THE EFFECT OF IMPURITIES, SMOOTHENERS AND OTHER FACTORS ON THE RECOVERY OF COPPER FROM SOLUTIONS

by

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submitted in fulfilment of the requirements
for the degree

MASTER OF TECHNOLOGY

in the subject

CHEMICAL ENGINEERING

at the

UNIVERSITY OF SOUTH AFRICA

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December 2008

DECLARATION I

This thesis, submitted for degree purposes at the University of South Africa, has not previously been submitted for degree purposes to any other institution of higher learning. The work, ideas and presentations in this document are entirely mine except for the sources that have been acknowledged particularly in literature survey.

F. W. Ntengwe December 2008

DECLARATION II

I declare that The Copperbelt University provided me with laboratory facilities which were used in carrying out experiments from April 2006 to December 2007 for the sole purpose of facilitating the carrying out of work towards the Masters programme registered with UNISA.

Felix William Ntengwe	December 2008
Head of Chemical Engineering	December 2008
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DEDICATION

This study is dedicated to my wife Leya,

my children

Thomas, Susan, Margret, Ruth and Mundalila

For their moral support during the preparation
of the proposal and write up of the Thesis

and

my grand parents

Mundalila Ntengwe and Jenny Mbale
Chambulamemba Mpharo and Jenny Banda

For their support and care
during my kinder-garden days.

ACKNOWLEDGMENT

This study was constituted as a result of my registration in the Masters of Technology (Chemical Engineering) programme in the College of Science, Engineering and Technology at the University of South Africa during the year 2006. The study was research based. As is the case with all research-based studies, one is bound to come across literature of studies and publications, which are used for comparison, strengthening of one's approaches, identification of gaps and adoption of methodologies used. I have come across a number of writing skills, which though different in the approach have conveyed important messages. The origin of the writing is what makes it different. In research, one is therefore reminded of the fact that when one uses other people's ideas and publications, such works need to be acknowledged. It is not often deliberate that one does not acknowledge what has been used from other authors because it is human to forget. It is for this reason that I wish to remind the readers of this manuscript that effort has been made to acknowledge all works of other authors that have been used in this document. I wish, therefore, to acknowledge and thank authors whose ideas have been used as reference keys in the effort to make my ideas not only clear to readers but to strengthen the manuscript as well.

In addition, I wish to thank the University of South Africa for providing the support and guidance during the preparation of the proposal and during the entire research period. I wish to thank Dr N Mazana and Pr Eng F Samadi, in particular, for providing guidance and the direction during the period of my study at the University. I also would like to thank the Copperbelt University for providing the laboratory, equipment and in some cases chemicals and Chambeshi Metals Plc for providing copper sheets which were used as cathodes and anodes during the study. Lastly I wish to acknowlwdge the assistance received from Mr Chipili Protasho who assisted in the preparation of standard solutions and the organization of equipment that were used during the evaluation.

ABSTRACT

The electrochemical refining of copper was investigated at different temperatures, distances between electrodes, different levels of overvoltage, current density, metal impurities, smootheners, electrode-active area and concentration of electrolyte using the parallel-plate model. The purpose of the investigation was to evaluate the effect of smootheners, impurities and other factors on the recovery of copper from solutions. The results showed that the metal impurities, with more negative oxidation potentials, did not affect the electro-deposition of copper whilst metals with oxidation potentials close and equal to that of copper reduced the current efficiency. The current density increased with the increase in temperature, overvoltage and concentration of electrolyte. The increase in overvoltage and current density above limiting values produced increased rates of deposition resulting in efficiencies greater than 100% to be attained. The increase in the limiting current density at concentration below 10.8g/L produced low values of current efficiency ranging from 100 to 30%. The 2 and 3cm distance between electrodes produced stable efficiencies of between 92-100% and 96-100% respectively. The temperature was found to have indirect effect on the current efficiency but direct effect on the dissociation of electrolyte in solution, current density and overvoltage. An increase of 20cm^2 of electrode active area reduced the current efficiency by about 40%. The increase in concentration of electrolyte produced an increase in the current density and efficiency ranging from 75-100%. The use of smootheners; thiourea and EDTA (Ethylenediaminetetraacetic acid) reduced the current density and current efficiency (100>CE>30%). However increased concentration of K-glue, B-glue and G-Arabic in conjunction with EDTA or thiourea and NaCl improved the current efficiency even at increased levels of overvoltage to levels of 96-100%, 100% and 90-100% respectively. Therefore, the presence of impurities, the use of high current densities, inadequate distance between electrodes, and too low concentration of electrolyte and the absence of glue disadvantaged the recovery process while the presence of K-glue and B-glue reduced the inhibition effects of thiourea and EDTA and thus improved the recovery of copper from solutions.

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LIST OF ABBREVIATIONS (ACRONYMS)

a	Number of moles of reactant A	mol/L
Aa	Factors for exponential function	-
A_g	Silver	-
[A]	Concentration of reactant A	mol/L
b	Number of moles of reactant B	mol/L
[B]	Concentration of reactant A	mol/L
c	Number of moles of reactant C	mol/L
C	Energy cost per kg of product, concentration	\$/kg, mol/L
Cd	Cadmium	-
C_E	Energy consumption	kWh/kg
Co^{2+}	Cobalt (II)	-
Co^{3+}	Cobalt (III)	-
Cu	Copper	-
[C]	Concentration of reactant A	mol/L
d	Number of moles of reactant D	mol/L
D	Diffusion coefficient	mol/m^2s
[D]	Concentration of reactant A	mol/L
e	Electron	-
E	Potential at any instant, energy consumption	Volts, kJ
E^o	Potential at initial conditions or equilibrium	Volts
F	Faradays constant	Coulomb
Fe^{2+}	Iron (II)	-
Fe^{3+}	Iron (III)	-
H^+	Hydrogen ion	-
Hg	Mercury	-
H_G	Hydrogen in glass	-
H_2O	Water molecule	-

H_2SO_4	Sulphuric acid	-
I	Current	Amps
I_L	Limiting current	Amps
j	Current density	A/cm^2
J	Flux	mol/m^2s, kg/m^2s
J_{conv}	Flux due to convection	mol/m^2s, kg/m^2s
$J_{diff.}$	Flux due to diffusion	mol/m^2s, kg/m^2s
J_{migr}	Flux due to migration	mol/m^2s, g/m^2s
k	Rate constant	s^{-1}, ms^{-1}
k_L	Mass transfer coefficient	ms^{-1}
K	Kohlrausch constant	$ohm^{-1} m^{7/2} mol^{-3/2}$
K	Equilibrium constant	-
L	Distance	cm
m	Mass flow rate of water, mass deposited on cathode	kg/hr, g, kg
m_A	Rate of change of mass on anode or cathode	kg/hr^{-1}
M_a	Weight of anode	kg
M_A	Mass of anode or cathode at any instant	kg
M_{Ao}	Mass of anode or cathode at initial conditions	kg
M_c	Weight of cathode	kg
M_T	Theoretical mass according to Faraday's Law	kg
M^{2+}	Metal ion	-
n	Number of moles	-
O_2	Oxygen molecule	-
Ox	Oxidised	-
P	Price of water	$/kg
q	Charge passed	A s, Coulombs
r	Rate of change of volume, reaction rate	m^3/hr^{-1}, mol/s
R	Gas constant, resistance	kJ/kmol,K, Ohms
Red	Reduced	-
SO_4	Sulphate ion	-
t	Time	s

T	Temperature	^{o}C, K
v	Speed	ms^{-1}
V_A	Volume of anode or cathode at any instant	m^3
V_{Ao}	Volume of anode or cathode at initial conditions	m^3
V_c	Cell Voltage	V
V_n	Neutral Voltage	V
V_r	Volume of reactor	m^3
w	Mass deposited	g
x	Distance between electrodes	cm
X_A	Conversion	%
z	Number of electrons taking part in the reaction	
?	Time of cathode build up or anode degradation	hr
?	Current efficiency, electric field strength	%, Vm^{-1}
?	Molecular weight	kg
?	Ionic conductivity	ohm^{-1} m^2 mol^{-1}
μ	Chemical potential	Volts
η	Overvoltage	Volts
α	Degree of dissociation	-
Λ	Molar conductivity of electrolyte	ohm^{-1} m^2 mol^{-1}

CHAPTER 1

INTRODUCTION

1.0 Introduction

This chapter deals with the background to the study. It presents the objectives which played key roles in the implementation of the study and the realisation of the results. It also covers brief description of the methods used and the expected relationships between different variables that were used during the study.

1.1 Approach

A holistic approach to the recovery of copper from solutions was considered. The recovery of copper was investigated using electrorefining process that uses electrodes of the same material, one acting as cathode and the other as anode. The deposition, in this process, occurs at the cathode while the dissolution at the anode. The ions in solution were considered to play a key role in the recovery of copper as the conductivity of the electrolyte depends on the ionic strength. The movement of the ions from solution to the cathode and from the anode to the solution was assumed to be potential dependent. The migration and diffusion of ions were considered to occur in the Gibs Helmholtz layers at the electrodes. The conduction and convection of heat to and from the reactor was controlled by steady heat supply from the water bath. The strength of the current on the electrode was assumed to be dependent on the size of electrode-active area while the rate of deposition was assumed to be current-density and voltage dependent. It was also assumed that the impurities, temperature and smootheners would play a role in the deposition process. The recovery was therefore assumed to depend on the factors temperature, concentration of electrolyte, electrode-active area, level of smoothening agents, impurities, current density and applied potential. If the current efficiency depended on these factors, it means that the current efficiency (F; %) was assumed to be a function (f) of each of these factors and therefore a model relationship could be determined from equation (1.1) where C (g/L) is the concentration of electrolyte, smoothener and impurity while A is the electrode-active area, T (K, ^{o}C) is the temperature, j (mA/m^2) is the current density and V (volts) is applied potential. The relationship between the current efficiency and the factors can be modelled using exploration, data mining and classical methods in the Latin Square as in bivariate correlations.

$$\Phi = f\{C_{electro}; T; A; C_{Smooth}; j; V; C_{impur}\} \qquad (1.1)$$

1.2 Objectives

The main aim of the study is to evaluate the recovery of copper by electrochemical method using constructed cell arrangements, so that parameters that could lower production would be identified and optimised in order to increase the efficiency. The specific objectives were:

1. To evaluate the effect of overvoltage on the rate of deposition and the effect of current density on the current efficiency in order to determine optimum values,
2. To establish the effect of temperature on current efficiency in order to determine the optimum value at which the current efficiency is greatest,
3. To determine the effect of distance between electrodes on current efficiency in order to establish the optimum distance for the electrodes,
4. To examine the effect of electrolyte concentration on the current and production efficiencies in order to establish the level that provides adequate recovery with less impurities,
5. To determine the effect of metal and other impurities on the current efficiency in order to establish the level that would provide no competition to copper ions in electrolyte,
6. To determine the effect of electrode area on current efficiency in order to establish the optimum electrode area in relation to the current density and efficiency and

7. To determine the effect of smootheners on the current efficiency in order to establish the best smoothener.

1.3 Methodology

The parallel plate model in circular reactor was used in this study assuming that the back and sides of both anode and cathode did not take part in chemical reaction. It was also assumed that the geometry of the reactor did not have any effect on the chemical reaction. By maintaining the temperature at fixed value, thermodynamic effects due to heat loss could be assumed to be at steady state. Convection effects were assumed to be negligible since stirring was conducted prior to the chemical reaction in order to make the concentration of additive to be distributed evenly and not during the electrodeposition process. Although the migration and diffusion processes contribute greatly to the process, and have been discussed in literature, the evaluation of such mechanisms can be achieved by the deposition or mass transferred to the cathode as the efficiency is dependent on the effectiveness of migration and diffusion of the ions in solution in addition to the driving force. The electrochemical refining of copper was thus investigated at different temperatures, distances between electrodes, different levels of overvoltage, current density, metal impurities, smootheners, electrode-active area and concentration of electrolyte using the parallel-plate model in order to establish the effect on the current efficiency.

1.4 Thesis Outline

A total of six chapters have been presented in this document covering the literature review, the overview of electrochemical engineering, the problem and its setting, the methodology for the investigation and the results. The discussion, conclusion and recommendation make up the last chapter. The appendix section includes the information on the crude data obtained during the study, and the apparatus as viewed through the camera. Acronyms are defined within the document and are listed after the list of figures and tables.

CHAPTER 2

LITERATURE SURVEY

2.0 Introduction

Many countries in the world, including Zambia, largely depend on copper as the backbone of their economies. Copper is the most widely mined mineral in Zambia though a few other minerals such as gold, cobalt and silver are also exploited. Copper producing companies have acknowledged the importance of producing high quality copper in order to satisfy the market demands and requirements. Copper refining by electrochemical reaction (electrolysis) is one of the very important components in the production of high quality metals in the mining industry and other small-scale ventures that contribute to sustainable development. There are two methods of electrochemical refining. Electrorefining is one method that produces high quality copper from 98% to 99.98% copper while electro-winning is used for the recovery of copper from dilute solutions. The methods make use of electrolytic reactors that contain the cathodes and anodes which are connected to electrical power at appropriate level, acting as the driving force, to allow for the electrochemical reaction to proceed smoothly. Various models have been developed to describe the behaviour of the electrodes (Rousar *et al.*, 1986). Many authors have presented mathematical models for such reaction systems. Bisang (1997) developed the mathematical model of the parallel plate reactors, which take into account the diffusion layer adjacent to the working electrode and the convective layer in bulk solution. The results for copper electro-winning showed agreement with the transient equation for the diffusion layer in the convective region. The parallel plate model is widely used for copper recovery particularly in the copper mining companies. The objective of this chapter is to cover the introductory topics of electrochemical process, the main objectives, the benefits of the study, approach, thermodynamics of cells and the properties of electrolytes that enable the electrochemical process to proceed.

