THE UNIVERSITY OF ZAMBIA

SCHOOL OF MINES

DEPARTMENT OF METALLURGY AND MINERAL PROCESSING

FINAL YEAR PROJECT REPORT-MM 590

DEVELOPMENT OF AN IMPURITIES BASED PROFILE OR MODEL FOR NCHANGA ELECTROWON CATHODES

REPORT SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF BACHELOR OF MINERAL SCIENCES (B.Min.Sc) IN METALLURGY AND MINERAL PROCESSING OF THE UNIVERSITY OF ZAMBIA

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DEVELOPMENT OF AN IMPURITIES BASED PROFILE OR MODEL FOR NCHANGA ELECTROWON CATHODES

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COURSE NAME: FINAL YEAR PROJECT

COURSE CODE: MM 590

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DATE OF SUBMISSION: 30TH APRIL 2010

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AKNOWLEDGEMENTS

I sincerely thank God almighty for graciously giving me strength of doing this project. Heartfelt thanks to my family for their emotional, spiritual and financial assistance. I thank also Mr C.Sakala (senior metallurgist), Mr. Mbewe (Technical services) and the rest of the staff at Tank houses of Tailing leach plant in Chingola for their cooperation, advice and data they provided for my research.

Special thanks go to all my classmates for their contributions on this research. I would also like to thank the University of Zambia, School of Mines Department of Metallurgy and Mineral processing staff for their professional advice.

Lastly, I thank my supervisor for his inspiration and guidance during the time of writing of the project.

May the almighty God bless you all abundantly.

ABSTRACT

The project was carried out at the Tailings Leach Plant of Konkola Copper Mine Plc in Chingola Zambia. The major objectives were to establish regions on the surface of the cathode that were prone to impurities such as lead, iron, sulphur and oxygen and to evaluate an existing mathematical model or develop a new one that computed the extent of affected regions on the cathode surface.

This came from the background of having poor quality cathodes that did not meet market specifications. The poor quality cathodes revealed the exact locations of the said impurities through the study of their concentrations on cathodes. A square grid was plotted to cover the entire cathode surface and each grid point was analysed for the major impurities that have been contaminating the cathodes.

The results were used to develop a physical model (Figure 4.3) and also to evaluate the existing mathematical models in literature (equations 4.2.1 and 4.2.2).

The need to estimate or quantify the levels of impurities occurring on electrowon copper cathodes at Nchanga Tailings Leach Plant is important.

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ABREVIATIONS

KCM	Konkola Copper Mines
TLP	Tailings Leach Plant
CT	Current Tailings
RT	Reclaimed Tailings
TD	Tailings Dam
KBC	Kabundi Copper Cathode
LME	London Metal Exchange
Emf	Electromotive Force
gpl	Grammes Per Litre
ppm	Parts Per Million

1.0 Introduction

1.0 INTRODUCTION

Konkola Copper Mines (KCM) PLC; a subsidiary of Vedanta group of companies is one of the major producers of copper in the world and operates a Tailings Leach Plant (TLP) in Chingola on the Copperbelt province of Zambia. TLP has since inception utilized Leach-Solvent-Extraction-Electrowinning process treating current tailings (CT) from the concentrator reclaimed tailings (RT) stockpiled since the 1930s in four paddock type tailings dams (TD 1 to 4).

Nchanga concentrator has a capacity to treat 750,000 tonnes per month of ore from both the open pit and underground operations. The concentrator tailing generated together with 660,000 tonnes per month of reclaimed tailings are treated through TLP.KCM produces copper of approximately 99.9979% purity and has a target of producing 500,000 tonnes of copper at 80 cents per pound by 2011.

The Nchanga Ore is mixed Oxide-Sulphide mineralization, the most important minerals being chalcolcite and malachite, with significant proportions of bornite, azurite, chrysocolla, pseudo-malachite and cupriferous vermiculite.

The TLP metallurgical process is divided into six main sections as follows:

- Current tails and reclamation tails material preparation (Dewatering and Pre-leach Filtration).
- Leaching and Solution Copper Washing by Counter Current Decantation.
- Post Leach Filtration.
- Solvent Extraction.
- Electrowinning.
- Solid Residue Neutralization and Disposal.

1.1 Brief description of Tailings Leach Plant

1.1.1 Process Description

Electrowinning is an electrolytic extraction process in which cathodic reduction is used to recover the sought metal from the electrolyte which is derived from a leaching process. The conventional process of copper is carried out from acid sulphate solutions containing the metal as the copper (II) ion. These electrolytes originate from leaching solutions which in a few cases may be sufficiently free from impurities to allow direct electrowinning. The electrowinning of Copper from the advance electrolyte carrying 40 to 60 gram per liter copper and 140 to 160 grams per litre sulphuric acid is conducted in two tank houses that is the new and the old. The spent electrolyte has the composition of 32 to 34 grams per litre copper while sulphuric acid is in the range 140 to 200 grams per litre.

1.1.2 Process Flow Sheet

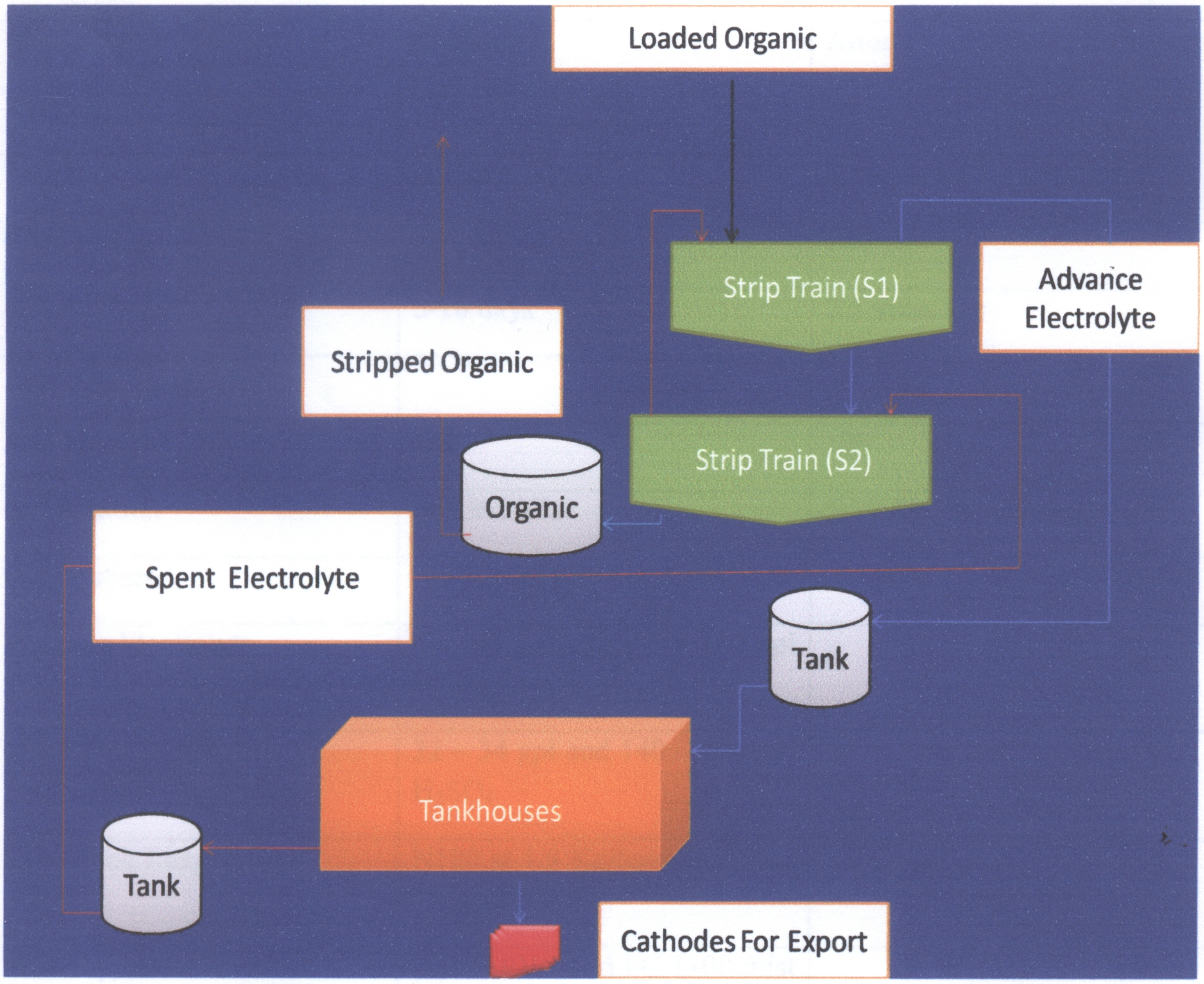

Figure 1.1.2 Flow sheet of the materials

1.1.3 New Tank house

The new tank house has the capacity of up to 300 tonnes per day of cathode copper. There are three units, unit I and Unit III has 80 cells each, unit II has 160 Cells making a total of 320 cells. A cell size is (L x W x D) of 6.72 x 1.12 x 1.35 cubic metres. The maximum unit amperages are 36 kilo amperes on each of the units. Maximum current densities are 250 amperes per square metre in the units. The cell voltages are 1.8 to 2.0 and cell temperatures 38-46 degrees Celsius. Currently the current efficiency varies between 80-95%.

