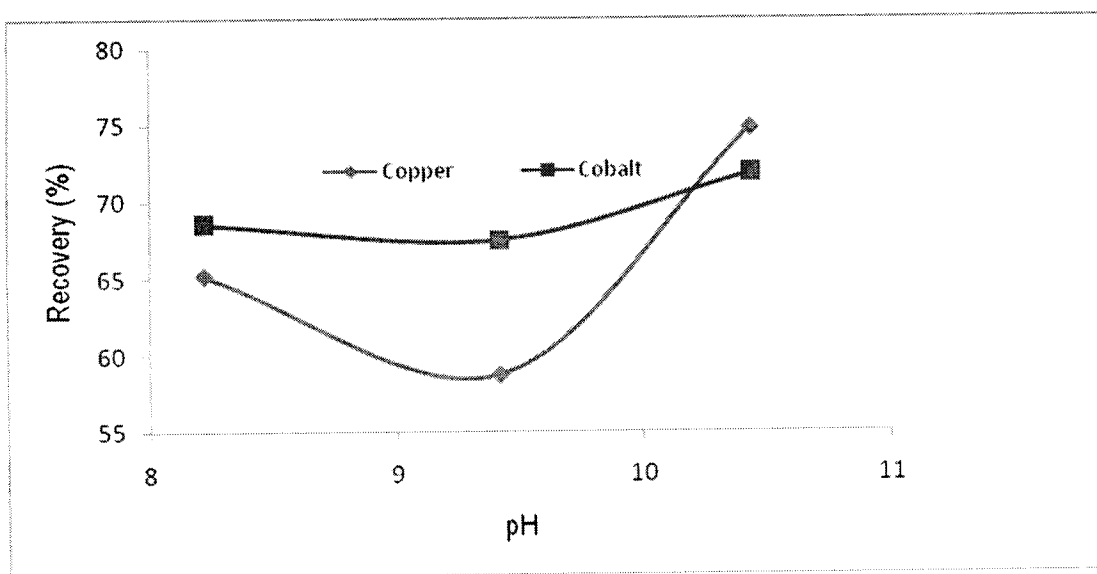
Figure 5.28: Flotation of Cobalt Ore at different pH values using SIPX

The recoveries of both copper and cobalt registered lowest recoveries at pH 9.44 whereas pH 10.5 had the highest recovery as shown in Figure 5.28. This pattern does not agree well with the findings in hallimond tube flotation for both Carrollite and chalcopyrite mineral in which maximum recoveries were attained at pH 9 and 3 respectively. The possible explanation to this may be the presence of other copper sulphide and oxide minerals which may interact differently with SIPX. The presence of

other copper and cobalt minerals may have caused galvanic interactions and possibly having surface properties which would improve recoveries of cobalt and copper at pH 10.45.

Table 5.7: Statistical Analysis of Flotation Results

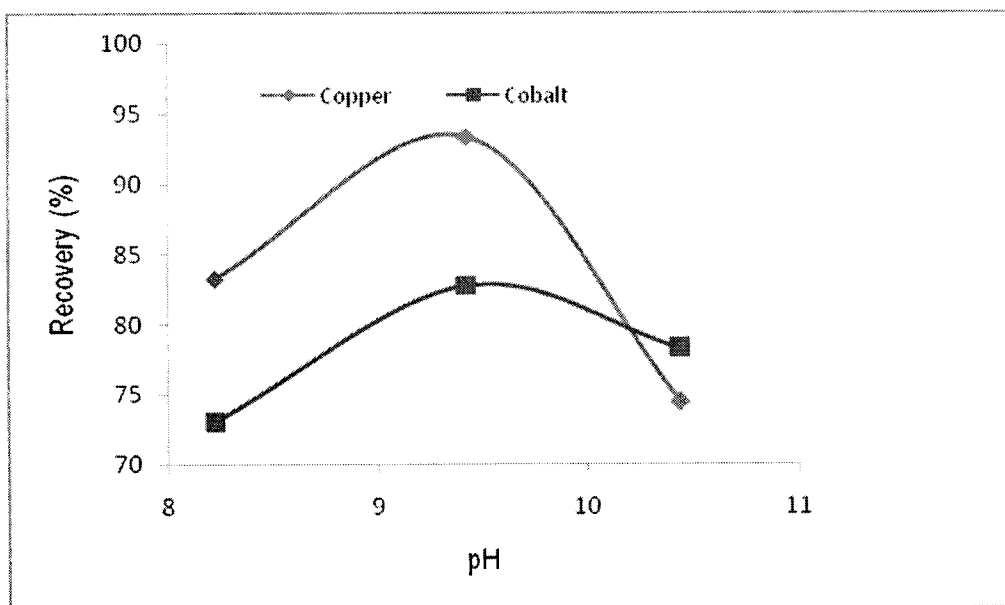| pH	Test 1	Test 2	Test 3	Test 4	Test 5	Average	Standard Deviation	Coefficient Of Variation.
Copper Recovery Using SIPX :PAX								
8.22	83.6	83.3	83.4	82.9	82.9	83.2	0.4	0.5
9.42	93.8	93.4	93.6	94.1	91.9	93.4	3.1	3.3
10.44	74.6	74.0	74.5	74.2	74.8	74.4	0.4	0.5
Cobalt Recovery Using SIPX :PAX								
8.22	73.0	72.5	72.8	72.1	74.6	73.0	3.5	4.8
9.42	82.5	83.1	82.6	82.7	82.9	82.8	0.2	0.3
10.44	78.5	78.3	78.7	78.8	77.0	78.3	2.1	2.7