2.1 Electrochemical Process

The electrochemical process uses electrodes, power supply and electrolyte solution, which may be heated by an external source such as steam in a heat exchanger or directly by steam flow through jackets around cell baths. One pair of electrodes forms a cell, which acts as an electrochemical reactor. The electrochemical reactor uses the voltage as the driving force for the chemical reactions at the electrodes. If the electrodes that form the cell are made of different materials then the cell deposits metal ions from solution onto the cathode. The anode does not dissolve. This method can use solutions of fairly low concentration. Such a process, called electrowinning, is usually used to make the starting sheets which are then used in other processes. If the electrode pair is made of the same material then the cell formed creates an electrorefining process. The electrorefining process is where the anodes release the metal ions into solution and are later deposited onto the cathode producing efficiencies of above 92% (Gana *et al.*, 1993). The electrolyte releases oxygen atoms on the anode (Bellino *et al.,* 2001). The potential applied across the reactors results in polarization of electrodes to anode (positive) and cathode (negative). Polarization is caused by various factors: shape, composition of electrodes, type of electrolyte, temperature, flow rate, level of current and type of species in electrolyte. Concentration polarization is the formation of ions around the cathode or anode created by potential. The film of ions allows the dissolution or deposition of copper on anode or cathode if the potential changes. If concentration polarization sets in, the deposition of copper ceases until the voltage increases. The film then allows the deposition of metal again. Polarization results in the development of voltage drop across two electrodes, which obeys Ohms Law as described in Koryta and Dvorak (1987:90-92). The Law is given by equation (2.1).

$$j = b(d\Phi) \tag{2.1}$$

Where j is the current density (mA/m^2), F (%) is the current efficiency and b is the constant given by the ratio $zFka/RTl$. At low levels of current, the voltage-current relationship is linear while the resistance remains constant. At high values of current there is a marked departure from linearity (Skoog and West, 1976). Polarization results in the deposition of metal and evolution of gas at cathode and anode respectively as shown in anode and cathode reactions in equations (2.2) and (2.3) and the overall reaction in equation (2.4). If the anode is soluble, then the reaction is as given by equation (2.5).

$$2SO_4 + 2H_2O - 4e = 2H_2SO_4 + O_2 \tag{2.2}$$

$$Cu^{2+} + 2e = Cu \tag{2.3}$$

$$2CuSO_4 + 2H_2O = 2Cu + 2H_2SO_4 + O_2 \tag{2.4}$$

$$Cu - 2e = Cu^{2+} \tag{2.5}$$

The advantage of this method is that power is available and the measuring instruments can easily be found. The other advantage is that it produces high purity product, as stated earlier, and can be conducted at fairly low values of voltage. But a number of factors may affect the electrorefining process. The factors such as the separation of electrodes, temperature, concentration of electrolyte, concentration of impurities, electrode-active area, overvoltage, current density and type and quality of surface smoothener play a significant role in the recovery of copper. In a study by Ling *et al.* (1994), the operating conditions that were used during the operation of electrolytic reactors include conditions that are mentioned above. The efficiency may increase or decrease depending on the levels of such parameters used during electrolysis. It is therefore necessary to consider such factors when evaluating the recovery of copper, for commercial purposes, by the electrochemical method.

The stability and efficiency of electrochemical process depends on the type and properties of electrolyte. An electrolyte is a solution containing ions, which are able to move to and from the electrodes upon the application of potential across the electrodes. An electrolyte may also be a melt, which is the solid electrolyte. If the electrolyte is poor then a low efficiency of electrolysis will be achieved. However, if the electrolyte is good, the efficiency of electrolysis can be high. A good electrolyte is one that offers little resistance to the flow of current. The behaviour of electrolytes depends on the properties of dissociation, conductivity and how much resistance the ions offer to the flow of current in the system. The two groups of ions that play an important role in electrolysis are the anions (-ve) and cations (+ve). The cations are attracted to the negatively-charged cathode and the anions to the positively-charged anode. The system so formed, called a cell, is heterogeneous in nature comprising the solid electrodes and liquid electrolyte. A solid-solid system can form when a melt is used in the electrochemical process. A pair of electrodes forms a cell, a group of pairs of electrodes in one cell bath form a battery. The anodes are usually arranged in series and so are the cathodes but anodes and cathodes are connected in parallel.

A good electrolyte should have good electrical conductivity properties. It must offer low resistance to the flow of electrons so that the application of voltage across it will allow the system to obey Ohm's Law as described in Koryta and Dvorak (1987:2). The product of resistance (R) and the current (I) gives the applied voltage according to Ohm's Law. The reciprocal of resistance of the electrolyte (conductance) and resistance are both concentration dependent. The resistance depends on the crossectional area and the length or distance through which the ions have to cover. The longer the distance the greater is the resistance. The resistivity (resistance per unit area and unit length) and the conductivity (reciprocal of resistivity) are also concentration dependent. An electrolyte can be said to be strong if its ions dissociate completely in solution and weak if its ions dissociate partially when in solution. According to Koryta and Dvorak (1987:2), "A weak electrolyte is present in solution as both ions and molecules". A strong electrolyte is present in solution as the corresponding ions. Temperature can contribute to the formation of ions in solution. For example, the temperature would affect the dissociation of ions in solution presenting a low effect at low levels and a high effect at higher values of temperatures. The conductivity of electrolyte, which is dependent on ions, would thus be affected and would make the solution to attain higher or lower conductivity of electrolyte (Koryta and Dvorak, 1987:2; AEM, 2004). The strength of an electrolyte described by both Ostwald's and Kohlrausch's applications (Koryta and Dvorak, 1987:2; Crow, 1994:26) represented by equations (2.6) and (2.7) where K is the equilibrium constant and K^1 is Kohlrausch's constant ($ohm^{-1}m^{7/2}mol^{-3/2}$), a is the degree of dissociation and c is the number of moles would thus depend on the anions (A^-) and cations (B^+) of the electrolyte compound AB.

$$K = [A^-][B^+]/[AB] = a^2 c/(1-a) \tag{2.6}$$

$$K^{'} = \Lambda^2 c / \Lambda^o[\Lambda^o - \Lambda] = a^2 c/(1-a) \tag{2.7}$$

When a solution is formed from a salt of the desired electrolyte (copper sulphate in this case), the heat of solution, though fairly small, is released which may be either exothermic or endothermic. From the thermodynamics point of view, the heat of solution is the result of the sum of the lattice and solvation energies (Crow, 1994:10-11). The ionic activity results in the generation of chemical potential in solution. Such potential is temperature dependent as is shown in equations (2.8) for the anode and (2.9) for the cathode. Where e (volts) is the chemical potential at any instant and e^o (volts) is the potential at equilibrium, T is the temperature (K), R (kJ/kmolK) is a constant and a^- is the activity of the solution representing the concentration. The potential so defined is in essence the free energy of the system when one mole of the uncharged particles (species) is added.

$$e = e^o + RTIn[a^-] \tag{2.8}$$

$$e = e^o + RTIn[a^+] \tag{2.9}$$

The effect of the charge on ions is to introduce the electrical potential in the system which is an additional change in free energy of the system given by the product of the charge of the specie ions (z), the Faraday constant (F) and the potential (E) as zFE giving the potential of the electrochemical system (ε) for copper sulphate solution to be as indicated in equations (2.10) and (2.11) where ? G (kJ/kmolK) is the free energy of the system.

$$e = e^{o} + RTIn[Cu^{2+}] + zFE \qquad (2.10)$$

$$e = \Delta G + zFE \qquad (2.11)$$

This potential, due to the transport of ions, creates the electrical migration due to the influence of an electric field. The total current carried by each ion is only a fraction of the current carried by the total ionic species in solution. The fraction of current carried by each ion is called the transport number (N_j^+) for the cation and (N_j^-) for the anion. The current carried by each ion per unit area (j) is given by equations (2.12) for the cations and (2.13) for the anions while the total transport number for both ions is given by equation (2.14). The sum of currents per unit area should not be greater than unity.

$$N_j^+ = c_+ v_+ z_+ F / F(c_+ z_+ v_+ + c\_z\_v\_) = j_+ /(j_+ + j\_) \qquad (2.12)$$

$$N_j^- = c\_v\_z\_F / F(c_+ z_+ v_+ + c\_z\_v\_) = j\_ /(j_+ + j\_) \qquad (2.13)$$

$$N_j = N_j^+ + N_j^- \qquad (2.14)$$

The ions in solution are driven by the electric field, which is induced by potential at the electrode. The speed of the ions is retarded, according to Crow (1994:53), by the retarding forces of asymmetry and electrophoretic effects and viscosity. The speed (v) of the ions is dependent on their mobility (u) and the field strength (F_s) as shown in equations (2.15) and (2.16) for cations and anions respectively.

$$v_+ = u_+ F_s \qquad (2.15)$$

$$v\_ = u\_F_s \qquad (2.16)$$

When the ions reach the electrode, they form layers. The positively charged ions form a layer near the cathode while the negatively charged ions form a layer near the anode. Since the anode is positive and the cathode negative, double layers form at each electrode consisting of positive and negative ions. The double layer, called Helmholtz Layer as described in Crow (1994:69) for the ions in electrolyte, can be observed in Figure 2.1.

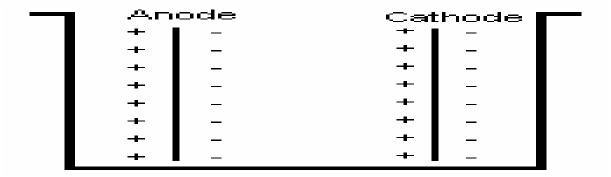


Figure 2.1 Description of the Helmholtz double Layer

The amount of mass deposited on the cathode gives the yield, which is dependent on the charge passed over the time by the applied voltage. This leads to the concept of current efficiency of the system. The current efficiency may depend on a number of factors such as the temperature of electrolyte, current density, overvoltage on the electrodes, impurities in electrolyte (may be particulate in nature) and electrodes which may affect the deposition process, the type of smoothener and its concentration which may affect the quality of electrode surface especially in industrial applications, the distance between the electrodes, and the concentration of electrolyte which may affect the deposition process. It was therefore important to investigate how and to what extent such factors affect the current efficiency in order to determine the optimum values that could be used for the smooth operation of electrorefining reactors.

2.2 Thermodynamics of Cells

Thermodynamics is the science that deals with the movements of heat energy from regions of high energy to regions of low energy. In machines, the energy is generated when the work is being done. The amount of energy generated is directly proportional to the work done. This leads to the First Law of Thermodynamics, which is the principle of conservation of energy that states that energy can neither be created nor destroyed but is converted from one form into the other. This is synonymous with the law of conservation of mass, which states that matter is neither created nor destroyed but is converted from one form into the other. For example, potential energy can be converted into kinetic energy and work energy can be converted into heat energy. The principle, according to Eastop and McConkey (1990:19-21), states that when a system undergoes a thermodynamic cycle the net energy supplied to the system from its surrounding is equal to the net work done by the system on its surrounding. Equation (2.17) is the mathematical expression of the First Law of Thermodynamics, which is the result of Joule's Experiments (Russell and Adebiyi, 1993: Chapter 6). In other words energy cannot be produced from nothing if work is not done. We see that the assertion by Eastop and McConkey (1990) agrees with the argument advanced by Russell and Adebiyi (1993).

$$\oint dQ = \oint dW \tag{2.17}$$

The systems obeying the First Law of Thermodynamics are perfect systems or ideal systems where all the energy that is generated from doing work is converted into heat energy. In practice, there are no such machines because friction takes up some of the energy resulting in the reduction of efficiency to less than 100 percent. Because of this, the First Law of Thermodynamics is modified to include the change in internal energy (dU) as indicated in equation (2.18).

$$\oint dU = \oint dQ - \oint dW \tag{2.18}$$

The Second Law of Thermodynamics, according to Eastop and McConkey (1990:100-101), states that it is impossible for a system to produce net work in a complete cycle if it exchanges heat only with bodies at single fixed temperatures. This means that work must be done at some point in the system, which will result in the change in temperature that results in the change in heat energy in the system. The change in heat energy results in the formation of high and low energy regions. Heat energy can then, according to the Second Law of Thermodynamics, flow to lower regions. It is indeed impossible for an electrochemical cell to exchange heat energy only with the surrounding if no work is done and there is no change in temperature of the electrolyte. Infact, Planck's and Clausius assertions, according to Russell and Adebiyi (1993: Chapter 7), agree with this argument. There must be an external load in order for the cell to do work, i.e., convert chemical energy into electrical energy, which is convertible into work energy. For example, a battery driving the starter motor converts chemical energy into electrical energy, an electrical motor driving a ball mill using electrical power converts electrical energy into work and kinetic energies, and a diesel engine converting fuel energy (chemical energy) into mechanical energy or work energy which is used to drive a motor that converts mechanical energy to electrical energy for home and industrial uses. The kinetic energy of water in a river is used to drive the turbine, which converts the kinetic energy into work energy and electrical energy. The heat transfer from cells can be achieved by conduction through the walls of the reactor, convection in electrolyte and radiation from the walls of the reactor and surface of the electrolyte (McCabe and Smith, 1976: Chapters 10, 11, and 12). The principle governing such heat transfer is Fourier's Law for heat transfer by conduction and the modified forms for radiation and convection.

The industrial applications of electrochemical cells involving copper electrorefining use Plug Flow Reactors (PFR) at steady states and open to the atmosphere at the top and batch reactors. The contributions of heat energy come from the heat of reaction, the free energy of the reaction, the loss of heat due to conduction, convection and radiation and the energy of the electrolyte before entering the reactor. For most practical applications, the contributions of most of these terms that are linked to loss of energy are not important because the cell generates heat energy, which results in rise of temperature. It is the temperature rise that may affect the recovery of copper. However, the heat of reaction and the free energy are important for purposes of assessing the magnitude of heat energy that would affect the temperature of the system.

The relation between the heat of reaction (ΔH), temperature (T) and the free energy (ΔG) has been developed by many authors who all agree that the relation is given by the Gibbs-Helmholtz equation as shown in equation (2.19) for the heat of reaction and equation (2.20) for the entropy of the system (Antropov, 1972:26-28; Bruce, 1995:216-217). Entropy is the change in heat energy of the system per unit temperature.

$$\Delta H = \Delta G - T(\partial \Delta G / \partial T) \tag{2.19}$$

$$\Delta S = (\Delta H - \Delta G)/T = zF(\partial E / \partial T) \tag{2.20}$$

Equation (2.21) shows the transformed form of free energy of chemical equilibria as stated by Barrow (1979:237-239). Where E_c and E_a are the potentials (volts) at the cathode and anode respectively. Barrow (1979:246-247) also asserts that the chemical equilibrium is related to the thermal-chemical property. The free energy of the cell reaction is the driving force for the reaction. The over-potential helps to liberate the ions in solution by providing an external electromotive force, which drives the ions from the metal into solution. The magnitude of such over-potential can be determined using equation (2.22) (Pletcher and Walsh, 1993:4-5,489; Heitz and Kreysa, 1986:94-95).

$$\Delta G^o = -RTInK_p \tag{2.21}$$

$$\Delta G = -zFE = -zF(E_c - E_a) = 0 \tag{2.22}$$

The values of ΔG, ΔH and ΔS can be obtained if the temperature is measured. The value of ΔG is obtained from the direct measurement of cell potential as indicated in equation (2.22). The values of free energy can be positive or negative. The sign of free energy gives the idea of what sign the electromotive force (emf) of the cell is going to be. For example, according to Perry and Chilton (1973:470-472), the emf is positive for a cell for which the value of the free energy is negative. This means that the cell reaction can proceed spontaneously. On the other hand the cell emf is negative for a cell for which the free energy is positive. The cell potential is normally greater than zero. It, therefore, means that the difference between the cathode and anode potentials is also greater than zero. The cathode should have more positive equilibrium potential than that of the anode in order for corrosion to occur. Thermodynamically, metals corrode by anode dissolution. The standard emf values of cell reactions for various solutions and electrode potentials are described in Barrow (1979:624).