Other important parameters are:

Parameter	**Cathode**	**Anode**
No. per cell	62	63
Size(l x w x d)	0.95m x 0.95m	1.12m x 0.88m x 0.12m
Weight(Kg)	46 - 76	180
Pulling Cycle	5-10 days	2.5 years life
Spacing(mm)	100	100
Composition	>99.97%Cu	5-7%Sb , 94%Pb (cast)
Starter sheet	5-6 Kg copper	
Advance Electrolyte	40 - 60 gpl and 140 - 160 gpl H_2SO_4	
Spent electrolyte	32 – 34 gpl and 140 – 200 gpl H_2SO_4	
Smoothing Reagents	N100 at 1.8 Kg/tone and Guar (on trail)	
Mist Suppressants	20mm PVC and FC 1100 mist suppressant at 0.28 Kg/ton	

Table 1.1.3a List of parameters

Cathode weight specification –KBC (Kabundi Copper):

From	**Minimum**	**Maximum**	**Nominal**
Deposited weight Kg/cathode	40	70	50
Gross weight (Deposited + Starting Sheet) Kg/cathodes	46	76	56
From	**Minimum**	**Maximum**	**Nominal**
K 91 – KBC (with loops) Kg/cathode	46	76	56
K 91 – KBC (loops guillotined) Kg/cathode	44	75	55
K 97 – KBC (top and bottom guillotined) Kg/cathode	37	62	46
K 91 –Export Bundle (40 pieces/bundle) Kg/bundle	1760	3040	2240

Table 1.1.3b Cathode weight specifications

1.1.4 Old Tank house

The old tank house has six units I, II and III are operational. They have 144 cells and each cell size is 4.55m x 1.05m x 1.20m. The maximum amperage on the units is 12 kilo ampere. The cell voltage is 1.80 – 2.0 volts and current densities of up to 220 ampere per square metre.

A cell has 40 cathodes and 41 anodes and has a pulling cycle of 5 – 10 days. The rest of the parameters are similar to those in the new tankhouse.

1.2 PROJECT BACKGROUND

Due to the presence of impurities such as oxygen, sulphur, lead and iron on the Kabundi Copper Cathode (KBC) surfaces, the quality of the final products is compromised. Certain areas on the cathode surface are more vulnerable to these impurities. Severely affected cathodes whose quality does not meet the London Metal Exchange specification are sent to the Smelter for further treatment. This increases the cost of production of KBC cathodes which also affects the general production of the company. It is for this reason that Konkola Copper Mines Nchanga Tailings Leach Plant in Chingola, in a pursuit to produce KBC cathodes that meet London Metal Exchange(LME) Grade A standards, embarked on a campaign to register and certify its Electrowon Cathode copper with LME. As part of its effort to secure the quality of copper, KCM has embarked on a project to generate a model, profiling impurities' distribution on the cathode surface.

1.3 OBJECTIVES

The main objectives of this investigation were to

- Establish regions on the surface of a cathode that are prone to impurities such as lead, iron, sulphur and oxygen.
- Evaluate existing or develop a mathematical model that computes extent of affected regions on the cathode surface.

2.0 LITERATURE REVIEW

2.1 Electrowinning

Conventional electrowinning of copper is carried out from acid sulphate solutions containing the metal as copper (II) ion. These electrolytes originate from leaching solutions which in a few cases may be sufficiently free from impurities to allow virtually direct electrowinning. Certain oxidized ores, and some sulphide ores after an initial oxidizing or sulphatising roast, may yield low impurity solutions on leaching, amenable to direct copper recovery. Iron is a common impurity and significant concentrations of iron (III) in the electrolytes can decrease the cathodes current efficiency drastically. If iron dissolution cannot be largely prevented during leaching, a separation process such as solvent extraction must be employed to provide a purified electrolyte. In the case of sulphide ores, roasting in the temperature range from 670 to 800 degrees Celsius favours the oxidation of iron sulphides to insoluble iron oxides whilst copper sulphides form a mixture of copper (II) oxides and sulphate, both of which are soluble in spent electrolyte.

Electrowinning is another term for plating. The solution to be electrowinned is recirculated (or agitated) past an anode (+) and cathode (-). A low voltage direct current is applied through the solution and metal ions are reduced at the cathode and water or another ion is oxidized at the anode. If a metal that can be plated is in solution, forms a coating on the cathode. Usually oxygen is formed at the anode from the oxidation of water molecules. The formula for electrowinning copper sulphate is:

$$CuSO_4 + H_2O \rightarrow CuO + H_2SO4 + O_2$$

The half reactions are:

At the anord

$$2H_2 + 2e \rightarrow 2O_2 + 2H$$

At the cathode

$$CuSO_4 + 2e^- \rightarrow CuO + SO_4$$

The efficiency of electrowinning is determined by the ability of the metal ion in solution to be reduced at the cathode. The lower the concentration of metal, the less likely it will be at the cathode to be reduced and hence lower efficiency. This result is due to the diffusion layer effect which is described as follows:

At the surface of a cathode is a thin film of water which is still. The thickness of this layer is determined by the agitation and temperature of the solution. Because this layer is still, the rate at which the metal ions transfer through by diffusion determines plating rate. The rate of diffusion and plating is determined by metal concentration, temperature, and/or agitation. Low concentrations, temperature, and agitation will reduce the plating rate.

In theory, most solutions can be electrowinned to some extent. The closer you get to zero metal in solution, the more current it takes to get the next increment of metal out. It is the law of diminishing returns. Some systems overcome this effect somewhat by placing very large cathode areas in the solution. Another way to overcome this effect is through very high agitation rates. The more solution you pass over the cathode, the more likely it is that a metal ion will be available to be reduced.

Integrated systems are compact. A 30 pound per day Copper recovery system will occupy an area 6' x 3'. No storage tank is needed except for your holding tank for future loads. Systems are designed to hold a single or double dump load (200-400 gallons) and recirculate this until it is plated out sufficiently.

Integrated systems are compact. A 13.608 Kg per day copper recovery system will occupy an area 0.1524m x0.0762m. No storage tank is needed except for your holding tank for future loads. Systems are designed to hold a single or double dump load (757.082 – 1514.164 litres) and recirculate this until it is plated out sufficiently.

Spent solutions are usually bled into the existing waste water treatment system or batch treated. Usually these solutions are high in acid content and may be used for pH adjust for other solutions.

There are many types of cells that have been tried over the years. There are presently 3 types in wide use that seem to be reasonably efficient and cost effective.

Parallel plate systems use an array of parallel anode and cathode pairs to provide a high surface area for electrowinning. These systems are inexpensive to design but have high labour costs associated with servicing the many contacts required. They are quiet efficient down to about 50ppm

Very High Surface Area Parallel plate systems use a mesh cathode to increase the surface area of the cathode. The contact maintenance problem is similar to the standard parallel plate system. The costs incurred with the mesh cathodes are very high. They are efficient to very low metal levels. Some of the major problems are plugging and very high costs associated with high metal recovery rates. These are best used in polishing applications where metal content is low and you have a clean stream.

Barrel plating systems use a polypropylene barrel with a "dangler" contact inside and a single anode outside. Mesh or drilled panels are used for solution transfer. The barrel has "BB" sized metal balls inside and a through wall cathode "dangler" to get the current inside the barrel. A conformal anode is mounted below the barrel. The barrel is rotated in the solution and this increase the mass transfer rate. High efficiency rates can be achieved with augmented solution transfer and the system can plate to very low levels. Only one anode and cathode contact is required to be maintained so the maintenance level is low. The barrel is emptied by lifting it up and dumping the contents into a trough that empties into the barrel.

The length of time to plate out a solution varies on the ion content, metal content, temperature, current density, and agitation. To produce copper plates of about 0.11907 Kg using 100 amps, it takes 1 hour. A 400 amp rectifier with a properly designed cell would plate up to 0.4536 Kg per hour.

Electrowon cathodes are suitable for all non-electrical uses. Most of the cathode impurities are caused by the occlusion of solid material arising from

a) Incomplete clarification of the leach solution

b) Corrosion products (Solid lead sulphate or lead oxide) from the lead anodes

The evolution of oxygen gas at the anodes create turbulent conditions in the electrowinning cells and this causes the particulate solids to reach the cathode surface where there is a high probability that occlusion will occur. Solids from the leach solutions are removed by clarification and filtration. The most common source of impurities is the lead anode which its surface is oxidized to form an almost insoluble oxide (PbO_2) layer. This layer tends to flake to a slight extent and they are carried over into the cathode deposit. Lead cause hot cracking or hot shortness in the copper cathodes. Flaking or corrosion of the anode are minimized by alloying lead with calcium(0.06%) or tin (6 to 15%).A controlled concentration of cobalt in the electrolyte is also effective in inhibiting flaking.

The principal organic additions to electrowinning solutions are flocculants which aid in the settling of solids thereby minimizing occlusion at the cathode. The impurity iron originates from the copper ore and its presence causes inhomogeneous in the properties of the copper cathodes if present.