Figure 5.29: Flotation of Cobalt Ore at different pH values using SIPX: PAX

The use of SIPX:PAX (3:1) as collector was based on the tests works which were conducted in the past and demonstrated higher recoveries and grade as opposed to using a single collector [32]. Synergism displayed a similar pattern as found in hallimond tube

flotation (Figure 5.27). The recoveries were maximum at pH 9.42, 93.82%TCu and 82.77%TCo as shown in Table 5.7.
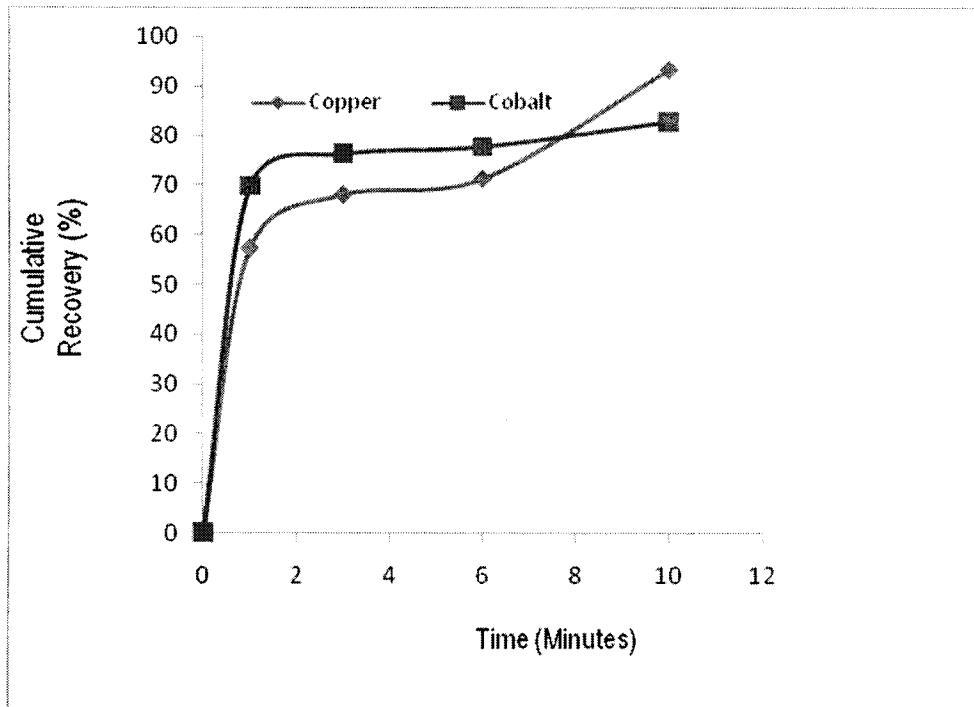
Figure 5.30: Flotation Kinetics SIPX: PAX

The first 1minute recorded the highest recoveries for both copper and cobalt as shown in Figure 5.30. This implies that the reactions between the minerals and collectors resulting in the formation of hydrophobic species were almost complete. The slight increase in recoveries from 6 to 10 minutes, as shown in Table 5.8, can be attributed to the addition of NaHS which targets the recovery of oxide minerals.