2.3 Study Model

Several models, as stated earlier, have been developed to describe the behaviour of electrodes (Rousar *et al.,* 1986). A mathematical model for parallel plates was studied in Bisang (1997). The parallel plate model used in this study was chosen for a number of reasons (Figure 2.2). Circular and rectangular reactors can accommodate such a model. The electrodes can easily be made from starting sheets. The cell baths are easy to make on a lab scale and it is easy to replace the electrodes and solution.

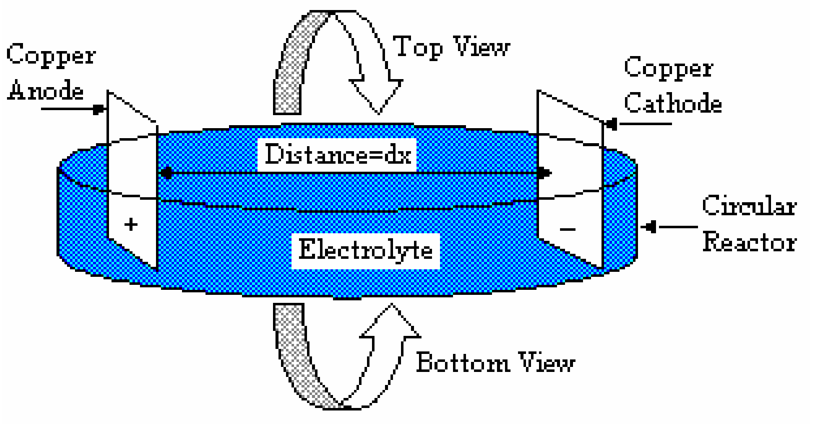


Figure 2.2: Reactor with electrodes immersed in Cu-sulphate solution

It is easy to control the distance between electrodes and to take measurements of overvoltage, current and electrode area. It provides for easy cleaning and assemblage of the cell components. The surface inspection for nodules is much easier for the parallel plate model than other models. The model is therefore suitable for the study of nodules and the effect of smootheners (inhibitors) on the recovery of metals. It has thus found many applications in industry. It is widely used in mining industries for the recovery of numerous metals by electrolysis. The recovery of copper, silver, cobalt, nickel and other metals uses this model to remove them from solutions although the anodes may be made of different materials in some operations. These are the existing benefits that the model has provided to human kind but the problems that have arisen as a result of the usage of this model has necessitated numerous researches of which this study is one. It is also easy to model the migration, diffusion, convection and overall mass transfer of ions from electrolyte to the electrodes and vice versa. Detailed discussions of the application of the model to the stated modes of mass transfer are described in Koryta and Dvorak (1987:90-92) and Bruce (1995). The kinetics of the other models are covered in Vetter (1967:117-119). In addition, the kinetics of the reactor deals with the reactions at the electrodes (Wan *et al.*, 1979). At equilibrium, the rate at the cathode is equal to that at the anode. If the cathode reaction is the one that is required then increasing the external potential (?) will drive the reaction (Barrow, 1979:645-652). The net current (I) of the system is defined by the current at the cathode (I_c) and that at the anode (I_a) as given by $I = I_c - I_a$ while the net overvoltage is given by $h = E_c - E_a$. It is the net current and net overvoltage that is used in the evaluation of the effect of current and overvoltage on the rates of deposition and current efficiency. The exponential increase of current with overvoltage is given by $I = Ae^{-(FE/RT)}$ at both the cathode and anode where A is the exponential factor. If the fraction of energy FE given by aFE drives the chemical reaction at the cathode then that driving the reaction at the anode is $FE(1-a)$ giving the currents in the system to be $I_c = k_c e^{-(FE-aFh)}$ at cathode and $I_a = k_a e^{-(FE+Fh(1-a)}$ at the anode where k_a and k_c are the rate constants (s^{-1}) at the anode and cathode respectively. These currents can further be reduced to $I_c = I_o e^{+aFh/RT}$ and $I_c = I_o e^{-Fh(1-a)/RT}$. The net current in the system can be used to evaluate the Butler-Volmer equation and hence the Tafel model $h = a + bInI$. When copper ions are reduced to produce an attached $M - Cu$ species, the current of the electrodes become $I_c = k_c[M - Cu]$ and $I_a = k_a[M - Cu^{2+}]$. Since the liberation of one atom of copper is associated with the liberation of two hydrogen atoms according to

Tafel's mechanism, the reaction is second order and therefore the current is given by $I = k[M - Cu]^2$.

In this model, the copper ions move to the cathode by either migration or diffusion or both. Convective movement occurs when there is provision for stirring or use of circulation using an external force or pump. Stirring also allows the concentration to be maintained at a constant value. The oxygen gas is evolved at the anode. The deposition of copper is via reductive mechanism where the ions receive electrons and are thus reduced in state while the evolution of gas is an oxidative process where the acid provides the electrons to the copper ions in order to reduce them.

The operation of the reactor assumes a one-dimensional mass transport model with two films, one on each side of the electrode which obey Ficks Laws (Coulson and Richardson, 1996), and a constant-operation temperature. The main reaction for modelling the reactor is the reduction of copper ions at the cathode. The copper ions diffuse, migrate and convect from bulk solution to the cathode where they are reduced. When this happens, a vacuum of ions is created in the films (L1 and L2) and hence in the bulk solution, which is filled by the ions released from the anode (Figure 2.3). This phenomenon allows the concentration of ions in bulk solution to remain unchanged and to provide adequate ions, dependent on the charge passed, to the surface of the cathode where the deposition takes place.

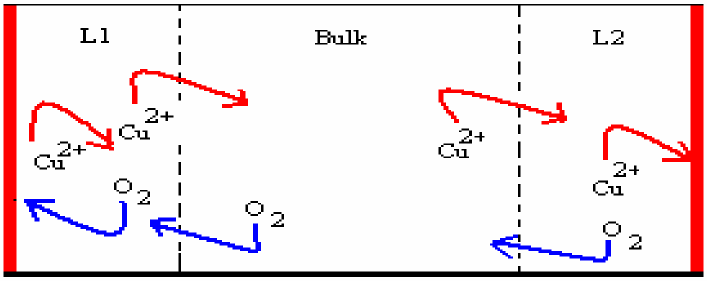


Figure 2.3: Movement of copper and oxygen species towards electrodes

The movement of ions in the vertical area towards the cathodes defines the flux (F_x) according to Ficks Law of diffusion and migration as indicated in equation (2.23) where D (mol/m^{2}s) is the diffusion coefficient, dc is the change in concentration and dx is the change in distance between the electrodes.

$$F_x = D(dc / dx) \tag{2.23}$$

This equation can be modified for material flux to give equation (2.24) where dN is the change in the number of mols, dt is the change in time (s)

$$F_x = dN / dt = D(dc / dx) \tag{2.24}$$

The mass deposited by the applied voltage at a particular current can be determined by equation (2.25) where m (g) is the mass deposited, M is molecular mass of the copper. If the deposition of copper on the cathode obeys Faraday’s Law then the current efficiency (F) is defined by equation (2.25).

$$dm / dt = \Phi MI / zFA = \Phi Mj / zF \tag{2.25}$$

A plot of (dm/dt) against the current density (j) yields a slope from which the current efficiency can be calculated. The current efficiency can also be determined from equation (2.26a) for a specified period of time, e.g., 15minutes as a modified version of equation (2.25). The temperature of the reactor increases diffusion, current density and the rates of chemical reactions. The mass transfer rates are enhanced when the viscosity of electrolyte is reduced (Pletcher and Walsh, 1993:95). In the case of the batch reactor, the rate of change of concentration is given by equation (2.26b).

$$\int dm = (\Phi MI / zF)\int dt \tag{2.26a}$$

$$dc / dt = -kC = k[Cu^{2+}] \tag{2.26b}$$

The effect of the volume (V_r) of the reactor electrolyte subjected to overvoltage on the concentration, for constant current, can be assessed by equation (2.27a). The substitution of I results in the introduction of current efficiency as indicated in equation (2.27b).

$$dc/dt = Iz^{-1}F^{-1}V_r^{-1} \tag{2.27a}$$

$$\int dc = (m/\Phi MV_r)\int t^{-1}dt \tag{2.27b}$$

The slope of equation (2.27b) gives the current efficiency at the specified time (t) interval for a change in concentration (dc) and the mass (m) deposited. When the current (I) is equal to the limiting current (I_L), which is equal to $k_L AzFC$, the rate of change in concentration with time is given by equation (2.28).

$$-dc/dt = k_L ACV_r^{-1} = k_L AV_r^{-1}[Cu^{2+}] \tag{2.28}$$

The distance between electrodes increases the polarity when the distance is small and lowers it when it is large. Whilst the Ficks Law applies to the films that develop near the electrodes, the distance between electrodes removes the bulk distance and the entire system is turned into a thin film between the two electrodes, which then allows the application of Ficks Laws of diffusion, and migration as shown in equation (2.29). It can be noted in equation (2.29) that the current is inversely proportional to the distance between the electrodes and the current efficiency can be obtained from equation (2.30).

$$-dN/dt = D(dc/dt) = I\Phi/zFA \tag{2.29}$$

$$D(C_0 - C)/x = \Phi I/zFA \tag{2.30}$$

In the case where there are dissolved impurities in the electrolyte; it is safe to operate the reactor if the potentials of such impurities (metallic) are higher than the element being recovered because competition would not be there. However, when the dissolved impurities have the potentials close to the element being recovered the chances of recovering impurities together with desired element are high. The efficiency of such a reaction can be modelled by considering the fraction attained by the limiting current in the system as given by equation (2.31). The value of I_F is usually less than unity. The conversion for the reaction is dependent on the initial concentration and the current as given in equation (2.32).

$$I_F = I\Phi / I_L \tag{2.31}$$

$$X_A = \Phi I / zFC_0 = (C_0 - C) / C_0 \tag{2.32}$$

When the reactor is operated under mass transport control it means that the current, which was at a value greater than the limiting current, drops to below the limiting value. The current efficiency falls with time while the decay of concentration is exponential with time. The current efficiency is now provided by equation (2.33).

$$\Phi = zFC_{(t)}k_L A / I_L \tag{2.33}$$

The current and current efficiency as a function of electrode-active area can be defined by equations (2.34a) and (2.34b). The slope of the plot of the change in current (dI) versus the change in active area (dA) gives the current efficiency. Confirmation of the result can be made using equation (2.34a).

$$dI = a^1 b^1 dA \tag{2.34a}$$

$$d\Phi = a^{11} b^1 dA \tag{2.34b}$$

Where the values of a^1, a^{11} and b^1 are given by $zF / Mt\Phi$, zF / MIt and $k_L C / V_r$ respectively. A plot of current versus the active area gives the correlation that represents the effect of active area on the current and current efficiency.

2.4 Benefits of the Study

The benefits of the study can be derived from different perspectives according to needs of the user or community or organization. One can foresee many organisations using the results to establish small-scale plants in order to forgo the trouble of having to buy copper from expensive sources or importing the commodity all the time. The mining sector and other users in the world would find the information from the study useful in the efforts to meet the challenge of technology advancement and mining sector copper improvement strategies. The academic fraternity and particularly students will find the information useful as one of their reference sources in the process of carrying out their project reviews. Other business entities particularly those that are into copper recovery may want to use the study as an opportunity to decide to venture into the copper recovery on a small, medium and large scale production depending on their capacities to invest.

The major benefit that the study provided was the introduction of new combinations of smootheners, which would enable the reactors to attainment high efficiency during the recovery of copper from solutions. Employment generation and sustainable development goes hand in hand with such innovations. If the study results are adopted they would provide job opportunities to many as a result of the expansions and creation of new organisations or provide an opportunity to sustain lives as the demand for copper in the informal sector for repairing equipment both in electrical and automotive small-scale industries is increasing. The study would therefore provide an easy method to purify copper from ore or scrap metals.

Wastewater treatment has experienced a number of problems. The removal of heavy metals and the metals higher up in the chemical series is becoming increasingly difficult as the pollution events are increasing due to faulty equipment and poor management systems. Electrolysis is one of the methods that can easily be applied in this area on a large scale to treat wastewaters before they are released into the environments. It is also a good method to remove precious metals; Gold and Silver. Metal recovery by electrochemical method provides a solution to the treatment of many industrial wastewaters (Pletcher and Walsh, 1993: Chapter 7). According to Pletcher and Walsh (1993:Chapter 7), the feeds to electrochemical cells may come from areas such as leaching of ores, leaching or run-off water, cells of electrowinning and electrorefining, rinse waters, and metal cleaning solutions. Heitz and Kreysa (1986:128, 206-208) agree with this concept. They argue that the packed and fluidised bed electrodes are suitable for the extraction of metals from low-grade ores and effluents. Although the method is a single metal recovery concept, a multi-metal recovery system could be designed if the levels of metals are high. Although the packed and fluidised bed electrodes are different in design when compared to the parallel plate type, the principle of metal removal from wastewaters is similar in that they both remove the undesired metals in wastewaters.

Electroplating using electrochemical process is used in many countries in the world and therefore is an already existing benefit to human kind. The objective of an electroplating process is to prepare a deposit, which adheres well to the substrate (Pletcher and Walsh, 1993: Chapter 8). The process of electroplating is exactly the same as that of electrowinning and electrorefining where two electrodes, one the anode and the other the cathode, are used to form part of the electroplating cell. The plating is done on the substrate, which is the cathode. The main areas of applications include corrosion protection, decorative appeal, wear resistance, hardness, electrical conductivity, solderability and thermal conductivity. In the electronics industry, the electroplating of circuit boards, electrical contacts etc., provides a solution to the conductivity of the metals. However there are many new emerging areas of applications that could benefit from this methodology.