The following are the factors influencing metal deposition in electrochemical production of copper cathodes:

- Electrolyte composition
- Temperature
- Current Density
- Impurities- soluble/insoluble

- Additives

Physical properties of copper are as follows:

Atomic weight	63.55
Density	8.96 * 10^3 Kgm^{-3}
Melting point	1083.4 ^0C
Boilling point	2567 ^0C
Crystal structure	f.c.c (face centred cube)

Table 2.1 List of physical properties of copper

2.2 Conditions for the deposition of copper

In an acidified solution of copper sulphate.A, copper forms ions with two valences: Cu^+ and Cu^{2+}.In the presence of copper, the process of the formation of monovalent ions is limited by the equilibrium:$Cu^{2+} + CU \leftrightarrow 2Cu^+$.The concentration of Cu^+ is always considerably lower than that of Cu^{2+}:**<u>According to literature</u>**, at 25°C,3.4 x 10^{-4}g atom of Cu^+ is an equilibrium with a molar solution of copper sulphate.A solution of $CuSO_4$ at an elevated temperature deposits metallic copper on cooling. The potentials of the electrochemical reactions in the formation Cu^+ and Cu^{2+} ions and the oxidation of Cu^+ to Cu^{2+} in solutions with normal concentrations are as follows:

$e_{1\,(Cu/Cu^+)} = +0.52$ Volts (2.2a)

$e_{\,(Cu^+/Cu^{2+})} = +0.34$ Volts (2.2b)

$e_{2\,(Cu^+/Cu^{2+})} = +0.17$ *Volts* (2.2c)

2.2.1 Electrolysis of copper

The electrolysis of copper is the sum total of the anodic and cathodic reactions.

<u>Cathodic reaction</u>:-Reduction

$Cu^{2+} + 2e = Cu^0$ (2.2.1a)

$$E^0_{Cu^{2+}/Cu} = 0.34 \text{ V}$$

The half cell potential is given by

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{RT}{nF} \ln \frac{1}{a_{Cu^{2+}}} \quad (2.2.1b)$$

Or $$E_{Cu^{2+}/Cu} = 0.34 + \frac{RT}{nF} \ln a_{Cu^{2+}} \quad (2.2.1B)$$

Where a_{Cu} = unity, being in standard state i.e. Solid

Anodic reaction: - Oxidation

$H_2O = H^+ + OH^- = 2H^+ + \frac{1}{2}O_2 + 2e$ (2.2.1c)

$E^0 2\, H^+/H_2O = +1.23\ volts$

The half cell potential is expressed as

$$E^0 H_2O/2H^+ = E^0_{H_2O/2H^+} - \frac{RT}{nF} ln \frac{a^2_{H^+} . P^{\frac{1}{2}}_{O_2}}{a_{H_2O}}$$

As oxygen and water are in there standard states $a_{H_2O} = 1$ atm and $P_{O_2} = 1$ atm.Therefore

$E_{H2O/2H^+} = -1.23 - \frac{2RT}{nF} ln a_{H^+}$ (2.2.1d)

The sum total reaction inclusive of sulphate ions is (2.2.1a) + (2.2.1c) or

$Cu^{2+}_{(aq.)} + SO^{2-}_{4(aq.)} + H_2O_{(e)} = Cu_{(s)} + 2H^+ + \frac{1}{2}O_{2(g)} + SO^{2-}_{4(aq.)}$ (2.2.1e)

The corresponding cell potential is given by

$E^0_{(1.6e)} = E^0_{Cu^{2+}/Cu} + E^0_{H2O/2H^+}$

$= +0.34 - 1.23 = 0.89\ volts$

The overall cell potential is given by the following expression.

$E_{(4.3e)} = E_{Cu^{2+}/Cu} + E_{H2O/2H^+}$

The above process is acid generating at the anode; oxygen is liberated while copper is deposited at the cathode. If equilibrium (2.2.1e) were carried out at standard conditions, a potential of 0.89v need be applied, however due to irreversible phenomena, a larger potential is applied. This irreversible phenomenon includes activation overvoltage, voltage drop due to electrolyte resistance and ohmic resistance owing to electrical leads and the electrodes themselves. The applied voltage lies in the range 2.0 – 2.5 volts. A high applied voltage will lead to high energy consumption according to the reaction:

$W = VIt$ (2.2.1f)

Therefore factors that lead to a high applied voltage should be minimized. The efficiency of the electrowinning process is measured by the ratio of the actual copper deposition to theoretical deposition expressed as a percentage

$CE = (W_{Cu\ (actual)}/W_{Cu\ (theoretical)}) \times 100$ (2.2.1g)

Due to irreversible phenomena, values of current efficiency calculated are lower than 100%.The mathematical form of Faraday's Law:

$$d\,(W_{Cu}) = \frac{MI}{nF}\,dt \qquad (2.2.1e)$$

this is the theoretical deposition of copper.

Where *M=molecular weight of copper* (*grams*)

I=current being passed (*amps*)

n=electron consumed (*number*)

F= Faraday's constant (*96500 Amps.secs*)

From expression (2.2.1e), the ampere hours required for electrodepositing 1 gram of copper will be:

$$1\ gram = \frac{63.54\ x\ It}{2\ x \frac{96500}{3600}}\,(A.hours) \qquad (2.2.1i)$$

$$It = 1x2x\frac{96500}{63.54x3600} = 0.844\ Ampere\ hours$$

Consumed by 1 tonne of copper (10^6grams) is therefore $0.844\ x10^6\ ampere\ hours$

Energy required $= VIt$

$$= V \times 0.844 \times 10^6\ watt\ hours/ton\ of\ copper$$

(If 100% current efficiency)

This implies that the energy used to produce a tonne of copper will generally be more than the above due to the irreversible phenomena and ohmic resistance.

Energy likely to be consumed therefore is

$$E = \frac{V \times 0.844 \times 10^6}{C.E/100}\,watt\ hours/tonne\ of\ copper$$

C.E. – current efficiency (as a percentage)

$$E\ (Kwh/tonne\ of\ Cu) = \frac{V \times 8.44 \times 10^5}{1000 \times C.E/100}$$

CELL TYPES, POTENTIALS AND IRREVERSIBLE PHENOMENA

Electrolytic cells are of two types

(a) Refining cells (transference cells)
(b) Production cells (non-transference type)

The principle of a transference cell is that if the anode and cathode reactions are added, we get the total cell reaction: $Cu = Cu$ i.e. the reaction has been the transfer of one mole of copper from the anode to the cathode and in this cell the two electrodes need not be identical. Very often a metal is transferred from an impure anode or alloy to a cathode of the pure metal. As for the production cell, an example is that on which the project is based. For instance

$Pb, O_2/Cu^{2+}, SO_4^{2-}, H_2O/Cu$

represents an insoluble anode of lead (Pb, O_2) on which oxygen is liberated. By conversion the above notation denotes a cell where the positive current flows from left to right. In the above case, the anode reaction is:-

$$H_2O = 2H^+ + \frac{1}{2}O_2 + 2e^-$$

And the cathode reaction:-

$$Cu^{2+} + 2e^- = Cu^0$$

The overall reaction is;

$$Cu^{2+} + H_2O = Cu + \frac{1}{2}O_2 + 2H^+$$

Thus in a production cell the electrolyte is consumed and the components deposited on the electrodes. This type of cell needs energy in order to proceed from left to right.

If an electrochemical reaction is carried out reversibly i.e. at infinitely low current density, the cell voltage is denoted by E and is called the electromotive force (emf) of the cell. We have in that case:-

$\Delta G = -nFE$ (2.2.2j)

Where ΔG is the change in Gibbs energy

n is the number of electrons transferred

F is the Faraday's constant

For non-transference electrolytic cells, E is negative an indication that the reaction is not spontaneous. If in a cell reaction all components are present in their standard state, the Gibbs energy is denoted by G^0 and emf by E^0.Thus for the reaction

$AX=A+X$ (2.2.1k)

$$\Delta G = \Delta G^0 + RT ln \frac{a_A \cdot a_X}{a_{AX}} \quad (2.2.1l)$$

$$E = E^0 - \frac{RT}{nF} ln \frac{a_A \cdot a_X}{a_{AX}} \quad (2.2.1m)$$

2.2.2 Irreversible Phenomena

The electromotive force of a cell can be measured only if the cell reaction takes place under reversible conditions; i.e. at infinitely low current density. In practical electrolysis, which occurs at a finite rate, there will be additional potentials. One of them being the voltage drop due to ohmic resistance in the electrolyte. A second voltage drop is due to ohmic resistance in the electric leads and the electrodes. These terms are proportional to the current and the resistance of the electrolyte leads respectively. In addition, there will be a voltage drop which is called the overvoltage n of the cell. Thus the total applied voltage may be expressed:

$$V = -E + (R_1 + R_2)I + n \quad (2.2.2a)$$

Here R_1 and R_2 are the resistances of the electrolyte and leads, and I the current. The e.m.f. is given with negative sign since it is by definition the voltage applied to the cell. For electrolytic cells,-E is positive, the additional voltage drop causes an increase in the applied voltage, where as for galvanic cells the additional voltage drops reduce the voltage from the coil.

The overvoltage, n, is caused either by the reactants not being supplied to the electrodes as fast as they are removed or by the reaction products not being removed as fast as they are supplied and it may be divided into concentration overvoltage and activation overvoltage.

2.2.3 Concentration overvoltage

This is the result of microscopic changes in the composition of the electrolyte in the vicinity of the electrodes. A good example would be in the electrolytic refining of copper, copper goes into solution at the anode and is deposited at the cathode. This creates a concentration cell, the emf of which works against and adds to the voltage needed for electrolysis.Concetration overvoltage may be reduced or eliminated by stirring of the solution, and it usually does not affect greatly the industrial electrolytic process.

2.2.4 Activation overvoltage

This is the phenomenon which occurs on a molecular or atomic scale on the electrodes, and its nature is only partly understood. It may be measured as the potential between a reversible electrode i.e.an electrode which does not carry any current, and a similar electrode with a certain current density. The overvoltage increases with increasing current density, and for many reactions and within a certain current range it is found to follow the TAFEL equation:

$$\vartheta = a + b\log(I/A) \qquad (2.2.4)$$

Where ϑ is the total overvoltage

(I/A) the current density

a and b are constants which are characteristic of the electrode reaction in question

The magnitude of the activation overvoltage differs greatly for different electrode reactions and is also a function of the material. It is generally large for the evolution of gases, particularly oxygen and hydrogen for aqueous solutions, but is known also for the evolution of carbon dioxide during aluminium electrolysis. The activation overvoltage may be reduced by giving the electrodes a spongy surface. It also decreases with increasing temperature. For the deposition of metals, both from aqueous and molten salt electrolytes, the overvoltage is usually small, but may be in certain cases being measurable.