Table 5.8: Recoveries using synergism SIPX: PAX (3:1)

Time (min)	0	1	3	6	10
Recovery Cu	0	57.29	68.02	71.27	93.35
Recovery Co	0	69.75	76.21	77.71	82.77
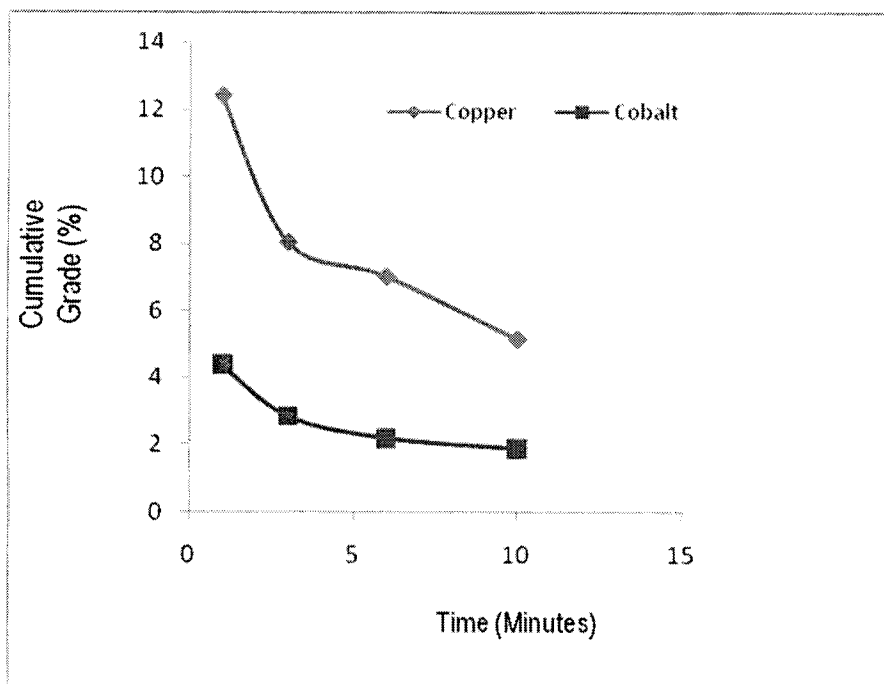
Figure 5.31: Concentrate grades for SIPX: PAX

The first 1 minute recorded the highest grades for both copper and cobalt as shown in

Figure 5.31. This implies that the selectivity of the collectors is best during this period,

beyond 1minutes, gangue minerals float as well, hence diluting the concentrate grade as

shown in Table 5.9.

Table 5.9 Recoveries using synergism SIPX: PAX (3:1)

Time (min)	0	1	3	6	10
Grade Cu	0	12.40	8.05	7.03	5.15
Grade Co	0	4.40	2.86	2.2	1.88

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

In acidic media more copper ions from both Carrollite mineral and ores go in solution which subsequently forms copper hydroxides and covellite (*CuS*) as compared to cobalt ions. In alkaline media there are more cobalt ions in solution as compared to copper ions. However, the amount of metal ions is insignificant (ppm). The loss of metal ions in water is very minimal.

Carrollite and Chalcopyrite surfaces acquire a negative charge from pH 3 − 11. The sulphide minerals lose electrons to oxygen in the water as the metal ions go in solution thereby forming oxy-hydroxides (*OH*) which covers the metal deficient sulphide (positively charged) surface. The presence of SIPX increases the negativity of the mineral surface. This is due to the presence of Xanthate anions which adsorb on the mineral surface. Oxidation of the Carrollite causes charge reversal at pH 7.5 and 10.5.

SIPX reacts with water to form xanthic acid at low pH. At pH 6 and above Xanthate ions are present in solution due to ionisation reaction. The presence of Xanthate ions in solution is a necessity to the formation of dixanthogen (X_2). Adsorption of Xanthate ions on mineral surface is in phases. A monolayer of Xanthate ions is achieved in the first 5minutes. This implies that conditioning collector (SIPX) with ores for 5minutes would be enough time to allow adsorption of Xanthate ions on the mineral surfaces. A second layer is formed after 30 minutes conditioning time. However, a monolayer is sufficient to induce the required properties.

The oxidation states of copper, cobalt and sulphur in Carrollite fresh sample are Cu (I), Co (III) and S (I) S (II). Carrollite is fairly stable in acidic media, however, at pH 9 and 11 copper is oxidised to Cu (II) (*CuS*, *Cu(OH)$_2$* and *CuX$_2$*) whereas cobalt is reduced to Co (II) (*Co(OH)$_2$*, *CoS* and *CoX$_2$*). This behaviour is similar in water, SIPX and oxygen saturated solution. pH 3 has little effect on Carrollite mineral surface.