This study has attempted to use different combinations of smootheners in order to find the use and effectiveness of other types of smootheners that can be used in the recovery of copper. Many authors have reported the use of bone glue, inorganic salt and organic compounds as combination of smootheners (Yamamoto *et al.*, 2002; Fthenakis, 2003; Veilleaux *et al.*, 2003; Yousef *et al.*, 2004; Voros, 2006). The use of the combination of smootheners depends on the cost of such materials. A combination of Bone Glue, Thiourea and Sodium Chloride would cost differently from that of EDTA, Bone Glue and Sodium Chloride. The most popular combinations have been the organic Thiourea, Bone Glue and Sodium Chloride.

This research attempted to study the effects of other combinations such as Thiourea, K-Glue, and Sodium Chloride; Thiourea, B-Glue and Sodium Chloride; EDTA, B-Glue and Sodium Chloride and so on. The use of such combinations was meant to find a way of reducing the nodulation problem. Gum Arabic has been used in studies elsewhere (Gurmen *et al.*, 2004; Srinivasan and Bommaraju, 2006:93-186). In this study it was used as one of the smootheners in conjunction with the current inhibiting types (Thiourea and EDTA). It was also used in conjunction with the salt in order to determine its effect on the current density and current efficiency. Since most glue are manufactured from cellulose of trees Gum Arabic is a product from trees grown in North of Africa.

2.5 Summary

Copper refining by electrochemical reaction is one of the very important components in the production of high quality metals in the mining industry and other small-scale ventures. Electrical power is the driving force for the ions. The recovery of copper is by reductive and oxidative mechanism which is second order. The conductivity of ions is electrolyte and temperature dependent. The thermodynamics of the system allows heat loss from the reactor by conduction, convection and radiation. The stability and efficiency of electrochemical process depends on the type and properties of electrolyte and the type and concentration of additives which provide economic benefits.

CHAPTER 3

REVIEW OF ELECTROCHEMICAL ENGINEERING

3.0 Introduction

The reaction of atoms using the exchange of electrons is the mystery that resulted in the birth of electrochemistry and electrochemical engineering. Just as chemistry is the basis for chemical reaction engineering, electrochemistry is synonymous with electrochemical reaction engineering. The movement of the atom from solution or from one metal to the other, of the same material, without the application of an external voltage is not possible because a cell that is in equilibrium remains in equilibrium forever. The application of external voltage is the key factor in the deposition of the metal from the anode to the cathode or from solution to the cathode as the case may be. The mass transfer through migration, convection and diffusion in electrochemical reactors is the result of the applied overvoltage. This chapter dwells more on these issues including the problems of nodulation and the use of smootheners to reduce the occurrence of nodules during electrochemical operations.

3.1 Electrochemistry

Electrochemistry deals with the study of mutual conversion of chemical and electrical forms of energy (Antropov, 1972:22). It deals with reactions that proceed at the expense of electrical energy. The basic features of electrochemistry are the ionic interactions i.e. the way the ions affect each other when in solution because of the nature of electrolytes. The ion-ion and ion-solvent interactions, which can result in the evolvement of dissociation, solvation, and solution is one of the key features. The interaction, called ionic activity, is dependent on the chemical and electrochemical potential. The ionic activity can be evaluated using the Debye-Huckel theoretical model (Crow, 1994:16). What is also significant in ion interactions is the ability of electrolytes to ionise, dissociate and associate when in solution. The association can be determined from the Bjerrum Equation (Crow, 1994:19). The conductivity of ions is key characteristic in the classification of electrolytes. The weak, incompletely dissociated electrolytes exhibit low dissociation values and hence give low conductivity values. The strong, completely dissociated electrolytes exhibit high dissociation values and hence give high conductivity values. The movement of ions due to the applied potential by migration and diffusion, both of which are mass transfer processes, result in the generation of flux of ions flowing towards the electrodes. An interface is created near each electrode, which allows the diffusion and migration of ions to the electrodes. The interface is shown in Figure 3.1.

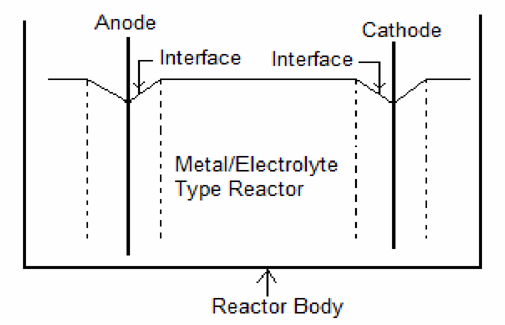


Figure 3.1: Electrochemical reactor with metal-electrolyte interfaces

There are various types of interfaces whose magnitude is a function of composition and the nature of the phase. For example, metal/metal, metal/electrolyte, electrolyte/electrolyte, and solution/membrane/solution are some of the interfaces that form part of half-cells. The reactions that take place in cells, i.e., a pair of electrodes, are driven by electric potential. If the electric potential is removed across the anode-cathode pair of the reactor then the anode-cathode pair reverts to equilibrium. If the external load is attached to the anode-cathode pair dipped in electrolyte then the chemical potential is converted into electrical potential, which is used to drive the external load. If the external load is removed and the external electric potential is reapplied then the chemical reaction is driven to increase the chemical potential, a process called charging, to make available more energy for use by the external load. The potential developed by the anode-cathode pair is electrolyte and electrode material dependent. Different pairs of electrodes give different potentials in different electrolytes. Barrow (1979:625-626) has listed values of potentials developed by different pairs of electrodes in different electrode-electrolyte systems.

When the cell reactor is in equilibrium its potential across the electrodes can be determined from the Nernst Equation as shown in equation (3.1) where K is the equilibrium constant. If the equilibrium constant is large then the value of the cell potential would be low. If it is small then the cell potential would be large. Since the equilibrium constant is dependent on the concentration of reactants and products, the reaction $aA + bB = cC + dD$ would yield a large constant only when the reaction favours products. For example, equation (3.2) shows how the concentrations can be used in place of the equilibrium constant in the evaluation of cell potential in the Nernst equation as described in Antropov (1972), Skoog and West (1976) and Crow (1994). When the values of [C] and [D] are large compared to values of [A] and [B] then the value of InK would be large and therefore the cell potential would be low. This is why the use of external potential is necessary to help maintain the driving force and the continuous supply of cations into solution.

$$E = E^o - (RT / zF) InK \tag{3.1}$$

$$E = E^o - (RT / zF) In([C]^c [D]^d / [A]^a [B]^b) \tag{3.2}$$

The electrode potentials in terms of the activities of ions in electrolyte can be determined from equation (3.3) for the anode and (3.4) for the cathode, which is a replacement of the concentration terms in equation (3.2). A plot of the natural logarithm of the activities versus the anode potentials at different isothermal temperatures can lead to the description of the behaviour of electrode potential with temperature. It can also provide information on the effect of temperature variations on the current efficiency.

$$E_a = E_a{}^o + (RT / zF) \ln a^+ \tag{3.3}$$

$$E_c = E_c^{\,o} + (RT/zF)\ln a^- \tag{3.4}$$

The fact is that positive electricity flows from right to left which means that electrons flow from the metal to the ion species in solution giving negative electrode potential (cathode). The opposite takes place at the anode. The other types of electrodes can be seen in Table 3.1.

Table 3.1: Types of electrodes and their reactions

No	Eelectrode Type	Chemical reaction	Electrode potential
1	Type 1: 1st kind	$M^{2+} + 2e = M$	$E = E^o + (RT/2F)Ina_{M^{2+}}$
	Ag^+/Ag	$Ag^+ + e = Ag$	$E = E^o + (RT/F)Ina_{Ag^+}$
	Cu^{2+}/Cu	$Cu^{2+} + 2e = Cu$	$E = E^o + (RT/2F)Ina_{Cu^{2+}}$
2	Type 2: 2nd kind	$MA + 2e = M + A^{2+}$	$E = E^o - (RT/2F)Ina_{A^{2-}}$
	$Cl^-/Hg_2Cl_2, Hg$	$Hg_2Cl_2 + 2e = Hg + 2Cl^-$	$E = E^o - (RT/2F)Ina_{Cl^-}$
	$Cl^-/AgCl, Ag$	$AgCl + e = Ag + Cl^-$	$E = E^o - (RT/F)Ina_{Cl^-}$
	$OH^-/HgO, Hg$	$HgO + H_2O + 2e = OH^- + Hg$	$E = E^o - (RT/2F)Ina_{OH^-}$
3	Type 3: Gas		
	$H^+/H_2, Pt$	$2H^+ + 2e = H_2$	$E = E^o - (RT/2F)InP_{H_2}$
4	Type 4: Amalgum		
	$M^{2+}/M_m, Hg$	$mM^{2+} + 2me = Mm(Hg)$	$E = E^o + (1.2RT/mF)Ina^m_{M^{2+}}$
	$Cd^{2+}/Cd, Hg$	$Cd^{2+} + 2e = Cd(Hg)$	$E = E^o + (2.3RT/F)Ina_{Cd^{2+}}$
5	Type 5: Redox		
	$\mathrm{Re}\,d, Ox/Pt$	$Ox + 2e = \mathrm{Re}\,d$	$E = E^o + 1.2RTIn(a_{Ox}/a_{\mathrm{Re}\,d})$
6	Type 6: Glass		
	H^+/H_G	$H^+ + M^+_G = H^+_G + M^+$	$E = E^o + (2.3RT/F)In(a_{H^+}/a^+_G)$

There are various types of electrodes, depending on the material used, which have a characteristic chemical reaction. The types include whether it is of the First kind, Second kind, Glass type, Gas type, and mercury composite called Amalgam, Redox and Glass electrodes. Each electrode behaves according to the chemical composition making such an electrode.

The system that has been chosen for the study is a $Cu/Cu^{2+}/Cu$, which falls under Type 1, the electrode of the first kind. The electrodes are easy to make and the electrolyte is readily available. There is a general similarity in the entire electrode systems described in Table: 3.1. The general similarity is that there is a metal to act as electrode and electrolyte to provide the much-needed ions that are used during the exchange of electrons in order to produce the desired effect. The Nernst equation given by equation (3.1) can be applied to any of the systems. Therefore electrochemistry is the basis for electrochemical engineering. It provides the fundamental principles on which chemical engineering unit operations of mass transfer that includes migration, diffusion and convection, are constituted. A list of the examples of such electrodes can be seen in Table: 3.1 below.

3.2 Kinetics of Cells

The reaction rates at the anode and cathode are potential and temperature dependent. The rate of oxidation and reduction are given by equations (3.5) for the anode and equation (3.6) for the cathode. The rate is dependent on the concentration of Cu^{2+} ions (C^{+}) in the case of the cathode and oxidizing species C^{-} as in the case of the anode. The geometry of the reactor is assumed to have no effect on the reaction which is assumed to be unidirectional.

$$r_a = k_a C^{-} \tag{3.5}$$

$$r_c = k_c C^{+} \tag{3.6}$$

The rate constants are given in terms of Arrhenius equation as indicated in equation (3.7) for the anode and (3.8) for the cathode where A is the pre-exponential factor and ΔH is the activation energy while T is the reaction temperature and R is the constant. These expressions have been discussed in works of many authors (Glasstone and Lewis, 1960:627-628; Levenspiel, 1962: Chapter 2; Walas, 1989:13-14 and Crow, 1994:133). It is much easier to evaluate the reaction rate of the chemical reaction once the rate constants are known or obtained from these expressions. One notable feature in these expressions for the evaluation of rate constants is that there is a temperature dimension, which explains why the rate of chemical reaction is dependent on temperature. If the temperature increases, the rate constant increases and hence the rate of chemical reaction will increase. The opposite would also be true. This means that the rate of deposition of copper onto the cathode would increase with the increase in temperature.

$$k_a = A_a \exp(-(\Delta H_a / RT) \qquad (3.7)$$

$$k_c = A_c \exp(-\Delta H_c / RT) \qquad (3.8)$$

In terms of free energy, since ΔH is equal to ΔG at isothermal conditions, the rates of chemical reactions at the cathode and the anode yield equations (3.9) and (3.10). The values of k_{ao} and k_{co} include the value of the A_c and A_a. Since the gas is evolved at the anode the value of A_aC^- reduces to A_a as $[H_2]^0$ is unity and hence k_{ao}. However, at the cathode, the value of A_c is equal to k_{co} as the concentration term $[Cu^{2+}]$ is so significant to be incorporated into the constant because the chemical reaction in electrochemical reactors depends on the concentration of copper ions, which is dependent on the temperature.

$$r_c = k_{co}[Cu^{2+}]e^{-\Delta G_c / RT} \qquad (3.9)$$

$$r_a = k_{ao}e^{-\Delta G_a / RT} \qquad (3.10)$$

At the equilibrium, the rates are equal, i.e., $r_a = r_c$. Therefore, equating equation (3.9) to equation (3.10) gives equation (3.11), which makes the rates of the reaction at the anode and cathode to be equal. This is an important aspect of the electrochemical reactions since the depletion of copper ions in electrolyte can result in the reduction in ion concentration which could result in the increase of the operating current and hence overvoltage. Such increases could bring about the rise in temperature due to increased generation of heat energy, which is associated with the reduction in current efficiency. A steady rate of dissolution of copper at the anode accompanied by steady deposition of copper at the cathode would maintain a steady concentration of electrolyte.

$$k_{co}[Cu^{2+}]\exp(-\Delta G_c / RT) = k_{ao}\exp(\Delta G_a / RT) \tag{3.11}$$

If equation (3.11) is rearranged then equation (3.12) is obtained which leads to equation (3.14). In order to reach equation (3.13), we revert to the Arhenius expression for the value of the rate constant (k) at each electrode. This reduces the numerator to $k[Cu^{2+}]$. Then by taking natural logarithms on both sides of the equation, equation (3.13) is thus obtained. In both the equations (3.12 and 3.13), the dependence of copper ion concentration in electrolyte on the overvoltage or overpotential is significant. It is the overvoltage that drives the ions in electrolyte in order to effect the deposition of the metal onto the cathode.

$$(k_{co} / k_{ao})[Cu^{2+}]\exp\{-\Delta G / RT\} = \exp\{zFE / RT\} \tag{3.12}$$

$$(zFE / RT) = In\{k_{co} / k_{ao}\} + In[Cu^{2+}] \tag{3.13}$$

We can also observe in equation (3.13) that multiplying throughout by zF and dividing throughout by RT yield equation (3.14) which again shows the dependence of potential on the concentration of ions or the dependence of ions on overvoltage as the reaction proceeds. Equation (3.14) leads to a very important expression, the Nernst equation as indicated earlier in equations (3.1), (3.3) and (3.4), when the term containing the rate constants is taken as E^0 to give equation (3.15).