2.2.5 Kinetic of Electrolysis

In any chemical process, Kinetics determines and controls the rate of a reaction and as such, their study is beneficial to the understanding of the overall processes. Briefly, reactions occurring at an electrode are heterogeneous ones that differ from other such reactions in that electric current is passing at the solid-liquid interface.Similiar to the other heterogeneous reactions, a boundary layer also exists at the interference of the electrodes as the result of the existence of the boundary layer diffusion process. For example, the discharge of hydrogen ions at the cathode may be represented by the following steps

i. Diffusion of ions through the boundary layer
ii. The dehydration of the ions
iii. The discharge of the ions
iv. Formation of hydrogen molecules
v. The desorption of gaseous hydrogen from the electrode
vi. The diffusion of hydrogen away from the electrode

Any of the above may be the rate determining step. Since the first and last are diffusion processes, therefore like any heterogeneous reaction, an electrode process may be diffusion controlled, chemically controlled, or intermediate controlled.

2.3 Diffusion Controlled Electrode Process

As a result of the discharge process at the cathode, the concentration of the metal ion is decreased at the interface. This loss is compensated for by diffusion of a fresh supply of metal ions from the bulk of the solution. The rate of diffusion is given by:

$$\text{Rate of diffusion} = \frac{DA}{d}(C - C_1) \qquad (2.3a)$$

Also the rate of discharge of the ions by the current is given by:-

$$\text{Rate of discharge} = \frac{I}{nF} \qquad (2.3b)$$

Where *I= Supply current* (*Amps*)

n= number of electrons consumed

F=Faraday's constant (*96500 Amps.secs*)

D= diffusion coefficient (Cm^2/sec)

A= area of diffusion (Cm^2)

d=thickness of boundary layer (*Cm*)

C_1= *Concentration of the ion species at particular time* ($moles/Cm^3$)

The above equation shows that with increasing current density I/A, the value ($C-C_1$) should increase rapidly since the metal ions at the interface will be rapidly depleted. The same equation also shows that at constant current density, when electrolyte is stirred, thus decreasing the thickness of the boundary layer d, the difference ($C-C_1$) should decrease i.e.O: increases

2.4 Kinetic Parameters of Metal Deposition

The rate of metal deposition according to Faraday's laws depends only on the current applied and not on other factors such as temperature, concentration; etc.Metal deposits are always crystalline but vary from large-grained coarse adherent deposits to fine-grained loosely adhering powder. The form of the deposits depends on many factors. Two processes are usually taking place during electrolysis

i. Nucleation, and
ii. Crystal growth

Grain size depends on the ratio of the two processes. If the rate of nucleation is much larger than the rate of growth of crystal, the product will be fine powder. On the other hand, if the rate of nucleation is smaller while that of crystal growth is larger, the product will be coarse grained. When C_l the concentration of the metal ion at the interface tends to zero i.e. when the process becomes diffusion controlled, the rate of nucleation becomes much larger than that of crystal growth, thus favouring the deposition of powders. In other words powder formation occurs when the electrode process is diffusion controlled and coarse grained deposits occur when the process is chemically controlled.

Factors that affect the concentration of ions at the electrode-electrolyte interface are:-

i. **Current density** – At low current densities, the discharge of ions is slow i.e. the process is chemically controlled. The rate of crystal growth is much greater than the rate of nucleation. The product will be a coarse deposit. At high current density the opposite will be true.
ii. **Concentration of the electrolyte** – At low electrolyte concentration, the rate of diffusion is slow usually governs the whole process which becomes diffusion controlled and powder formation is favoured.The opposite is true at high electrolyte concentration. The figure below shows the effect of current density on particle size distribution. It can be seen that at current density 10.5 amp/m^2 the most common size of electrodeposited metal powder is 0.1 mm while at 18 amp/dm^2 it only 0.05mm.

Table (4.9b)

Cu^{2+} (g/litre)	Apparent density (g/cm^3)	Particle size analysis (%)	
		<74mm	<44mm
5	0.420	82.3	62.4
10	0.663	68.2	33.9
20	0.776	66.9	32.8
30	1.060	59.0	25.1
40	2.040	47.7	21.0
50	2.440	29.2	11.8

From Principles of Extractive Metallurgy' Habashi- Table (1-3) shows that the more dilute the electrolyte is the more fine particles of the metal deposited.

iii. **Temperature** – Increasing the temperature has two effects:-
   a. the rate of diffusion is increased

b. the rate of crystal growth is increased

Both factors favour the formation of coarse deposits. Therefore increasing the temperature, results in the formation of coarse deposits.

iv. **Stirring the bath** – The higher the speed of stirring, the coarser the deposited particles, because under these conditions the thickness of the boundary layer is decreased, resulting in an increased rate of diffusion. The process becomes chemically controlled.

v. **Presence of an indifferent electrolyte** – An indifferent electrolyte does not react at the cathode but decreases the transference number of the cation deposited. A decrease in the transference number will decrease the diffusion process to such an extent that it becomes rate controlling, thus favouring powder formation.

vi. **Presence of Colloidal substances in electrolyte** – Small additions of gelatin, agar, glue, peptones, sugars etc.result in the formation of smooth fine grained deposit. If however the concentrations of such additions exceeds about 0.05g/litre, a loose deposit is obtained. The reason being that such colloids are absorbed on the nuclei of metal crystals, thus preventing their growth, and the ions are compelled to start new nuclei.

2.4.1 Current efficiency

This is said to increase with increasing current density e.g. hydrogen overvoltage increases with increasing density of current. Therefore the ratio of the metal deposited to hydrogen will rise. Chemical short circuiting is mainly a result of continuous oxidation of the reduction of iron. At the anode, in addition to oxygen evolution, the ferric ions diffuse to the cathode where they are reduced to Fe^{2+}.Thus one Faraday has passed through the cell without any metal deposition. The part of the current which is transferred this way depends on the rate of diffusion and convection in the electrolyte. For a given cell this occurs at a more or less constant rate whereas the deposition of iron on the cathode increases with increasing current density. Thus again the current efficiency is increased by increased current density. One way to reduce chemical short circuiting is to insert a semi-permeable diaphragm between the anolyte and the catholyte. This cuts down the diffusion of the ferric ions and maintains a high concentration of ferrous ions in the catholyte. On the other hand the diaphragm causes a considerable increase in ohmic resistance.

2.5 Practical Application of Electrolysis

For both Electrowinning and electro refining processes the same type of cell equipment is used. The cells are rectangular tanks with a cross section of about 1m x 1m and a length which can be varied with the desired capacity, but which is usually 5 and 10m.The electrodes may have a section of about 0.9m x 0.9m and are suspended vertically in the tank. Anodes and cathodes are placed alternatively. In order to give a low resistance but without danger of metallic contact, the distances between anode and cathode may be 3-5 cm.An exception is represented by a process with diaphragms where the distances may be 10cm.Usually all the anodes and cathodes in one tank are connected in parallel, making the voltage drop for the whole tank equal to the voltage drop between each set of electrodes. Since this voltage drop is much less than the available DC voltage several tanks are connected in series until they correspond to the voltage of the DC source. An exception is the so called series system for refining of copper. Here a number of electrodes of impure copper are placed in the cell, and the DC source is connected only to the two electrodes at the end of the tank, these acting as anode and cathode respectively. The electrodes act as anode on one side and cathode on the other. This system has the advantage of a higher voltage drop per cell, and is suitable for small plants. Its disadvantages are many however, and the system is not much used anyway. The current density for most aqueous plants is between 100 and 500 A/m^2, and is adjusted by means of the applied voltage as well as by the temperature and acidity of the electrolyte. The electrolyte is usually made to flow from one tank to tank partly to circulate the electrolyte between leaching and electrolysis and purification of the electrolyte.

2.6 Electrolytic Winning of Copper

From leaching solutions, the winning of copper is a relatively simple process, copper being a rather noble metal, and impurities such as zinc or iron will remain in the electrolyte. Also the electrolysis may be done from highly acid solutions and above room temperature without danger of hydrogen evolution. Copper is deposited on copper cathodes (starting sheets) and oxygen is liberated on insoluble (lead) anodes. For the electrolysis of a one molal $CuSO_4$ solution at pH = 0, the theoretical emf is -0.09 volts. In practice about 2.5 volts are used. Owing to the presence of ferrous and ferric ions in the solution the current efficiency is only about 80-90%.This energy requirement is about 2.5 KWh per Kilogramme of copper produced.

If the electrolytic plant works in combination with a leaching plant (as in Nchanga), the spent electrolyte which is still contains appreciable amounts of copper, is re-circulated. Eventually the contents of impurities build up to a level where some electrolyte has to be withdrawn. The remaining copper may then be precipitated by cementation on scrap iron.

2.6.1 Advance Electrolyte

The composition of the electrolyte for the electrolysis of copper is an aqueous solution of copper sulphate and sulphuric acid. The conductivity of the electrolyte increases when the concentration of the copper sulphate is increased to a certain limit. When this limit is exceeded, it begins to decrease. The solubility of copper sulphate is affected by the concentration of sulphuric acid contained in the electrolyte. The solubility of copper sulphate increases with increase in temperature.