Contact angles at low pH were below **30^0** whereas at pH 9 maximum angles were **33.5** ^{0} and **49.8^0** for untreated and treated in SIPX respectively. This implies that hydrophobic species are formed at pH 9 and SIPX improves hydrophobicity.

The recoveries and grades using SIPX were relatively low (74.7% TCu and 71.8% TCo recovery at 10.31%TCu and 2% TCo concentrate grade) as compared to SIPX:PAX (93.35% TCu and 82.77% TCo at 12.40% TCu and 4.40% TCo concentrate grade) at pH 9 -10.5. However, both scenarios gave better recoveries to what is currently achieved (45%TCo recovery and 2%TCo grade) on the plant. This implies that the range of pH 9 – 10.5 is expected to give maximum recoveries and grades for both SIPX and SIPX:PAX. Flotation kinetics indicates that a good grade and recovery is achieved in the first 1 minute, beyond this there is dilution of grade. This implies that the concentrate recovered in the first 1 minute can directly be reported as final concentrate whereas the remaining 9 minutes can be utilised to upgrade the recovery and grade through scavengers, cleaners and re-cleaners cells.

6.1 Recommendations
To achieve good cobalt recoveries and grades the following should be done:

- The optimum pH for cobalt recovery and grade is 9.5 – 10.5, therefore, conditioning pH should be within this range.

- Further synergism tests should be conducted using various collectors and frothers at different ratios.

- Since the knowledge on Carrollite mineral is in its infancy, further research work should be encouraged to gain a deeper understanding on the behaviour of the mineral in different conditions.

REFERENCES

1. Young R.S., 1960. "Cobalt, its chemistry, Metallurgy and Uses". Reinhold publication corporation, New York, 16 - 17

2. http://www.londonstockexchange.com/prices-and-markets/markets/prices.htm. updated on 15th April, 2011 [Accessed June, 2011]

3. Witika L.K., 1995. "Investigation of the electrochemical, electrokinetic and adsorption properties of Carrollite and chalcopyrite from Zambian ore in relation to their flotation behaviour". DSc Thesis, University of Regensburg, Germany.

4. Alan N.B., William M.S. and Harmer S.L., 2009 "Electronic environments in Carrollite, determined by soft X-ray photoelectron and absorption spectroscopy. Science Direct. *Geochinmica et Cosmoschimica Acta* 73 , 4452 – 4467.

5. Woods R., 1972. "Electrochemistry of sulphide flotation". In "flotation". Ed.M.C. Fuerstenau. AIME. New York, 298-333.

6. Woods R., 1984. "Electrochemistry of sulphide flotation". In "Principles of Mineral Flotation". Ed.M.H. Jones, J.T. Woodcock. The Australasian Institute of Mining and Metallurgy, Victoria, Australia, 91–115.

7. Heyes G.W. and Trahar W.J., 1977. "The Natural floatability of Chalcopyrite". International Journal of Mineral Processing, 4, 317-344.

8. Fornasiero D., Fullston D. and Ralston J., 1999. "Zeta potential study of oxidation of copper sulphide minerals". Colloids and surfaces, 146, 113-121.

9. Subrahmanyam T.V. and Forssberg K.S.E.,1993. "Mineral Solution Interface Chemistry in Minerals Engineering". Minerals Engineering, 6,5, 439-454.

10. Rao S.R., Moon K.S. and Leja J., 1976."Effect of Grinding on Media on the Surface reactions and flotation of heavy metals". SME AIME,9, 17, 509.

11. Berglund G. and Forssberg K.S.E., 1987. "Pulp Chemistry measurements in Sulphide Mineral Flotation". Erzmetall, 40(4), 189.

12. Adam K. and Iwasaki I., 1984. "Pyrrhotite-Grinding Media Interaction and its effect on Floatability at different applied potentials". Minerals and Metallurgical Processing,1, 81.

13. Yelloji M.K., Rao and Natarajan K.A., 1989. "Effect of Electrochemical interaction among Sulphide minerals and grinding medium on Chalcopyrite Flotation". Minerals and Metallurgical Processing, 6 (3), 146.

14. Pozzo R.L., Malicssi A.A. and Iwasaki I., 1990."Pyrite – Pyrrohotitte Grinding Media Contactand Effect on Flotation". Minerals and Metallurgical Processing, 6, 120-139.