$$E = (RT / zF)\,In\{k_{co} / k_{ao}\} + (RT / zF)\,In[Cu^{2+}] \qquad (3.14)$$

$$E = E^o + (RT / zF)\,In[Cu^{2+}] \qquad (3.15)$$

The free energy at the cathode and the anode, as indicated in equations (3.11) and (3.12), are used to effect the reduction and oxidation at the cathode and anode respectively. The free energy is the energy the system produces after doing some amount of work. It is a function of work. That means that the amount of energy that can be converted into work corresponds to the free energy of the reaction system (Antropov, 1972:540-541). In electro-chemical engineering, the work is the result of the passage of current by the overpotential that drives the metal ions from the anode into solution to the cathode where they are deposited. Their values can be obtained from a number of equations. Specifically, the magnitude of such free energy is given by equations (3.16) and (3.17). In these equations, according to Crow (1994:135), the a is the transfer coefficient and the overvoltage plays two roles. Part of it (a fraction a) is used to assist the cathode process while the other fraction (1- a) retards the anode process.

$$\Delta G_c = \Delta G_c^o + azF(E - E^o) \qquad (3.16)$$

$$\Delta G_a = \Delta G_a^o + (1 - a)zF(E - E^o) \qquad (3.17)$$

The reaction rates can also be expressed in terms of the free energy of the system as represented by equations (3.18) for the cathode and (3.19) for the anode. These equations show how the free energy contributes to the chemical reaction in the reactors. The small increase in free energy would result in a small increase of the reaction rate. On the other hand, if the free energy increase were large then the reaction rate would increase which would increase the rate of deposition of the metal at the cathode and the rate of dissolution of the metal at the anode as the desired effects.

$$r_c = k_c[Cu^{2+}]\exp\{-[\Delta G_c - anF(E - E^o)]/RT\} \tag{3.18}$$

$$r_a = k_a \exp\{-[\Delta G_a - (1 - a)nF(E - E^o)]/RT\} \tag{3.19}$$

Since E-E^o is the overvoltage or over-potential (η) at the respective electrodes, the overvoltage has, therefore, an effect on the reaction rate of the systems at the two electrodes. The rate constants can also be expressed in terms of potential as represented by equations (3.20) for the anode and (3.21) for the cathode respectively. The determination of the overvoltage and temperature would then lead to the evaluation of the rate constants and hence the rates of reaction at the electrodes. This would lead to the evaluation of the rate of reaction for the cell reactor.

$$k_a^1 = A_a \exp\{-[\Delta H_a^o - (1 - a)nF(E - E^o)]/RT\} \tag{3.20}$$

$$k_c^1 = A_c \exp\{-[\Delta H_a^o - anF(E - E^o)]/RT\} \tag{3.21}$$

Therefore the rate constants k_a^1 and k_c^1 can be determined based on the initial values of k_a, k_c, E and E^o in equations (3.22) for the anode and (3.23) for the cathode where E-E^o is the over-potential or overvoltage (η). The over-potential across the cell comprises the contributions of resistance, activation and polarization over-voltages. Koryta and Dvorak (1987:262) argue that the passage of current in the cell results in electrodes attaining different values of electrode potentials and this creates polarisation. The degree of polarisation is defined in terms of overvoltage, which is equal to the electrode potential (E) minus the equilibrium potential (E^0) of the same electrode ($h = E - E^0$). The value of the transfer coefficient (α) is taken as 0.65 at the cathode and 0.35 at the anode when z is unity. However, when z>1 it is better to use α at the cathode and (1-α) at the anode since the sum of values of α at the anode and cathode is not unity.

$$k_a^1 = k_a \exp\{-(1-\alpha)zF(E-E^o)/RT\} \qquad (3.22)$$

$$k_c^1 = k_c \exp\{-\alpha zF(E-E^o)/RT\} \qquad (3.23)$$

According to Antropov (1972:335-336) the overpotential can be understood by assuming that the overall electrode reaction to which there corresponds the reversible potential involves chemical steps. The chemical steps in cell reactors are the dissolution of the anode and the deposition on the cathode. Heitz and Kreysa (1986:101,214), Pletcher and Walsh (1993:75-78), and Crow (1994:143-147) have also provided full explanations of the role of the overvoltage in electrochemical reactions. Equations (3.24) and (3.25) give the cell voltages (V_{cell} and E_{cell}) in relation to the electrode overvoltage as described in Heitz and Kreysa (1986:101) and Pletcher and Walsh (1993:75) respectively. More of electrochemical kinetics is covered in Vetter (1967:117-119.).

$$V_{cell} = V_o + \eta_a + \eta_c + \sum IR \qquad (3.24)$$

$$E_{cell} = E_c - E_a - IR_{cell} - IR_{circuit} \qquad (3.25)$$

Heitz and Kreysa (1986:100-101) have alluded to the fact that the cell overvoltage can be divided into several contributing parts; the ohmic potential drop at the electrode-electrolyte interface consisting of the equilibrium potential (E_o) and the overvoltage (η), the diffusion overvoltage (η_d) in the diffusion boundary layer on the electrode surface, the ohmic potential drop in electrolyte, the activation energy (E_A) and the potential rise at the other electrolyte-electrode interface as is indicated in Figure 3.2. These potentials act together in order to realign the ions in the direction required.

The kinetics of electrode processes can be considered in two dimensions: the current-limited control and mass transport control. At the current-limited control, i.e. constant current, the change in concentration is given by equation (3.26). The change in concentration is current and time dependent. The increased time would induce an increased drop in concentration. Because of such effect it would be reasonable to operate the reactor with constant concentration in order to minimise the effects of increased overvoltage and current on the current efficiency. Effects such as increased heat generation; resistance and the associated temperature rise have a negative effect on the efficiency of the reactor.

$$dm = \{\Phi / zFV\} I dt \tag{3.26}$$

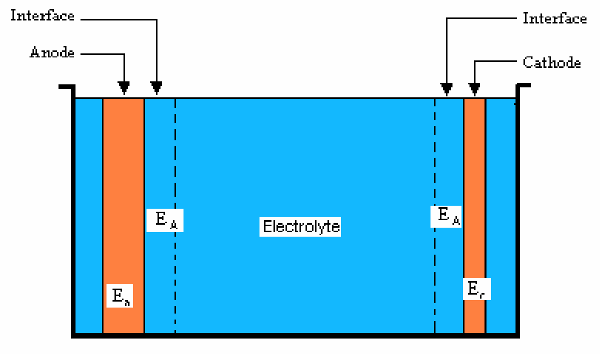


Figure 3.2: Electrochemical reactor with regions of energy generation

The rate of chemical reaction (r_c) can thus be determined from equation (3.27), which shows that it is concentration and time dependent. It is also dependent on the Current (I). As the concentration drops, the rate of chemical reaction reduces until when the current and overvoltage increase in order to drive more ions into solution so as to balance up the driving force. The effect would be increased current and overvoltage that would result in irregular deposition on the cathode. The material balance for the system can be represented by equation (3.28) as described in Fogler (1986:8-10) and Levenspiel (1962:101-103). The material balance is a form of conservation law which takes into account what goes in and what comes out of the system.

$$r_c = (dC / dt) = (\Phi / zFV) I \tag{3.27}$$

$$F_o - F_A + rdV = (dN / dt) \tag{3.28}$$

3.3 Temperature and Energy

During electrolysis, some of the electrical energy is converted into heat energy. The heat energy causes the temperature of the electrode and cell electrolyte to rise. The rise in temperature can result in overheating which causes the gas to evolve at the electrode. The evolution of gas causes the irregular deposition of the metal thereby rendering the surface to become rough. A rough surface causes irregular distribution of current density on the electrode. The overall effect is the development of passivating sites, which contribute to reduced deposition of the metal and hence reduced current efficiency. The current efficiency can respond to changes in temperature in two ways. Firstly, it can decrease with the increase of temperature in which case cooling the electrolyte can be the solution to the problem or secondly, it can increase with increasing temperature. In the second case, it might be necessary to determine the optimum temperature so that the cell electrolyte does not decompose with rise in temperature.

The rise in temperature increases the dissociation of the electrolyte, i.e., allows the formation of more ions in solution and at the same time increases the solubility. The increase in the number of ions can produce an increase in current flow which could increase the deposition rate that may then render the reactor to operate at reduced concentration, which could result in overheating. The cost of electrolysis would increase when the system uses high overvoltage and current density, which would result in increased heat generation in the system. Equation (3.29) shows the correlation between the heat energy (Q) and the cell voltage (V) and the current (I). Since the reactor is operated at steady state, the heat flow from the cell is equal to heat generated by the cell.

$$Q = I(V_c - V_n) \tag{3.29}$$

It is obvious that when the temperature is increased in the cell, the cell resistance would decrease and hence the cell overvoltage required to drive the ions in solution would increase since more ions would form at high temperature. This would then increase the heat generation in the reactor. It is also obvious that the cooling of the system would increase the operational cost. Equation (3.30) relates the cost of cooling (C) to the period of operation (t). Increased periods result in increased costs as the coolant (m) removes more and more heat energy from the system.

$$C = pmt \tag{3.30}$$

The energy cost can be evaluated in terms of energy consumption (E) and the unit energy price (P_E) as indicated in equation (3.31). The higher the energy consumption the higher would be the production cost. Similarly, the higher the unit price of energy the higher would be the production cost. Therefore, there would be a response to the high unit price of energy by instituting cost saving measures that would allow the high unit price to have less or little impact on the profits. There are a number of ways in which the energy consumption would increase. Firstly, the operation of the reactors at temperatures higher than the normal operating conditions, a situation that could occur when the monitoring regimes are relaxed or faulty as is the case where the temperature control systems fail. The other way is when the plant demand increases. Increased capacity and resistance in the reactors can increase the demand for energy. Here the forces of demand and price could play a key role in the management of energy. Most importantly, the optimisation of the process would reduce the cost of energy.

$$C_e = EP_e \tag{3.31}$$

The heat flow from the cell to the surrounding can be evaluated using equation (3.32). In this equation the temperature difference and the values of the mass (m) of the cooling-process streams determine the magnitude of the heat flow from the reactors. If large amounts of process streams are used then the value of heat energy (Q) will increase. The opposite will also be true. On the other hand, the larger the difference in temperature, the larger the increase on the value of heat flow and vice versa. Since the chemical reaction is more efficient at the normal operating conditions, the operation of the reactors at other temperatures would result in the reduction in efficiency of the reactors. The operation of the reactor at temperatures above 70^{o}C would damage the properties of the materials being used such as glue whose structure would break down into pieces and therefore would not be able to provide the function it is intended to do during electrorefining. Most importantly is the current efficiency, which would be affected if the chemical reaction is not efficient. In the same token, the non-cooling of the process stream in order to maintain a stable operating temperature would equally result in the reduction of efficiency since the poorly-removed heat energy would result in further increase of temperature which would then result in the instability to set in the system.

$$Q = mC_p(T_o - T_i) \tag{3.32}$$

The time for the reaction can be calculated from Faraday's Law as shown in equation (3.33) but the direct relationship between the current density and the temperature and the current efficiency requires investigation since the literature review has not revealed any model of the variation of temperature with current efficiency.

$$dm = (M / zF)\Phi I dt \tag{3.33}$$

The cell resistance of the system is given by equation (3.34) or using Ohms Law ($V = IR$) where V is Voltage, I is the current and R is the resistance.

$$R = R_o\{1 + a(T_c - 298)\}^{-1} \tag{3.34}$$

$$\Phi = a - bT_c + cT_c^2 \tag{3.35}$$

The effect of temperature on the current efficiency can thus be investigated using equation (3.35) or data exploration method. For the electrochemical system, the change in work (dW) is equal to the change in heat energy (dQ) and this is related to electrical energy generated as a result of the application of overvoltage. According to Antropov (1972:25-29), the work energy, the heat energy and the Gibbs free energy, if electrical in nature, will be equal to zFE. Equation (3.36) shows such a relationship. However, due to heat effects, the values will be different at different temperatures as shown by equation (3.37), which is the Gibbs Helmholtz equation. This equation yields the same values for constant volume and constant pressure systems that are reversible at isothermal conditions. The cell potential can thus be obtained by dividing equation (3.37) with zF to give equation (3.38).

$$\int dW = \int dG = Q = zF \int dE \tag{3.36}$$

$$zFE = Q + zFT\{\partial E / \partial T\} \tag{3.37}$$

$$E_{cell} = (Q / zF) + T\{\partial E / \partial T\} \tag{3.38}$$

3.4 Diffusion of Ions in cells

Diffusion is defined in different ways depending on the area in which it is applied. In Physics, it is defined as the spontaneous movement and scattering of particles (atoms and molecules) of liquids, gases and solids while in the Electrical environment it is defined as a method of producing a junction by diffusing an impurity metal (Lapedes, 1978:451). Diffusion in liquids, which comprises positive and negative ions or molecules, results in the generation of chemical potential (Coulson and Richardson, 1991:873). This link is in agreement with that described in Crow (1994:12, 51) as expressed in equations (3.39) and (3.40).

$$dm = VdP + (\partial m / \partial C)dC + zFdE \tag{3.39}$$

$$m = m_o + RTIna + zFE \tag{3.40}$$

The diffusion of molecules has been cited in Coulson and Richardson (1991:507, 1996:495-496). Coulson and Richardson (1991:819) further argue that the diffusion potential in liquids is created when a film of molecules forms near the cathode. The circumstances under which this could happen is when there is an electrostatic layer of charged molecules, which interacts weakly with the cathode. The diffusion potential arising from the electrostatic differences and the driving force accelerate the ions towards the cathode. The ions then diffuse through the electrostatic layer when the overvoltage is applied across the reactor. Inhibitors are thought to form a film of ions near the cathode and the cations are allowed to diffuse through such a layer in order to hit the cathode where they are deposited. The diffusion flux of ions from the electrodes into solution and vice versa can thus be modelled as described in Koryta and Dvorak (1987), Coulson and Richardson (1996:504) and Bruce (1995) using Ficks Law of diffusion as expressed by equation (3.41).

$$J_{diff} = -D(dc/dx) \qquad (3.41)$$

Fick's Law describes regions of high and low concentrations of ions. It means that the flux of ions is driven from regions of high to regions of low concentrations. The cathodes in electrochemical reactors act as sinks where the cations are sunk into solid and therefore the cathodes act as regions of low concentration. It also means that the cathodes are regions of low electrochemical potential. Thus spontaneous movement of ions, according to Crow (1994:51), will take place from regions of high to regions of low electrochemical potential. The rate of movement of ions is governed by the gradient $(\partial m/\partial x)$, which is proportional to the rate of movement (v) as is expressed in equation (3.42). The cation has to be driven by the gradient if it has to move the distance x. That is that the rate of movement is dependent on the chemical potential (μ).