Table (5-3)

H_2SO_4 Concentration (grams/litre)	$CuSO_4.5H_2O$ Solubility(g-eqvi/litre)
7.291	347.40
20.619	328.67
42.532	306.59
65.905	289.50
91.924	272.15

The solubility of copper sulphate is also reduced by the presence of impurities in the electrolyte. Nickel has a particularly marked effect. Since 1 part of nickel is equivalent to 1.67 parts of sulphuric acid, it must be considered that with a nickel content of 10 grams in 1 litre of electrolyte, the content of free sulphuric acid increases by 16.7g and the solubility of $CuSO_4.5H_2O$ decreases accordingly. Other impurities present in the electrolyte also reduce the solubility of copper sulphate. In practice the concentration of $CuSO_4.5H_2O$ must be kept between 130 and 160g/litre depending on the current density. The resistance of the electrolyte increases with further increase in the acidity. Practice and research have shown that the maximum concentration of sulphuric acid for an electrolyte temperature of 50 – 70^0C is 220g/litre.A small amount of chloride ions (Cl^-) is added to the electrolyte; this is necessary partly to precipitate the antimony and arsenic and also to prevent silver from passing into solution.Moreover,it is known from works practice that, in small quantities, chloride ion has the useful effect on the structure of the cathode deposit; too much chloride leads to the production of a circular cathode deposits. The concentration of chloride ions is kept between 20 and 40mg/litre, which correspond (with an electrolyte density of 1.2g/Cm^3) to 0.0017 – 0.10033%.Forcing loss of chloride ions, compensation is made for by the additions of hydrochloric acid or common salt to the electrolyte. If the water added to correct the electrolyte contains chlorides, or HCL or common salts need not be added.

2.6.2 Some Parameters Affecting Electrolysis

Careful control of certain prime parameters leads to a high efficiency of operation during electrolysis.

2.6.3 Temperature of electrolyte

Electrolyte temperature is one of the most important parameters of electrolysis of copper. With increase in temperature the mobility of all the ions presents in the electrolyte increases and consequently the conductivity of the electrolyte increases. The dependence of conductivity on the temperature may be described by the equation:

$$X_t = X_{20}(1 + x(T - 20) \qquad (2.6.3a)$$

T = temperature

X_t = conductivity at a given temperature ohm^{-1}

x = the temperature coefficient of the conductivity for an increase of 1^0C in the temperature.

The relationship above does not give accurate results for solutions at the temperatures above 45^0C, and can therefore be used only as an approximation.

Since with distance of 100 – 120 mm between the centres of like electrodes at a temperature of 40^0C the resistance of the electrolyte amounts to about 75% of the total resistance of the cell, so even a slight change in temperature is reflected significantly in the electricity consumption. It is not however possible to keep the temperature above certain limit the following reasons:

i. At the temperatures, the electrolytes evaporate rapidly and the air above the cells is saturated not only, with water vapour but also with the finest droplets of electrolyte which affects the health of the workers.
ii. At high temperatures the crystal structures of the cathode deposit becomes much coarser, and the density of the cathode decreases.

It has been found that raising the temperature within permitted limits affords to carry out electrolysis at high current densities, since the mobility of the ions increases. This increased current density reduces the unfavourable effects of high temperature on the crystal structure of the cathode deposit.Largely, temperatures of the range 45 – 70^0C are suitable.

2.6.4 Electrolyte Circulation

During electrolysis, the solution near the cathode is continuously being depleted of the copper ions. There may come a time when the ions at the cathode become insufficient for the normal passage of current. And in to avoid the separation of the electrolyte into layers and to equalize the concentration of copper ions in the cell, it is necessary to mix the electrolyte all the time. The electrolyte is mixed by continuous circulation and this is achieved by use of the centrifugal pumps. The electrolyte is introduced at one end of the bath and removed at the other end of the other end. Logically it could be supposed that the introduction of the electrolyte at the top and withdrawal at the bottom would improve the deposition of the slime at the bottom of the bath.

To achieve better agitation of the electrolyte, it must be directed (towards) parallel to the electrodes. In this case the need arises for constant filtration of the electrolyte since as it passes parallel to the anode (in the case of electrorefining), it carries away a large amount of slime. The electrolyte circulation rate is one of the most important parameters of the technological process.

The more vigorous the motion of the electrolyte, the better the copper ion concentration is equalized. In addition with higher circulation rates, the temperature drop between the electrolyte entering and leaving the cell decreases. The criterion for the circulation rate is the time in which the electrolyte in the cell is completely replaced. Practice has shown that for the current densities employed, the optimum electrolyte replacement time is 2.3→ 5 hours. Therefore optimum circulation rate should be:

$$R = \frac{Cell\ volume}{(2.5\ x\ 60) mins} \qquad (2.6.4a)$$

2.6.5 Impurities and their effect

Impurities and their effect largely depend on their source, whether they come from a leaching circuit or a solvent extraction stage. The most troublesome impurity however is iron, present in both types of electrolytes. In the leach/electrowinning system, the presence of inert salts for example $Al_2\ (SO_4)_3$, $MgSO4$ etc. also play an important role. Poor quality deposits combined with low current efficiencies as well as problems associated with localized corrosion of electrode suspension loops have been related to the concentration of Fe, Al, Mg, Ca and suspended solids or gelatinous materials. There mode of control has been an art developed through experience but however attempts recently have been made to understand the relationship between solution composition, temperature, current density, agitation and the observed tank houses phenomena.

2.6.5.1 Iron Fe

Cyclic oxidation and reduction of iron consumes current and decreases the current efficiency. In the recent analysis of the variables in copper electrowinning it has been shown that the electrode reaction rates at a given current are determined by the diffusion of Fe^{2+} ions to the anode, and Fe^{3+} ions to cathode. A comprehensive equation relating the rate of diffusion of iron species to an electrode (i_L) and the operating parameters has been developed.

$$i_L = \frac{F K^{\frac{2}{3}} T^{\frac{2}{3}} V_{\infty}^{m} C}{(6\pi r_1)^{\frac{2}{3}} Kg\, n^{\frac{2}{3}} \left({}^{n}/_{p}\right)^{n}} \qquad (2.6.5.1a)$$

$Kg = constant\ for\ a\ given\ electrode\ geometry$

V_{∞} = Velocity constant of the electrolyte parallel to the electrode surface at a distance greater compared to the diffusion layer thickness.

${}^{n}/_{p} = kinematic\ viscosity\ of\ the\ solution$

m, n = are constants depending upon whether the solution flow is turbulent or laminar. For laminar flow n = 0.5 and 0.16 and for turbulent flow n = 0.9 and 0.57

$r_1 = radius\ of\ the\ diffusing\ species$

K =Boltzmann constant. Note that the term $^{KT}/_{6r_1 n} = D\ the\ diffusion\ coefficient.$

The above equation predicts that increases in temperature, solution velocity and copper ion concentration make important increases in i_L, whereas an increase in the viscosity and i_L. The limiting current for the reduction of Fe^{3+} increases with solution agitation which in turn, is influenced both by the circulation rate of the electrolyte through the cell and by the oxygen bubbles from the anode. It has been reported that the diffusion rate is proportional to the concentration of oxygen bubbles. Thus the overall effect of agitation is complicated depending on the cell design as well as the above mentioned factors.

2.6.5.2 Other Impurities

Impurity salts in the electrolyte,e.g.$Al_2\ (SO_4)_3$ and $MgSO_4$ increase the viscosity n of the solution and therefore impedes the diffusion of Fe^{3+}.The results of laboratory studies indicate that the term $n^{\frac{2}{3}}$ of equation (7.1a) makes a greater contribution than the$(^{n}/_{p})^{n}$ term to inhibiting the diffusion.

As a follow up to an earlier discussion on the influence of temperature in the electrolysis process, here it is seen that from equation (7.1a) increase in temperature increases i_L, both because $T^{\frac{2}{3}}$ increases and n decreases with an increase in temperature. It was concluded that the primary influence of temperature on i_L is on the diffusion coefficient $D = KT/6\pi r_1 n$ which is in agreement with the general finding that the diffusion coefficient of ions in solutions usually increases by about 2% per degree.

2.6.7 Current Efficiency Based on Operating Parameters

In addition to what was discussed on C.E. in earlier sections, below is another based on the parameters introduced in the preceding section. The dependence of the current efficiency on the operating parameters may be expressed by the equation.

$$C.E = \frac{1.0 - FK^{\frac{2}{3}} T^{\frac{2}{3}} V_{\infty}^{m} C_{Fe^{3+}}}{(6\pi r_1)^{\frac{2}{3}} Kg n^{\frac{2}{3}} (n/p)^{n} i_C} \qquad (2.6.7a)$$

Where i_C is the applied current density. Thus both the concentration of ferric ion and the applied current density have a strong influence on the current efficiency. Increasing the current density increases the current efficiency because the rate of reduction of Fe^{3+} is diffusion controlled, so that any increase in the C.D must be sustained by an increase in copper deposition. Note also that increases in salt concentrations such as $Al_2\ (SO_4)_3.MgSO_4$ of the electrolyte tend to increase the viscosity of the electrolyte and hence increase the current efficiency.