15. Shaw D.J., 1980. " Introduction to Colloid and Surface Chemistry". 3rd Edition,Spottiswoode Ballantyne Ltd.

16. Leja L., 1982. " Surface Chemistry of Froth Flotation". Plenun Press, New York.

17. Willard H.H., Merritt L.L.Jr., Dean J.A. and Settle F.A. Jr.,1988. "Instrumental Methods of Analysis". Wardsworth publishing Company, Belmont, Califonia.

18. Chau T.T., Bruchard W.J., Koh P.T.L. and Ngunyen A.V., 2009. "A review of Factors affecting Contact Angles and Implications for Flotation Practice." Advances in Colloid and Interface Science, 150, 106-115.

19. Adamson A.W. and Gast A.P., 1986. "Physical Chemistry of Surfaces". New York, Wiley Interscience.

20. Chander S., 1988." Electrochemistry of Sulphide Minerals Flotation". Minerals and Metallugical Processing, 104.

21. Chen K.Y. and Morris J.C., 1972. " Kinetics of Oxidation of Aqueous Sulphide by Oxygen". Environmental Sci. Technol, 6, 529-537.

22. Gaudin A.M., Miaw K.L. and Spedden H.R., 1957. " Native Floatability and Crystal Structure". "2nd International Congress of Surface Activity, Ed. J.H. Schulman, Butterworth, London, 201-219.

23. Guy P.J. and Trahar W.J., 1985. " Effect of Oxidation and Mineral Interaction of Sulphide Floation". Development in Mineral Processing ,6.

24. Heys G.W. and Trahar W.J., 1986. " Oxidation Reduction Effects in Flotation of Chalcopyrite and Cuprite". Internal Journal of Mineral Processing.

25. Guy P.J. and Trahar W.J., 1985. " The Influence of Grinding and Flotation Environment on the laboratory batch Flotation of galena". International Journal in Mineral Processing

26. Plaskin I.N. and Bessonov S.V., 1957." Role of Gases in Flotation reactions". 2nd International Congress on Surface Activity, 3, 361-367.

27. Pitard F.F., 2009. " Pierre Gy's Theory of Sampling and C.O. ingamell's poisson process approach". Doctorial Thesis.

28. Jain S.K., 2001. "Mineral processing", 2nd Edition CBS Publishers and Distributors, New Delhi, India.

29. Crozier R.D., 1992. "Flotation; Theory, Reagents and Ore Testing" 1st Edition, Pergamon Pressplc, Headington Hill Hall, Oxford, England.

30. Sasaki K., Takatsugi K., Ishikura K and Hirajima T., 2010. " Spectroscopic study on oxidation dissolution of chalcopyrite, enargite and tennantite at different pH values" Hydrometallurgy 100, 144 – 151.

31. Garip F. and Ozdag H., 1998. "The Adsorption of Potassium Ethyl Xanthate on pyrite and Effect of Na2S on the Concentration of Xanthate ion in the Potassium Ethyl Xanthate Solution" Internal Journal of Mineral Processing, 55, 129-137.

32. Zimba N., 2005." Optimization of Reagents on Konkola Ores (KCM), Nchanga Oxide and Sulphide Ores". B.Sc.Min., University of Zambia.

33. Ralston J., 1991. "Eh and its consequences in Sulphide Mineral Flotation". Minerals Engineering, 4, 7-11, 859 – 878.

34. http://www.chem.qmul.ac.uk/Surfaces/Scc/Scat5.htm. updated on 15 April, 2011 [Accessed on June, 2011].

35. Finch J.A., 1997. "Xanthate adsorption on lead contaminated pyrite." International Journal of Mineral processing, 49, 207 – 221.

36. Rao S.R., 1971."Xanthates are related compounds". Marcel Dekker, New York, 497.

37. Bushell C.H.G. and Malnarich M., 1956." Reagent control in flotation". Minerals Engineering, trans., AIME, 734 -737.

38. Nagaraj D.R., 1990. "Chemistry sulphide collectors, Recent Advances". American Cyanamid Company.

39. Garip F., 1995. "The Adsorption , the thermal desorption at the Potassium Ethyl Xanthate – pyrite interface and the re-adsorption of desorbed Xanthate ions on pyrite surface." PhD. Thesis in Mineral processing, Osmangazi University, Eskisehir 82.

40. http://en.wikipedia.org/wiki/langmuir. updated on January, 2011 [Accessed on 15 June, 2011].