$$v = k(\partial m/\partial x) \qquad (3.42)$$

The rate of movement of ions as flux (J_{diff}) can be obtained from equation (3.43). It is important to note that the diffusion of ions in electrolyte is temperature dependent. The flux can further be expressed according to equation (3.44) since the flux is also equal to $dn_i / dt = c_i v_i$.

$$J_{diff} = k_i\{RT(\partial Inc_i / \partial x) + z_i F(\partial E / \partial x)\} \tag{3.43}$$

$$J_{diff} = k_i c_i\{RT(\partial Inc_i / \partial x) + z_i F(\partial E / \partial x)\} \tag{3.44}$$

The above equations reduce to Ficks Law of diffusion when the gradient (∂E/∂x) is zero. The driving force, when the potential gradient is zero, is the concentration gradient and therefore equation (3.44) reduces to equation (3.45), since the numerator term (∂Inc) changes to the new term (∂c) thus giving the Fick's Law of diffusion (Crow, 1994:52).

$$J_{diff} = k_i RT(\partial c / \partial x) \tag{3.45}$$

The value of diffusivity (D_i) is equal to k_iRT and the constant (k_i) is equal to D_i/RT. The longer the distance (x), the smaller the gradient and the lower would be the flux. In order to create a large flow of flux, a smaller value of ∂x is required. When the concentration gradient is zero the flux can be expressed in terms of potential as shown in equation (3.46) where the values of c^1, c^{11} and d^1 are given by $k_i c_i z_i$, $c_i z_i F$ and D_i / RT respectively.

$$J_{diff} = c^1 RT(\partial E / \partial x) = c^{11} d^1 (\partial E / \partial x) \tag{3.46}$$

The charge that is passed through electrolyte, due to the flux, can be determined from equation (3.47). The conductivity of the ions can be expressed in terms of the charge (I) and the field strength (F_s) represented by the gradient (∂E/∂x) as indicated by equation (3.48).

$$I = z_i F J_{diff} = c_i d^1 z_i^2 F^2 (\partial E / \partial x) \qquad (3.47)$$

$$k = I(\partial E / \partial x)^{-1} = IF_s^{-1} \qquad (3.48)$$

On the other hand when the concentration gradient is zero then the flux (J_{diff}) exhibits linearity with the potential gradient for a single component ion (i) as is indicated in equation (3.49). The value of the constant (k_i) can be replaced by its equivalent value d^1. It can be observed that the equation reduces to Fick's Law when it is expressed in terms of potential. It can be observed also that the longer the distance (x) the smaller the gradient ($\partial E/\partial x$) and the weaker will be the flux of ions. In order to conduct electrolysis effectively, a stronger flux is required and this can be obtained when the distance (x) between electrodes is small.

$$J_{diff} = d^1 c_i z_i RT (\partial E / \partial x) = D_i c_i z_i (\partial E / \partial x) \qquad (3.49)$$

The flow of flux from either the solution to the cathode as in electrowinning or from the anode to the cathode as in electrorefining, by the mechanism of diffusion, contributes to the mass transfer of the metal using the cathode collection mechanism. Each of the laws of diffusion by Stefan and Plank contribute to the transport of the metal from electrolyte to the cathode as described by Fick's Law (Coulson and Richardson, 1996).

3.5 Convection of Ions between Electrodes

The convection of ions in cell reactors can be defined, according to Koryta and Dvorak (1987:86), as the transport of streaming in the system produced by the action of external forces. Pletcher and Walsh (1994:132) define the convection as the movement of species of ions due to mechanical force. The external force which is usually mechanical in nature as a result of stirring or flow due to pumping of electrolyte drives the ions to the electrodes. In non-stirred systems the convection is absent and the ions move by diffusion and migration forces. It means that the use of batch systems may require stirring in order to create convective mass transfer while the use of Plug Flow Reactor

(PFR) relies on the convective currents created by the pumping of electrolyte. For example, the rotating disc reactor creates convection currents by the rotating action due to the torque applied on it by the motor.

The modelling of the transport of ions by convection is based on Fick’s Second Law. Since both diffusion and convection take place at the same time, the model is thus modified to include the convection component as shown in equation (3.50). The change of concentration of ions with time is thus defined where the term $D_i\{d^2c_i / dx^2\}$ and $v\{dc_i / dx\}$ are the diffusion and convection components respectively.

$$dc_i / dt = D_i(d^2c_i / dx^2) - v(dc_i / dx) \tag{3.50}$$

The flux of ions make available to the electrodes the ions required for the reduction or oxidation as given in equation (3.51) which conforms to Fick’s first Law of diffusion.

$$J_{conv} = -Ddc / dy = 0.62D^{2/3}V^{-1/6}w^{1/2}(c^2 - c^1) \tag{3.51}$$

The convective flux can also be defined by equation (3.52) where (v) the number of ions and the concentration of component (i) is represented by c_i. The value of v_i is given by $v = 0.51n^{-1/2}w^{3/2}x^2$. When the reactors are operated at steady state, the diffusion is equal to convective flux and equation (3.52) is reduced to equation (3.53).

$$J = vc_i \tag{3.52}$$

$$D_i(d^2c_i / dx^2) = v(dc_i / dx) \tag{3.53}$$

3.6 Migration of Ions between Electrodes

Migration is defined as the movement of cations and anions through a solution under the influence of applied potential between electrodes placed in that solution (Crow, 1994:132). Pletcher and Walsh (1993:18) defines it as the movement of charged ion species due to the potential gradient. The two definitions show similarity in that they both refer to the potential that is used to drive the ions in the electrolyte. In order to understand the concept of migration of ions in the electrolyte, the salt of the electrolyte must dissociate to some degree when dissolved in solution so that the ions so formed (negative and positive) must respond to the applied potential or the electric field. The response to the electric field is the independent movement from regions of high to regions of low potential. The positive ions move to the cathode independent of the negative ions. The independence of each ion type is inherent in the type of electrolyte and hence different electrolytes exhibit different strengths of ions when they dissociate in solution. The Law of Independent Migration (LIM) of ions in the electrolyte also known as the Kohlausch Law of Independent Migration (KLIM) represented by equation (3.54) demonstrates the importance of the contribution of ion species in the electrolyte. The conductance of the electrolyte is the sum of the contribution of the positive and negative ions. In order to quantify the charge, we need to know the number of moles of the ions (n^+) for the cations and (n^-) for the anions so that the conductivity, according to LIM or KLIM, is then determined from equation (3.55).

$$\Lambda_o = l_+^o + l_-^o \tag{3.54}$$

$$\Lambda_o = n^+ l_+^o + n^- l_-^o \tag{3.55}$$

In order to model the movement of ions we assume the velocities (v_+) and (v_-) for the cations and anions respectively and that the ions travel a distance (L) between two points through an area (A) as is shown in Figure 3.3.

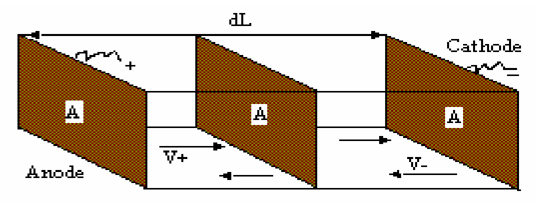


Figure 3.3: Migration model for the ions in electrolyte

Given this scenario, there exists between the electrodes an electric field gradient in the electrolyte. The potential gradient created by the electric field results in a force that develops a velocity (v_+) and (v_-) for the cations and anions respectively. The relation between the electric field and the potential gradient is shown in equation (3.56).

$$\Phi = -dE / dL = \Delta E / L \tag{3.56}$$

The movement of each component ion (i), by the electric force (F_e), given by equation (3.57), is in the direction parallel to the electric field. The friction force (F_s), given by equation (3.58), is thus created which retards the movement of the ions. In order to overcome the friction force the electric force must be greater.

$$F_e = -q_i \Phi \tag{3.57}$$

$$F_f = k_i v_i \tag{3.58}$$

The acceleration of the ions as a result of the imbalance between the electric and the frictional forces is dependent on the mass of the ion. The force acting on the ion can then be quantified according to Newton's Law of motion as indicated in equation (3.59).

$$m_i a_i = q_i \Phi - k_i v_i \tag{3.59}$$

Since the acceleration is the rate of change of velocity as indicated in equation (3.60), therefore equation (3.60) can be substituted in equation (3.59) to give equation (3.61).

$$a_i = dv_i / dt = d^2 L / dt^2 \tag{3.60}$$

$$m_i (d^2 L / dt^2) dL + k_i v_i dL = q_i \Phi dL \tag{3.61}$$

Equation (3.61) can further be simplified to give equation (3.62) from which an important conclusion is drawn. The electric force $(q_i\Phi dL)$ is used to develop the kinetic energy $d(\frac{1}{2}m_iv_i)$ in the ions and overcome the frictional force (k_iv_idL) in order to deliver the ions to the electrodes where their fate is determined either by being deposited as metal or discharged as a gas to the atmosphere.

$$d(\tfrac{1}{2}m_iv_i)+k_iv_idL=q_i\Phi dL \tag{3.62}$$

The integration of equation (3.61) gives equation (3.63) for the general case, which is another important equation of ionic migration in an electrolyte. The value of the term $e^{(-kt/m)}$ is usually small and therefore can be neglected. Equation (3.63) thus reduces to equation (3.64) for a single component ion.

$$v=(q\Phi/k)\{1-e^{(-kt/m)}\} \tag{3.63}$$

$$v_i=q_i\Phi/k_i \tag{3.64}$$

The velocities of cations and anions in the copper sulphate electrolyte can therefore be determined from equations (3.65) and (3.66) where e^1 and e^{11} represent the ratios z_+/k_+ and z_-/k_- respectively in which k_+ and k_- are the friction coefficients for the ions.

$$v_+=e^1(\Phi/L)=-e^1(dE/dL) \tag{3.65}$$

$$v_+=e^{11}(\Phi/L)=-e^{11}(dE/dL) \tag{3.66}$$

We know that the factors; concentration, potential and temperature gradients, and mechanical stirring affect the transport of ions by migration. The effects of these factors have already been discussed in Chapter 2. But the dissociation of the salt of the electrolyte is dependent on the temperature. The electrochemical potential (E_{ec}) created by the dissociation and migration of ions under an electric field due to the application of the external potential (E) is related to the chemical potential (E_c) in equation (3.67). If we include the concentration term (c_i), the effect of concentration gradient on electrochemical potential can be realised in equation (3.68).

$$E_{ec} = E_c + z_i FE \tag{3.67}$$

$$E_{ec} = E_c + RTInc_i + z_i FE \tag{3.68}$$

What this means is that there will be a spontaneous movement of ions from regions of high to regions of low electrochemical potential as stated earlier. The rate of movement of the ions as described in Crow (1994:51) is proportional to the chemical potential but inversely proportional to the distance through which the ions migrate as given by equations (3.69) and (3.70). It can also be said that the rate of migration depends on the concentration and potential gradients.

$$v_i = k_i (dE_{ec} / dL) \tag{3.69}$$

$$v_i = k_i \{RT(dInc_i / dL) + z_i F(dE / dL)\} \tag{3.70}$$

The flux of ions migrating to the electrodes can then be modelled over the area (A) and through the distance (dL) to give equation (3.71), which obeys Ficks Law of mass transfer.

$$J_{migr} = -zF(d\Phi / dL) = dn_i / dt = c_i v_i = k_i c_i \{RT(dInc_i / dL) + z_i F(dE / dL)\} \tag{3.71}$$

In the reduction of positive ions, the transport is achieved by migration, convection and diffusion but in the reduction of anions, the transport of ions to the cathode is achieved by convection and diffusion and they are removed from the electrode by migration

(Antropov, 1972; Crow, 1994). Most reactors are operated under unsteady state due to agitation but laminar conditions favour the yield in electrolytic reactors.

3.7 Mass Transfer in Cells

The transport in electrochemical cells is carried out in two ways; the transport of ions and that of electrons. It is the movement of mass from solution to cathode in the case of electrowinning and from the anode to the cathode in the case of electrorefining. The solution close to the electrode surface is the critical element in mass transfer. When the conditions are right, i.e., the material of the electrode and that of the electroactive solute are compatible, then the transfer of electrons takes place according to the Frank-Gordon Principle (Crow, 1994:132). The electron transfer takes place only when the two compatible materials have electrons at the same energy level; a process called isoenergetic electron transfer (Koryta and Dvorak, 1987:278). The transfer of electrons accompanies the transfer of ions on the cathode and the release of the oxidised at the anode. According to Faraday's Law, the current passing through the electrode is equivalent to the mass flux of the electroactive species (Koryta and Dvorak, 1987:289).

The mass transfer takes place when the electroactive species disappear in the electrode reaction when acted upon by the current. This means that the current density (j) is proportional to the mass flux (J) as described in equation (3.72).

$$j = zFJ \quad \text{(general case)} \tag{3.72}$$

The relation at the cathode with the reduced species is given by equation (3.73) while that at the anode is given by equation (3.74). The current density is thus related according to the strength of the flux of the reduced and the oxidised.

$$j = -zFJ_{\mathrm{Re}d} \tag{3.73}$$

$$j = zFJ_{Ox} \tag{3.74}$$

When the value of the flux (J) for the reduced and oxidised are substituted in equations (3.73) and (3.74) equation (3.75) is obtained which defines the mass transfer according Fick's Law of diffusion and migration of electroactive species in electrolyte at or near the electrode when the distance of the interface (x) is zero. It also provides the relationship between the current density and the concentration of electroactive species. The change in concentration with time, as indicated by equation (3.76), gives the Fick's Second Law of diffusion as described in Pletcher and Walsh (1993:20-23).

$$j / zF = D_{\mathrm{Re}\,d} (dc_{\mathrm{Re}\,d} / dx)_{x=0} = -D_{Ox} (dc_{Ox} / dx)_{x=0} \tag{3.75}$$

$$dc / dt = D(d^2 c / dx^2) \tag{3.76}$$

One can therefore predict the relationship between the concentration and the distance between electrodes. If the concentration decreases as the reaction proceeds then the initial concentration is higher than that after the lapse of time. The comparison of the reduced and the oxidised concentration shows that as the reduced increases, the oxidised decreases. If the volume or mass lost at the anode is equated to the volume or mass gained then the variations in volume can be given by $V_{Ao} - V_A + r_A t = (dV / dt)$ while that in terms of mass can be given by $M_{Ao} - M_A + m_A t = (dM / dt)$. Faraday's Law, according to Heitz and Kreysa (1986), can also give the rate of mass transfer as $(dm / dq) = I(M / zF)$. The rate of anodic dissolution of copper in phosphoric acid above the potential where oxygen evolution takes place was studied in Sedahmed *et al.* (1980). The variables investigated were oxygen discharge rate, phosphoric acid concentration and electrode position. The mass transfer coefficient of the anodic dissolution of copper in phosphoric acid was related to the oxygen discharge rate and the physical properties of the solution. Copper was thus observed to move from the anode into the solution and to the cathode. Copper can thus be deposited at the cathode with no change in concentration of solution. Newton (1959) showed that the electrolysis of metals undergoing electro-refining do not produce any change in concentration and all cathode reactions result in the deposition of metal at cathode.