It is technically possible to improve the current efficiency in copper modeling by decreasing the temperature, increasing the inert salt concentration decreasing the Fe^{3+} concentration, increasing the current density and decreasing the electrolyte agitation. The most effective of these methods however is to decrease, Fe^{3+}, since it is the only method which does not deteriorate the quality of the deposit. The various methods for decreasing Fe^{3+} include

a) Solution purification by **hydrolysis**, precipitation, solvent extraction, etc.
b) Reduction of Fe^{3+} by SO_2,Cu^0 etc.to Fe^{2+}
c) Increase in the bleed stream volume
d) Use of the diaphragm cell

The above methods have their advantages and disadvantages.

2.7 Role of Additives in Copper Electrowinning

The major factor that counteracts the negative effects of concentration polarization is the activation or charge transfer polarization and it is a function of the current density only. This activation polarization is often artificially and increased by addition of leveling agents to the electrolyte. Since the leveling agent is transported to the electrode surface by diffusion, the increased flux of leveling agents towards imperfections may actually suppress their growth relative to the rest of the cathode. For this reason addition agents such as glue, thiourea and chloride ions are added to copper electrowinned solutions. Although the concentrations of these substances in the electrolyte are several orders of magnitude less than the concentration of Cu^{2+} of free H_2SO_4,these addition agents have a profound effect on the deposit, quality through their leveling action and grain refinement.

These addition agents can be organic (glue, thiourea) or inorganic in nature. Their presence in the electrolyte generally has physical as well as metallurgical effects on the deposit. These can be changes in deposit characteristics such as brightness, hardness, grain refinement and surface smoothness. Addition agents can also increase the limiting current density for electrodepositing process. Their action has been associated with various properties, such as their ability to form complex ions, become colloidal dispersed in the electrolyte, or absorbed on the cathode surface. The additives modifying the properties of the deposit do so by virtue of their effect on the microstructure and on the nature and distribution of deposited impurities, since these two factors are determined by the nucleation and growth of the deposit, it is the effect of any addition agent in these respects which is important.

Among the organic agents used as additives, the effects of thiourea, glue, gelatin, glycine, cystine, dextrin and sulphonated products have been studied. Among the inorganic ions are Co^{2+},Mn^{2+},Mg^{2+},Al^{3+},Cl^-,SO_4^{2-} and also Cl_4^-, fluoroborate and NO_3^- are such others used. The optimum effect of these additives is realized when a complete monolayer is formed on the surface of the cathode. The concentration of thiourea required is about *5-10mg/litre* depending on the volume of the tank houses liquor and cell design. The overall effects of the above additives on copper deposition vary from its kinetics, orientation of the metal lattice, with *(100)*,*(110)*,*(111)* being observed. High concentrations may lead to nodular depositions, *75mg/litre* and above in the case of thiourea.

2.8 Physico-Chemical Properties of Copper Electrowinning Electrolytes

Physico-chemical properties of winning and refining solutions such as density, viscosity, electrical conductivity and heat capacity are vital to the smooth operation of the tank houses. These properties of the electrolytes affect the purities of the product metal and the energies consumed by the winning process. Recently main researches have made studies of the $CuSO_4$ – H_2SO_4 – H_2O system, with regard to the constituents such as copper, arsenic, iron and free sulphuric acid.

2.9 Mathematical Model

A mathematical model uses mathematical language to describe the system. Mathematical models are used not only in the natural sciences and engineering disciplines (such as physics, biology, earth sciences and engineering) but also in social sciences (such as economics, psychology and political science); physists, engineers, computer scientists and economists use mathematical models most extensively. The process of developing a mathematical model is termed a "Mathematical Modelling".

Mathematical models can take many forms, including but not limited to dynamic system, statistical models, differential equations, or game theoretical models. These and other types can overlap, with a given model involving a variety of abstract structures. Engineers analyze the system to be controlled or optimized by using the mathematical model. In analysis, engineers build a descriptive model of the system as a hypothesis of how the system could work, or try to estimate how an unforeseeable event could affect the system.Similary, in control of the system, engineers try out different control approaches in simulations. A mathematical usually describes a system by a set of equations that establish relationships between variables. The values of the variables can be practically being anything; real or integer numbers, Boolean values or strings, for example. The variables represent some properties of the system, for example, measured system outputs often in the form of signals, timing data, counters, and event occurrence. The actual model is the set of functions that describe the relations between the different variables.

There are six basic groups of variables: decision variables, input variables, state variables, exogenous variables, random variables, and output variables. Since there can be many variables of each type, the variables are generally represented by vectors.

Decision variables are sometimes known as independent variables. Exogenous variables are sometimes known as parameters or constants. The variables are not independent of each other as the state variables are dependent on the decision, input, random, and exogenous variables. Furthermore, the input variables are dependent on the state of the system (represented by the state variables).

Objectives and constraints of the system and its users can be represented as functions of the output variables or state variables. The objective functions will depend on the perspective of the model's user. Depending on the context, an objective function is also known as in index of performance, as it is some measure of interest to the user.Although,there is no limit to the number of objective functions and constraints a model can have, using or optimizing the model becomes more involved(computationally).

Many mathematical models can be classified in some of the following ways:

1. **Linear vs. nonlinear:** Mathematical models are usually composed by variables, which are abstractions of quantities of interest in the described systems, and operators that act on these variables, which can be algebraic operators,functions,differential operators,etc.If all the operators in the mathematical model present linearity, the resulting mathematical model is defined as linear. A model is considered to be nonlinear otherwise. The question of linearity and nonlinearity is dependent on context, and linear models may have nonlinear expressions in them. For example, in a statistical linear model, it is assumed that a relationship is linear in the parameters, but it may be nonlinear in the predictor variables. Similarly, differential equation is said to be linear if it can be written with linear differential operators, but it can still have nonlinear expressions in it. In mathematical programming model, if the objective functions and constraints are represented entirely linear equations, then the model is regarded as the linear model. If one or more of the objective functions or constraints are represented with a nonlinear equation, then the model is known as a nonlinear model. Non linearity, even in very fairly simple systems, is often associated with phenomena such as chaos and irreversibility. Although there are exceptions, nonlinear systems and models tend to be more difficulty to study than linear ones. A common approach to nonlinear problems is linearization, but this can be problematic if one is trying to study aspects such as irreversibility, which are strongly tied to nonlinearity.
2. **Deterministic vs. probabilistic (stochastic):** A deterministic model is one in which every set of variable states is uniquely determined by parameters in the model and by sets of previous states of these variables. Therefore, deterministic models perform the same way for a given set of initial conditions.Conversely.in a stochastic model, randomness is present, and variable states are not described by unique values, but rather by probability distributions.
3. **Static vs. dynamic:** A static model does not account for the element of time, while a dynamic model does. Dynamic models typically are represented with difference equations or differential equations.

4. **Lumped vs. distributed parameters:** If the model is heterogeneous (varying state within the system) the parameters are distributed. If the model is homogeneous (consistent state throughout the system), then the parameters are lumped. Distributed parameters are typically represented with partial differential equations.

A crucial part of the modeling process is the evaluation of whether or not a given mathematical model describes the system accurately. This involves several different types of evaluation. Usually the easiest part of model evaluation is checking whether the model fits experimental measurements or other empirical data. In models with parameters, a common approach to test this fit is to split the data into two disjoint subsets: training data and verification data. The training data are used to estimate the model parameters. An accurate model will closely match the verification data even though this data was not used to set the model's parameters. This practice is referred to as cross-validation in statistics.

Defining a metric to measure distances between observed and predicted data is a useful tool of assessing model fit. In statistics, decision theory, and some economic models, a loss function plays a similar role. While it is rather straightforward to test the appropriateness of parameters, it can be more difficult to test the validity of the general mathematical form of a model. In general, more mathematical tools have been developed to test the fit of statistical models than models involving differential equations. Tools from nonparametric statistics can sometimes be used to evaluate how well data fits a known distribution or to come up with a general model that makes only minimal assumptions about the model's mathematical form.Assesing the scope of the model that is, determining what situations the model is applicable to, can less straight forward. If the model was constructed based on a set of data, one must determine for what systems or situations the data is the typical set of data from. The philosophical consideration of the validity of the model rests not only on its fit to empirical observations, but also on its ability to extrapolate to situations or data beyond those originally described in the model. One can argue that a model is worthless unless it provides some insight which goes beyond what is already known from direct of the phenomenon being studied.

3.0 METHODOLOGY

3.1 Sample collection and preparation.

A random selection of cathode samples from the tank houses was achieved by using a computer generated random number table. For each lot of copper pulled on a particular day about 1% of the weight was sampled.

Pulling Copper Cathodes

Punching Copper Cathodes

3.2 Procedure

- Random number tables were obtained from the sectional Chemist (They are generated on the computer by the Senior or Sectional Chemist and they identify cathodes in random order to be pulled on any pulling day).
- Section numbers from the shift foreman of each tank houses were obtained.
- The section numbers were entered against the randomly selected cathode numbers.
- The loops of the selected cathodes were painted whilst selecting alternate cells in the sections resulting in the sampling of three cathodes per section

The Old Tank houses is set up in sections and each section has six cells (as shown below) and one cell carries 40 cathodes.

A	D	E
B	C	F

Sampling was commenced with cell A and repeated for cell C and E. Sample selection changed with each pulling cycle as follows:

Cycle	**Pattern to start with**
1	A,C,E
2	B,D,F

Sample selection at the New Tank houses was carried out from alternate cells based on the pulling cycle as shown below

Cycle	**Pattern to start with**
1	1,3,5,7,etc
2	2,4,6,8,etc

3.2.1 Preparation of Sample Cathodes for Analysis

A square grid was planned to cover the whole surface of the sample cathode. The dimension of the cathode is 0.91m x 0.91m. With a view to reduce wastes, only two lines were marked on each sample cathode. In the first round, horizontal lines were labeled from A to N while vertical lines were from A1 to N1.Each line was investigated for the four elements (lead, iron, sulphur and oxygen). The investigation of elements for analysis was alternated on the lines. For the second round, horizontal lines were relabeled as A2 to N2 while vertical lines as A12 to N12.Where lead with iron was investigated in the first round, in this round, it was sulphur with oxygen and vice versa. The loops were labeled as loop 1(left) and loop 2(right) and all the elements were investigated in pairs stated earlier. Both horizontal and vertical lines were 0.025m from the edges of the cathode surface and from each other.

Sample cathodes were punched and the resulting discs were melted in an induction furnace to produce ingots for lead and iron analysis. For the analysis of sulphur and oxygen the resulting discs were sent without being melted.

4.0 RESULTS AND DATA ANALYSIS

Sample date	Sample code	Iron (ppm)	Sulphur (ppm)	Lead (ppm)
08-06-09	7302,Cell52B, Vertical A	4.1	5.4	0.1
08-06-09	2228,Cell304, Vertical B	4.0	4.0	0.1
08-06-09	2228,Cell245, Vertical C	4.2	3.1	0.1
08-06-09	2228,Cell262, Horizontal A	7.5	5.2	0.1
09-06-09	2228,Cell244, Horizontal B	7.1	5.5	0.1
09-06-09	2228,Cell261, Horizontal C	7.2	3.8	0.1
20-06-09	7305,Cell51A, Loops	7.5	3.1	1.8
Average		5.943	4.936	0.15
Maximum Limit		10	15	7

Table 4.1 Levels of iron, sulphur and lead on the Kabundi copper cathodes

Sample date	Sample code	Oxygen (ppm)
08-06-09	7302,Cell52B, Vertical A	40
08-06-09	2228,Cell304, Vertical B	40
08-06-09	2228,Cell 245, Vertical C	50
08-06-09	2228,Cell262, Horizontal A	60
09-06-09	2228,Cell244, Horizontal B	40
09-06-09	2229U1D,Cell261, Horizontal C	80
09-06-09	2229U1,Cell17, Vertical D	70
10-06-09	7302U3East, cell50B,Horizontal E	120
11-06-09	7303U3West,Cell50D,Vetical F	30
11-06-09	7303U3West,Cell62,Horizontal E	50
15-06-09	7303U3East,Cell50D, Vertical F	120
15-06-09	2235U3A,Cell301, Horizontal F	100
18-06-09	2236U1C,Cell305, Horizontal G	130
18-06-09	2236U1C,cell52, Vertical G	120
20-06-09	2236U1C,Cell53, Horizontal H	130
20-06-09	2305,Cell51A, Loops	30
Average		81
Maximum limit		400

Table 4.2 Levels of Oxygen from Kabundi copper cathodes

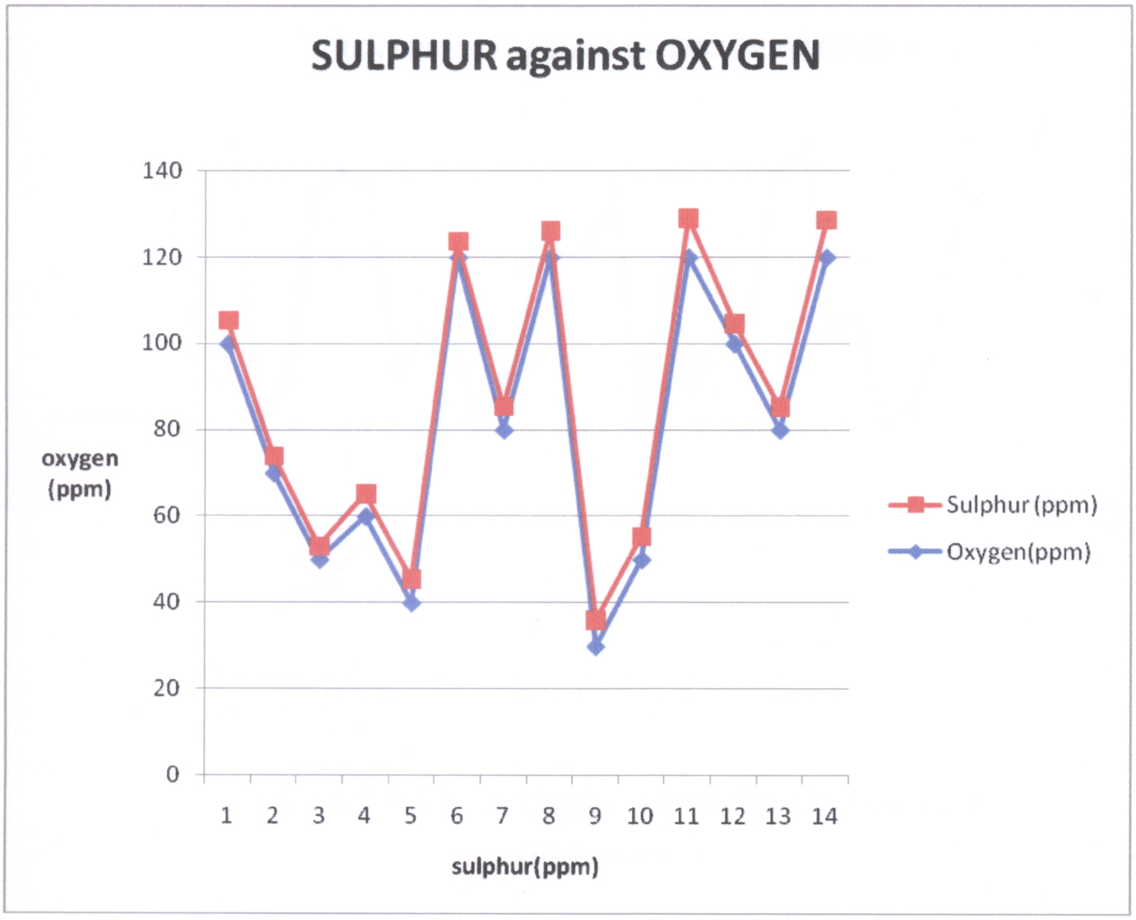

Figure 4.1 Sulphur and Oxygen levels in Kabundi copper cathodes (KBC)