However, if the anode is not soluble, then the concentration can vary as more ions of metal migrate and deposit at the cathode. The potential across the reactor will thus be affected by changes in concentration.

In order to maximise the mass transport optimum conditions must be attained. The use of high currents may cause overheating in the electrolyte, which may lead to uneven potential distribution as described in Pletcher and Walsh (1993:110). The operation of the reactor at a current that is less than that of the limiting value ($I=I_L$) may result in the reduction of current efficiency when changes in the electrolyte conditions occur. For example, a decrease in electroactive species at the inlet of the reactor may result in the current being greater than the limiting value, which may result in the birth of side reactions. However the advantage of using high current density is that the reactor performance is enhanced as evidenced by the increased fractional conversion and space-time yield. The composition of the electrolyte in the bulk must be the same as that near the electrode in order to avoid the depletion of the reduced at the interface. It is important also to maintain uniform current at the electrodes in order to reduce the secondary reactions and maintain the current efficiency and hence increased mass transfer to the cathode. The control of the temperature allows the chemical reaction to be fixed as the concentration of ions in solution is temperature dependent and so is the dissociation of electrolyte.

3.8 Current Density and Overvoltage

The movement of fluxes results in the generation of and flow of current. The current enables the anode to dissolve and to deposit metal at the cathode. If the area of the anode is the same as that of the cathode, then the current per unit area, which is the current density, will be the same for both electrodes (Newton, 1959). If the current is reversed, then the chemical reactions at the electrodes will be reversed. Skoog and West (1976) support this argument. They argue that cells that can reverse chemical reactions are electrochemically reversible and that those that give different products upon reversing current are irreversible. The reversing of current removes nodules on the surfaces of electrodes.

If the systems behave according to Faraday's Laws then the rate of reaction divided by the charge that is used to react one-gram equivalent (zF) of the element becomes the definition of the current density. The current density, the current per unit area of electrode, plays a key role in electro-refining (Lapedes, 1978). It is caused by the distribution of charges due to migration of electrons and ions. The current distribution is not uniform in most practical situations and so is the current density. This is due to a number of factors; the geometry of electrochemical reactors, conductivity of electrolyte, electrode and concentration over-potentials, which are controlled by the circulation of electrolyte and mass transfer of metal to cathode. The determination of current density provides a means of assessing the optimum current densities that give best process operating conditions. Over-potential is the difference between electrode potential and equilibrium potential at the electrodes. The current density is limiting if it is independent of potential over a large range. For example, if the current is uniformly distributed, it is expected that the deposition of the metal will behave according to Faradays Law that states that one gram-equivalent of a material is chemically altered at each electrode for every 96,500 Coulombs passed through an electrolytic reactor (Newton, 1959). The current densities at the anode and cathode have fully been described in Crow (1994:133-137) and Subramanian and White (2000). They can then be compared to measured values. Any increase in current density results in increased voltage and therefore power consumption and capital costs are decreased due to reduced electrode area (Heaton, 1986:137). This means that the electrode separation would have to be reduced as much as is possible in order to maximize the current density and efficiency.

Equation (3.77) is the starting point for the relation of overvoltage and current density. The relation of reaction rate and current density is therefore linear. Any increase in current density results in the increase in reaction rates. This means that increased values of reactions rates would be obtained at increased values of current densities. By the same token, increased values of deposited metal would be obtained at increased values of current density.

$$r_c = zFj \tag{3.77}$$

The current density is a function of concentration, free energy and overvoltage. Equation (3.78) shows the functionality of the terms concentration, free energy and overvoltage at the cathode. When the free energy of the chemical reaction and the overvoltage are increased the exponential term would increase and hence the value of the current density would increase. In practice the increased overvoltages increase the current density.

$$j_c = zFk_c[Cu^{2+}]\exp(\Delta G/RT)\exp(-anFh/RT) \tag{3.78}$$

The first exponential term can be denoted by a symbol (j_o) and therefore equation (3.78) reduces to equation (3.79) at the cathode. The value of the free energy is usually smaller and therefore the current density is increased or reduced by the exponential term, which includes the overvoltage. It is the overvoltage therefore that impacts the current density at each electrode. The overvoltage is therefore a critical element in maintaining a constant current density at the electrodes.

$$j_c = j_o \exp(-anFh/RT) \tag{3.79}$$

The above argument can be advanced at the anode also to give equation (3.80). As can be observed in the equation, the overvoltage induces heat energy that causes an increase in temperature. Increasing temperature may reduce the current density and hence reduce the chemical reaction. The reduced chemical reaction may result in reduced current efficiency. It is therefore important to investigate the effects of current density and overvoltage in the evaluation of current efficiency.

$$j_a = j_o \exp\{-(1-a)nFh / RT)\} \tag{3.80}$$

By taking natural logs on both sides of (3.79) and (3.80) and letting the overvoltage as the subject of formula, Tafel equations (3.81) and (3.82) for the cathode and anode respectively can be obtained which give Tafel plots when j/j_o is plotted against the overpotential. The Tafel plots give an indication of how the ratios of the current densities vary with overvoltage ($E\text{-}E^o$). The values of f^1 and f^{11} are given by the ratios RT / azF and $RT /(1-a)zF$ respectively.

$$h = E - E^o = -f^1 Inj_o + f^1 Inj_c \tag{3.81}$$

$$h = E - E^o = +f^{11} Inj_o - f^{11} Inj_a \tag{3.82}$$

The current for the electrochemical reaction is introduced from the external power supply, which provides the required overvoltage across the reactor including that which is created due to formation and movement of ions to the electrodes. Each electrode in the reactor receives the current. The current is then distributed on the entire electrode in order to polarise them. The distribution of the current over the electrode area results in the current density distribution over the area. The current is also an important element in the operation of the reactors. At the cathode, the overvoltage drives it. Similarly, at the anode, the overvoltage drives it. The current at the electrodes can be evaluated from equations (3.83) for the cathode and equation (3.84) for the anode. In these equations, it can be observed that any increase in overvoltage would result in an increase in current, which would result in increased chemical reactions, and hence increased conversion that would increase the current efficiency if and only if the temperature for the operation is right.

$$I_c = I_0 \exp\{-(anFh / RT)\} \tag{3.83}$$

$$I_a = I_0 \exp\{-(1-a)nFh / RT)\} \tag{3.84}$$

The difference between I_c and I_a, i.e., subtracting the value of current at the anode from that at the cathode gives the net current at the cathode while the difference between I_a and I_c, i.e., subtracting the value of current at the cathode from that at the anode gives the net current at the anode.

3.9 Current Efficiency

The current efficiency (ϕ), the efficiency at which copper enters the electrolyte from the anode, is a ratio of the weight of metal deposited to the weight of the metal that can be theoretically deposited (Newton, 1959; Lapedes, 1976:392). It is slightly higher than that of the cathode by about 0.5%. It can be determined from equation (3.85)

$$\Phi = M / M_T \tag{3.85}$$

The current efficiency is usually affected by high current densities, which produce passivity on the electrodes. Passivity is the non-deposition of copper on the electrodes and the creation of pits due to exfoliating surface of the electrode. On the other hand, low current densities are not effective in depositing metal on the cathode. It is important to note also that the maximum value of current efficiency is 100%. However, parallel deposition due to impurities can result in values exceeding 100% because impurities in solution and anode tend to interfere with the deposition process. Therefore the determination of current efficiency provides a guide on which to assess the performance of the reactors. Equation (3.85) can further be defined according to Faraday's Law as the current based yield. According to Pletcher and Walsh (1993:73), it is based on the charge (q) passed compared to theoretical charge (Q_T). Therefore equation (3.86) defines the efficiency based on the charge and thus obeying the Law of Faraday.

$$\Phi = q / Q_T \tag{3.86}$$

The charge passed through the electrolyte is dependent on the time. The longer the time, the more the charge that can be passed and the more deposit of the metal can be achieved. Equation (3.86) therefore provides the relationship between the charges used to deposit certain mass of the metal to that that can be used to deposit the theoretical amount according to Faraday. Equation (3.87) considers the valence and mass of the metal deposited and the theoretical charge that would deposit one molecular weight of the substance. The efficiency is also a function of concentration gradient or drop as indicated in equation (3.87).

$$\Phi = wzF / qM = mzF / q = (zFV / q)\int dC \tag{3.87}$$

The value of q can be calculated from equation (3.88). In this equation, the charge is a function of current and time. At the value of current the time determines the amount of charge passed. If there are impurities that have similar characteristics with the desired metal to be recovered then it becomes difficult to account for the charge passed over the specified time as some of it would be used to deposit such other metals. It would also be difficult to account for the current efficiency. It is thus important to ensure that the electrolyte used does not contain undesirable impurities.

$$q = \int_{I_o}^{I_t} Idt \tag{3.88}$$

As described in Antropov (1972:299-300) and Heitz and Kreysa (1986:218), the current efficiency is also defined as the amount of current passing through a cell, which accomplishes the desired-electrode reaction. The amount of electricity used to deposit the metal on the cathode plus that used to liberate gas on the anode should be equal to one gram-equivalent of the overall reaction. This means that the amount of electricity liberating the metal at the cathode is not always the same as that that liberates the gas on the anode. Antropov (1972:299) describes the reduction of zinc ions in acidified solution of zinc sulphate to be 60% and that of the oxidizing hydrogen gas ions to be

40%. The total charge to liberate one gram equivalent would therefore be equal to 100%.

The current efficiency is affected by the distribution of current on the electrode. If the distribution of the current (I) is uniform then it is possible to achieve 100% current efficiency. If on the other hand the distribution is non-uniform then the current density would be different at different points of the electrode-active area and therefore the undesired-reduced current efficiencies can be obtained which may cause a number of problems. According to Heitz and Kreysa (1986:54), the distribution of current density may cause variations of thickness of deposited metal, non-uniform corrosion of electrodes and poor energy efficiency. The current efficiency can also be assessed based on whether the operation is at constant or varying concentration in which case we speak of the Plug Flow Reactor (PFR) and Batch Reactor. In the case of a batch reactor, the current efficiency can be evaluated from equation (3.89).

$$\Phi = zF(C_o - C) / a_e I \int dt = kF(C_o - C) / I \int dt \tag{3.89}$$

The space-time yield (Y_{st}) is also an important parameter in the evaluation of current efficiency. If the mass (m) is deposited in time (t) in some volume (V_R) of electrolyte then the mass is directly proportional to the time but inversely proportional to the volume of the electrolyte ($Y_{st} = m/(tV_R)$). The substitution of concentration and the introduction of space velocity (u) yield equation (3.90).

$$Y = uM(C_o - C) = M(dC/t) \tag{3.90}$$

The rate of mass deposition of the substance is current-efficiency dependent and also current dependent as shown in equation (3.91). The increase and decrease in current would certainly increase and decrease the deposition rate respectively. The increase and decrease in current efficiency would also mean that the deposition rate increased and decreased respectively. There would be thus a linear relationship between the said parameters. Any changes to linearity would mean that impurities have accessed the electrolyte or the concentration behaviour has changed due to depletion of the ions in electrolyte or the current has become inefficient due to problems at source contacts or some other problems.

$$m/t = MI\Phi/zF \tag{3.91}$$

Equation (3.92) is the yield based on Faraday's Law and introduces the current density, which is a critical element in the electrolytic recovery of copper. We therefore see that the yield is dependent on the current density, the volume of reactant or reactor, the concentration of ions in solution of electrolyte and most of all dependent on the current efficiency. The electrode-active area is critical but the optimum yield requires optimum current density. The conversion of the ions during the electrochemical reaction on the cathode (X_A) is useful in quantifying the yield.

$$Y = AMj\Phi/zFV_R \tag{3.92}$$

The conversion of the chemical reaction in the reactors is concentration dependent. Equation (3.93) gives the conversion based on concentration. The initial and final concentrations are used for the evaluation of the conversion. In the case of PFRs, the inlet and outlet concentrations can be used as initial and final concentration while in the case of batch reactors the initial concentration is that at the feed time and the final concentration is that at any instant during the reaction or that at the end of cycle time excluding cleaning time. What is important however is to identify the limiting and excess reactant. The conversion is always determined based on the limiting reactant or component because the overall yield is dependent on such a reactant. Since the speed of the chemical reaction is dependent on temperature, different values of conversion are obtained at different temperatures signifying that the conversion is temperature dependent.

$$X_A = (C_o - C)/C_o \tag{3.93}$$

For the batch reactor, the yield for the reactant that can be converted to 0.9g-equivalent is given by equation (3.94). It is clearly indicated in this equation that the ratio of the initial (higher) and final (lower) concentrations determines the magnitude of the yield. The conversion also plays a role in that if the conversion is high then the number of gram equivalents would be low and if low then they would be high. Since the volume is kept constant in batch reactors, the yield is a critical element in maximising the current efficiency.

$$Y = (0.9IM\Phi / X_A zFV_R) In\{(C_o - C)/C)) \tag{3.94}$$

In PFRs, the ratios of the final (lower) and the initial (higher) concentrations are used in the determination of the yield. Obviously the ratio is less than unity and therefore the value of the yield would be smaller than that of the batch system. Maintaining a constant concentration can raise the value of the yield in this type of reactor. The yield is also dependent on the current efficiency as shown in equation (3.95) as it provides information on the level of current efficiency during the electrochemical reaction and therefore is a critical element in the evaluation of current efficiency in PFRs. The conversion plays a significant role in the determination of the reactor yield and therefore contributes to the current efficiency. The yield based on conversion is more useful than that based on space-time (Pletcher and Walsh, 1993:89). The values of h^1 and h^{11} in equation (3.95) are given as $0.9IM / X_A zFV_r$ and $In(C_i / C_o)$ respectively.

$$Y = h^1 h^{11} \Phi \tag{3.95}$$

3.10 Operation of Electrochemical Reactors

The operation of electrolytic reactors can, therefore, be either at constant potential or at constant current flow. If the concentration of ions that carry electrons (Cu^{2+}) changes, then the current will change with time. At low levels of concentration of electrolyte, more hydrogen ions will form and less deposition will take place. The increase in voltage will raise the current and more deposition will take place. On the other hand, maintaining the concentration of copper ions in electrolyte at constant value maintains the deposition at constant rate. This is how electro-refining cells can be operated at constant current or at constant electrode potential. At constant current electrolysis, Lingane (1949:2:589) and Skoog and West (1976) had shown that the variation of potential with time is not linear. On the other hand, the variation of current with time at constant potential was also not linear. This is in agreement with what Skoog and West (1976) had presented. This can, therefore, mean that electrolysis can be performed by maintaining a constant potential at the electrodes while varying the current at the expense of concentration or operating at constant current while varying potential at the expense of concentration. In practice the maintenance of constant concentration at a particular flow will enable the electro-refining process to be operated at constant over-voltage and current. This was the guiding principle for the study.