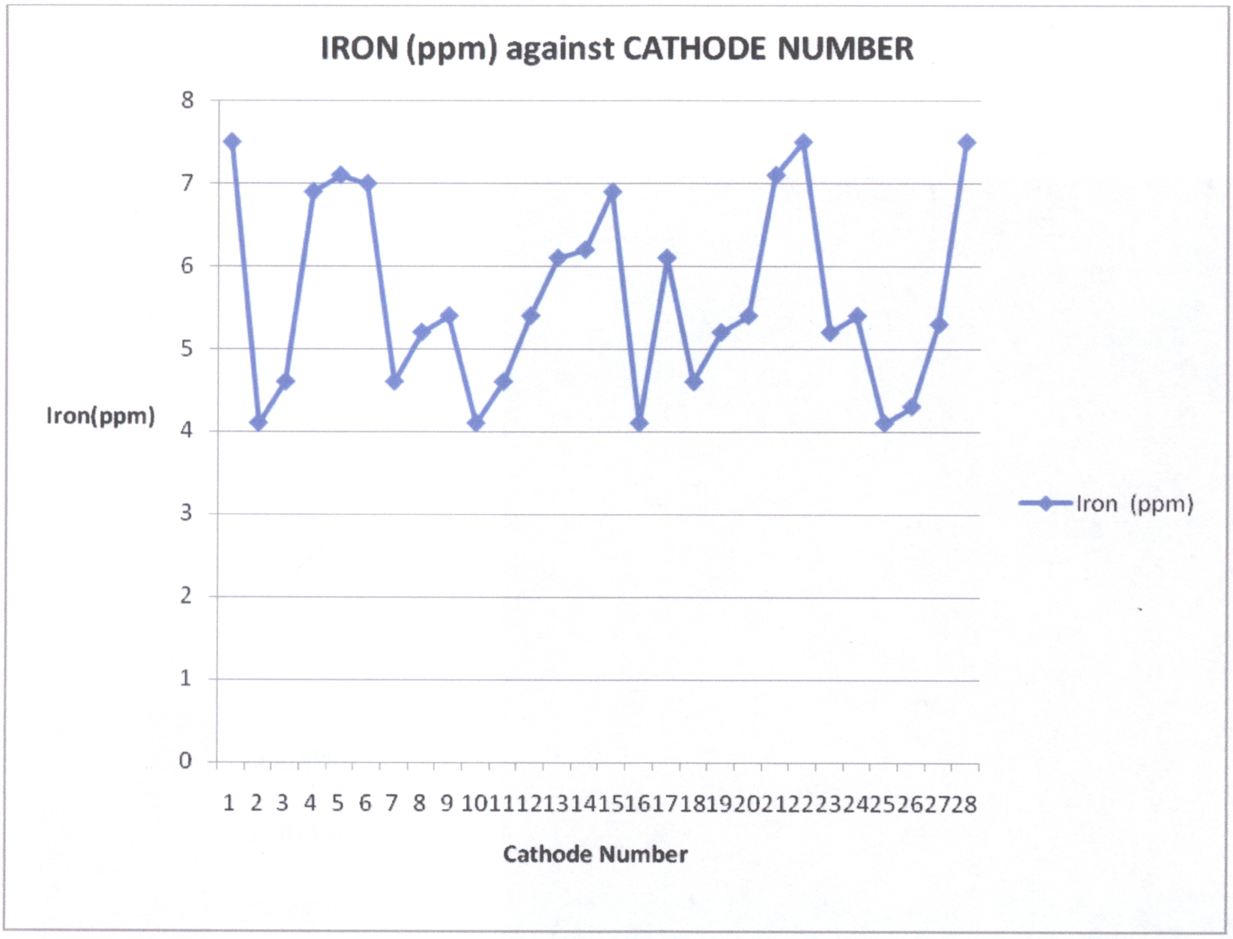

Figure 4.2 Distribution of Iron in the Kabundi Copper Cathodes

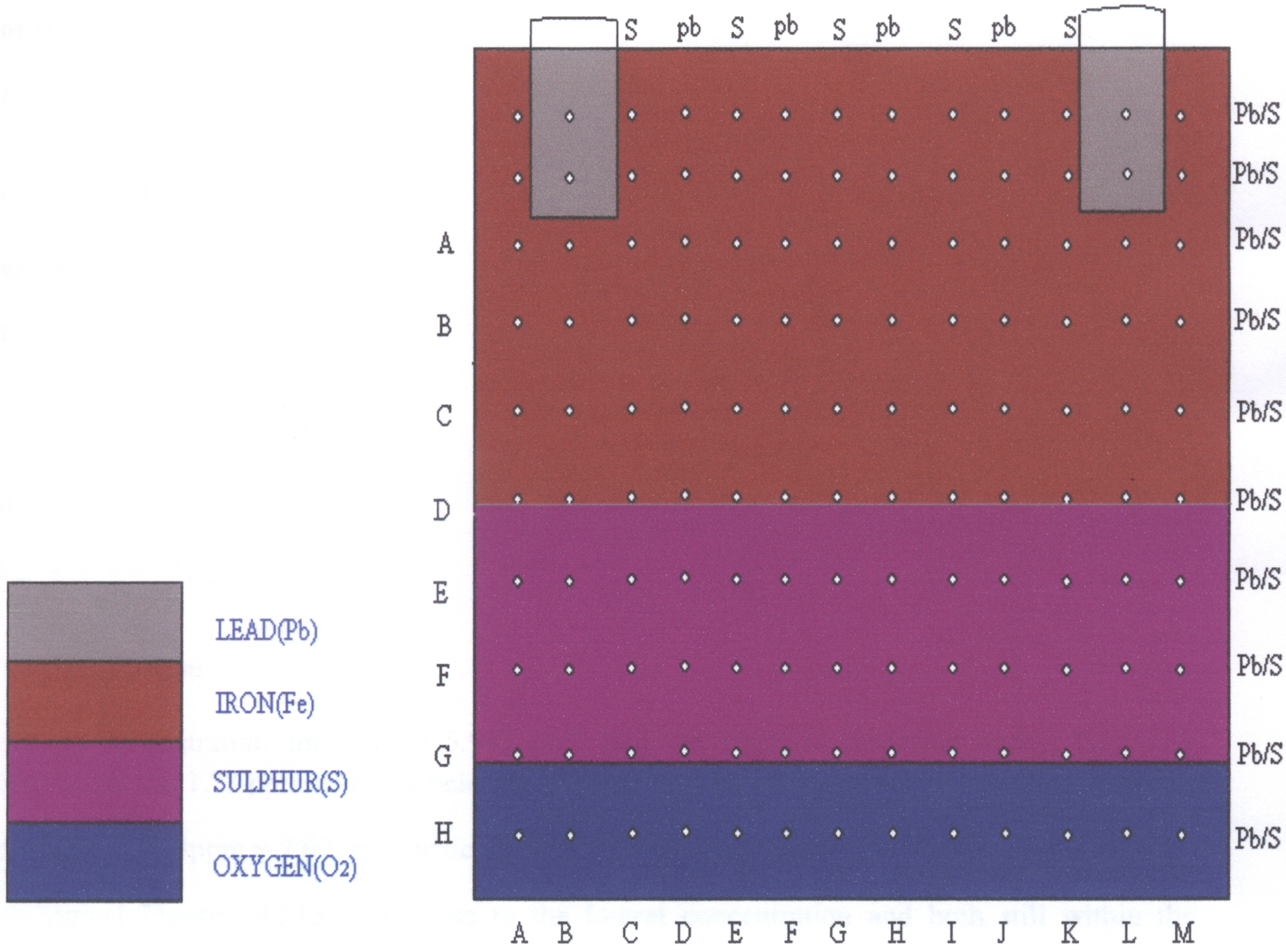

Figure 4.3 physical models showing the location of the investigated impurities on the copper cathodes.

4.1 Sample calculation

The standard deviation for the data can be computed as follows

$$S^2 = \frac{n\sum x^2 - (\sum x)^2}{n(n-1)}$$

where

n = total number of observations

$\sum x^2$ = sum of observations of the impurity

$(\sum x)$ = sum of the squared observations of an impurity

For iron

$$S^2 = \frac{7(265.2)-(41.6)^2}{7(7-1)}$$

$S = \pm 1.73$ ppm

For suphur

$$S^2 = \frac{7(136.1)-(30.1)^2}{7(7-1)}$$

$S = \pm 1.11\ ppm$

For oxygen

$$S^2 = \frac{16(88761)-(820)^2}{16(16-1)}$$

$S = \pm\ 55.82\ ppm$

Average concentration for iron is 5.943 ppm and the standard deviation means that each observation was 1.73 ppm above or below the mean.

5.943ppm + 1.73ppm = 7.673ppm which is close to the highest concentration of 7.5ppm while

5.943ppm-1.73ppm= 4.213 ppm close to the lowest concentration and both still within the acceptance limits.

For sulphur,

4.936ppm +1.11ppm = 6.046 ppm

4.936ppm – 1.11ppm = 3.826 ppm

For oxygen,

81 ppm + 55.82ppm = 136.82ppm

81 ppm – 55.82ppm = 25.18ppm

Both results are within the acceptance area.

Hence all the results remain within the acceptance area as can be observed from all the means of the impurities less than the maximum limit of each impurity concentration.

4.2 Evaluation of the existing literature models

1. Equation relating the rate of diffusion of iron species to an electrode (i_L) and operating parameters.

$$i_L = \frac{FK^{\frac{2}{3}}T^{\frac{2}{3}}V_\infty^m C_{Fe^{3+}}}{(6\pi r)^{2/3} Kgn^{2/3} (^n/_p)^n} \quad \text{.......} \quad (4.2.1)$$

Where

Kg = *constant for a given electrode geometry*

V_∞ = *velocity constant of the electrolyte parallel to the electrode surface*

$^n/_p$ = *kinematic viscosity of the solution*

m, n = *constants depending on flow(turbulent or laminar)*

r_1 = radius of the diffusing species

K = *Boltzmann constant*

Note that the term $\frac{KT}{6r_1 n} = D$ the diffusion coefficient.

V_∞ *can be obtained from the above equation*

2. Current efficiency may be less than 100% when there is the deposition of unwanted products such as iron.

$$C.E = \frac{1.0 - FK^{\frac{2}{3}}T^{\frac{2}{3}}V_\infty^m C_{Fe^{3+}}}{(6\pi r_1)^{\frac{2}{3}} Kg(^n/_p)^n i_c} \quad \text{.......} \quad (4.2.2)$$

where i_c is the applied current density.

Velocity constant of the electrolyte parallel to the electrode can be obtained.

Knowing V_∞ and the flow rate of the electrolyte, the area can be computed using the following relationship i.e.

$$A = \frac{Q}{V_\infty} \quad \text{.......} \quad (4.2.3)$$

Where Q(m^3/s)is the flow rate and A(m/s) is the area.

5.0 DISCUSSION, CONCLUSION AND RECOMMENDATIONS

5.1 Discussion

From the physical model (figure 4.3) developed based on the results of this research, it was found that impurities have specific locations on the cathode surface. The distribution of these impurities on the physical model in the research was determined by comparing the concentration levels, where the element with the highest concentration was assumed to occupy the point considered on the grid. This distribution of impurities on the physical model agreed with that locallised high current density causes the presence of lead in the loops while iron position is determined by the cementation of copper at solution line. The presence of sulphur and oxygen at the bottom of the cathode are due to the lower copper concentration at the bottom of the cell. Therefore the distribution of the impurities on the cathode surface was predicted.

In order to evaluate the mathematical model, measurements on current load, current efficiency, and temperature and flow rate data of the electrolyte should be available. The data was not available because the literature models (4.3.1 and 4.3.2) were not available at the data collection stage of this research and therefore could not also develop the mathematical model due to insufficient of data.

5.2 Conclusion

From the work done, the following were the findings;

5.2.1 Regions on the cathode surface prone to impurities under investigation were established. The presence of lead is in the loops and iron presence covers the cathode surface from the upper most to D, the 6th horizontal grid line. The presence of sulphur is from D to G, the 9th horizontal grid line while oxygen presence is from G to the lowest point of the cathode.

5.2.2 The extent of contamination of iron can be computed by using the relationship (4.2.3) of area (A), flow rate (Q) and velocity (V) of the electrolyte.

5.3 Recommendations

5.3.1 Measurements of fluidity should be done in order to determine the viscosity of electrolyte using the literature models (4.2.1 and 4.2.2).

5.3.2 Measurements of temperature, current efficiency and flow rate should be done in order to evaluate the existing literature models (4.2.1 and 4.2.2).

5.3.3 Same sampling method must be used but the spacing should be reduced below 2.5 cm in order to have many grid points which can allow having sufficient data for mathematical model development.

5.3.4 Computation of the extent of contaminated areas on the electrowon cathode be done using equation 4.2.3.

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