3.11 Smootheners and Metal Recovery

The chemistry of the surface reaction between the cathode and the smoothener is not quite clear from the many studies that have been conducted elsewhere. Many attempts have been made in the use of various inorganic and organic chemicals in combination, according to the determined proportions, in order to observe the effects on the deposition of copper on the cathode. The smoothness of the surface at the cathode has been improved when additives such as thiourea, gelatine and chloride and ethylene glycol and glycerine have been added to the electrolyte during electrolysis in order to promote a smooth deposit (Yamamoto *et al.,* 2002; Veilleaux *et al.,* 2003). The ethylene glycol (EG) and glycerine (G) were used in the ratios of 80:20 and 19.5:76 in the electrolysis using copper and zinc as electrodes. The results showed that the EG and G improved the smoothness and colour of the deposit in the presence of Ethylmethylimidizolium-zinc-bromide-molten salt (EMIB-ZnBr). The current efficiencies were found to be high (63-100%). In the electrolysis of molybdenum or carbon electrode in pure Sulphuric Acid using 15V ac, the smoothness of surface is improved by the addition of 0-6g/L of pyrazine (Voros, 2006). Additives such as animal glue have been observed to enhance smoothness of the resulting Cadmium Cathode during electrolysis (Fthenakis, 2003).

The influence of additive concentration and pulse electro-deposition parameters (current-on time, current-off time and surface morphology) was investigated in the study conducted by Yousef *et al.* (2004). The smootheners used were Poly-acrylamide (PA) and Thiourea (Tu). The results showed that at concentration of 0.7g/L of PA and 0.05g/L of Tu, the grain size decreased with increase of current-on time at constant current-off time and peak current density but increase in current-off time at constant current-on time and peak current density resulted in grain growth. The effect of additives such as Jaguar C13 on structure characteristics of copper deposits electro-won at 161Am^{-2} from aqueous chloride electrolyte was improved quality of deposit while additives such as glue and gelatine were found to be less effective (McKinnon *et al.*, 1985). The action of smootheners is to inhibit the formation of nodules and rough surface at the cathode. A study by Stelter *et al.* (2002) that used polyethylene glycol (PEG) as alternative additive to glue and thiourea for copper electro-refining produced a smoothening effect and the PEGs offered high thermal stability and slow chemical decomposition at higher temperatures with high cathodic polarisation. A study by Farndon *et al.* (1995) on the effects of Thiourea (TU), Benzotriazole (BTA) and 4,5-dithiaoctane-1,8-disulphonic acid (DTODSA) on the deposition of copper from dilute acid sulphate solutions using potential sweep techniques where Tafel slopes and exchange current densities were determined in the presence and absence of such organic additives revealed that TU and BTA were found to inhibit the copper deposition reaction. Increases in the BTA concentration gave a systematic lowering of the exchange current density, whilst TU behaved in a less predictable manner.

Although many tank-houses in the world use glue, thiourea and chloride as inhibitors, the action of such inhibitors is not yet clearly known but the disadvantages of such inhibitors include rapid decomposition of glue as a result of acidic hydrolysis at high temperatures and the deposition of part of thiourea sulphur in the cathode. In a study by Muresan *et al.* (2003) where the objective was to determine the kinetics of copper deposition in the presence of triethyl-benzyl ammonium chloride (TEBA), an attempt to explain the inhibition process was made but is still unclear. According to Muresan *et al.* (2004), the influence of TEBA on the kinetics of copper deposition was to block or to inhibit the deposition process but did not interfere with the reaction pathway. In essence, the TEBA competed for adsorption sites on the electrode.

In another study by Dow *et al.* (2005) the potential-dependent adsorption of chloride ion on the copper surface was found to be the determining and governing factors of the electrochemical effect of additives on the cathode which resulted in adsorption of inhibiting reagents (PEG + Cl^- + 3-mercapto-1-propanesulfonate and Junus Green B (JGB)) and the asymmetrical filling of copper deposit inside the microvias. The inhibition effect of PEG + Cl^- + C^+ and JGB was demonstrated. The dominance of the accelerator and suppressor of inhibition process depended on the chloride ion concentration and the convection due to stirring effect.

3.12 Nodulation

Nodulation on the cathodes is the result of formation of rounded projections on the surface of cathodes. The nodules may be started by an impurity or particle that may deposit on the surface of the cathode. Further deposition of copper on the particle results in an extended growth, which may create problems of shorting and rough surface. Nodulation studies conducted elsewhere have shown that the presence of Nickel (Ni) particles or atoms in the anode copper decreases the exchange current density as determined from the Tafel analysis of electrode reaction (Stankovic *et al.*, 2001). The use of improper proportions of smootheners can also result in the formation of nodules at the cathode surface as reported in the study by Veilleaux *et al.* (2003). The nodules of copper on the cathode can be detected by the use of galvanostatic technique which uses the value of the starting potential and the presence of the cathodic polarisation peak on the potential-time curve (Lafront *et al.*, 2002). Studying the morphology of the deposit using a scanning electron microscope at various magnifications can confirm the results. The inappropriate concentrations of additives (thiourea, gelatine, and chloride) are associated with current densities that generate intergranular microcracks due to absorption of additives and leads to the formation of nodules.

3.13 Impurities

The presence of impurities in solution has been observed to inhibit the deposition of copper on the cathode. Some metals likely to be found as impurities in solutions of electro-winning operations include Silver (Ag), Lead (Pb), Iron (Fe), Cobalt (Co) and Zinc (Zn) (Pletcher and Walsh, 1993). A study by Lozano-Morales and Podlaha (2004) showed that low particles of Aluminium Oxide (Al_2O_3) concentration (12.5g/L) resulted in inhibited deposition rate of copper while the high particle concentration (60g/L) inhibited the deposition rate at low over-potentials and accelerated it at high over-potentials. The cathode nodulation was studied by electro-depositing copper at $38mAcm^{-2}$ from acid sulphate baths containing $0.5gdm^{-3}$ of various suspended particulate (Andersen *et al.*, 1983). The results showed that the conductive particulates such as copper and graphite produced dense nodulation at 50 ^oC and less while Antimony and Silver powders caused pitting as well as nodulation. The non-conducting powders such as lead sulphate, lead dioxide and gypsum produced no nodulation. However the nodulation was found to increase with the increase in temperature particularly from 50 to 70 ^oC. Increasing the copper ion concentration, which was found to decrease the nodulation gnomically, could solve the problems of nodulation. On the other hand, the study by Ashiru (1995) where the objective was to assess levels of impurities during silver deposition in the presence and absence of additives showed that the brighteners were incorporated with the silver deposits and not the inhibitors like Thiourea etc. This could be one explanation to defend the use of additives.

3.14 Summary

The reaction of atoms using the exchange of electrons is the mystery that resulted in the birth of electrochemistry and electrochemical engineering. The application of external voltage is the key factor in the deposition of the metal from the anode to the cathode. The conductivity of ions is the key characteristic in the classification of electrolytes. An interface near the electrode aides the deposition process by selective diffusion and migration of ions.

The potential developed by the anode-cathode pair is electrolyte and electrode material dependent. The kinetics of the circular reactors is dependent on the rates of reaction which results in the dissolution and deposition of copper on the anode and cathode respectively. During the process, electrical energy is converted into heat energy. The ions diffuse in electrolyte according to Ficks Laws of diffusion. The current efficiency is inversely proportional to the distance between electrodes during migration of ions whilst the mass transfer takes place when the electroactive species disappear in the electrode reaction when acted upon by the current. The movement of ions, assumed to be unidirectional in the film, form fluxes of ions. The current efficiency is affected by high current densities, which produce passivity and nodulation on the electrodes. The passivity is the inactivity of the site while nodulation is the excessive growths of copper deposit at one point which may result in short circuiting. This problem can be solved when optimum conditions (optimum current densities) are maintained in the reactors. Therefore, the operation of electrolytic reactors can be either at constant potential or at constant current flow in order to achieve good results. Smootheners can help to stabilise the deposition of copper at low levels of current density whilst producing high current efficiency. Metals found as impurities include silver (Ag), lead (Pb), iron (Fe), cobalt (Co) and zinc. These may produce different levels of interferences on the deposition of copper.

CHAPTER 4

PROBLEM IDENTFICATION

4.0 Introduction

This chapter sets out the nature of the problems that can be encountered in the copper-recovery process using the electro-refining method and includes suggested solutions of how such problems can be solved. The major problems discussed here include the passivity created by conditions beyond normal such as effects of concentration, ineffective smootheners, and effects of electrode distance, active area, temperature, current density and overvoltage on the current efficiency. There are various approaches to solving the problems related to copper recovery as demonstrated by researches conducted elsewhere particularly on the use of inhibitors during electro-refining. The use of current inhibitors and smootheners from plant products opens up the way for cheaper products to be synthesised as the organic types are becoming increasingly costly.

4.1 The Problem and its Setting

The recovery of copper from ores and wastewaters by the electrolytic method is an important element in most copper mining industries. It is important because most applications of copper have a direct impact on society. The making and use of electrical cables for lighting community and business buildings enables the people to see and work at night or in dark places like the underground mine tunnels. The sale of copper has direct effect on the growth of the economy. The recovery of copper from wastewaters brings about a sustainable environment as copper destroys the micro-organisms that bring about its sustainability in the environment. The problems that exist are associated with the quality and quantity of the copper produced. The problem of quantity of copper produced is usually tied to the issues of sustainability in industry.

The more it is produced the more sustainable will be the industry if it is backed by increased sales. The sales depend on the quality and the demand for copper. Increased copper sales would boost the economy of a country. The quality is a key factor in the marketing of such products at the local and international markets.

The key factors that affect the quality and quantity of copper recovered by electrolytic methods are the overvoltage and current density. The potential and current densities are the main driving forces for the electrochemical reactions. Low values may not be effective while higher values would be more effective but may produce irregular deposits that could bring the phenomenon of nodulation, passivity and rough surfaces of copper cathodes (Lafront *et al.,* 2002). The other factors that reduce the quality of copper are passivity, inadequate concentration of electrolyte, the presence of impurities, ineffective smootheners, inadequate electrode-active area and inadequate distance between the electrodes. The most important is the use of inappropriate levels of the overvoltage and the current density. In order to obtain a good product from the copper recovery process, it requires the maintenance of the process parameters at optimum levels. For example, the optimum parameters for the electro-winning will slightly differ from those for electrorefining depending on whether the direct current (DC) or the Alternating Current Reversal (ACR) system is used. But when the parameter, overvoltage, is regulated such that the current induced results in the efficiency being increased, as determined by the amount of copper deposited on the cathode, then the overvoltage used is at the optimum level. The major problem in the recovery of copper by electrolysis in industry has been the reduction of current efficiency and hence the reduction in production. The attempts to solve the problems that occur during the recovery of copper by the electrolytic method should consider all the aspects of the process from the quality and type of electrolyte and material of electrodes to the variable parameters of overvoltage, current density, the distance between electrodes and impurities, ineffective electrode-active area and the temperature in a holistic approach to finding the levels that would give the best operating conditions in order to achieve a high level of the current efficiency. This therefore requires a careful choice of appropriate levels of the operating parameters.

4.1.1 Passivity

The creation of passivity on the electrodes where electro-deposition ceases due to high levels of currents and overvoltages is one factor. The electro-deposition ceases because the dissolution of the metal from the anode ceases or is markedly reduced due a number of factors. The use of high current densities and overvoltages is one factor, which can be resolved by using normal levels that favour the non-formation of passivity. The use of a number of trials of current densities and overvoltages can provide adequate information for the determination of the optimum values. The other factor is the change in concentration of electrolyte during electro-deposition. When the concentration of electrolyte drops, the current density may increase resulting in the development of passivity. This problem can be solved when the concentration of metal ions in solution remains constant (Pletcher and Walsh, 1993:401). An investigation at various levels of overvoltages can produce the overvoltage required for the evaluation of copper recovery. The third factor is the development of passivity due to the formation of a continuous film on the anode, which prevents the dissolution of the metal. The effect is that there is no deposition-taking place at the cathode. On the other hand a film of solid phase formed from salts or complexes of metals with solution components having a high resistivity, with minimum thickness, prevents the ions from entering the solution because the oxidation takes place at the metal-film interface (Koryta and Dvorak, 1987:363-364).

Passivation is used as a means of protecting the metal from corrosion. When the passivating film forms on the anode, the dissolution of metal ions from the anode ceases or is considerably reduced thus reducing corrosion. This point is in agreement with the argument advanced in Antropov (1972:532) that when the passive state region is reached, the rate of dissolution of the metal falls abruptly in the absence of external polarisation. This argument is based on the film and adsorption theories of passivation (Antropov, 1972:507). According to Antropov (1972:508), passivity is not necessarily connected to the formation of polymolecular-oxide film but can be achieved through retardation of metal-dissolution reaction caused by adsorbed oxygen atoms. The oxygen atoms, from the discharge of water molecules or hydroxyl ions, may appear on the metal surface at potentials much less than those that evolve oxygen or those that form oxides. Passivations on metals include the action of oxidizing agents such as nitric acid and anode polarisation. The anodic polarisation can be detected on the potentio-static curves of anode potential versus current density (Antropov, 1972:505).

4.1.2 Temperature Changes

The second factor is the variance of temperature as the deposition of copper progresses. It has been stated in Section 1.2 that the chemical reaction in an electrochemical process releases heat energy, which heats up the electrolyte resulting in the temperature to rise. The deposition process, i.e. recovery of copper, will not be effective until the right temperature called the optimum temperature is reached. According to Skoog and West (1976:433-434), the high temperatures inhibit concentration polarization because the mobility of ions is increased and the viscosity of electrolyte is reduced. In such situations, the overvoltage effects such as evolution of gas can easily be observed. This means therefore that the temperature plays an important role in electrochemical reactions and that the optimum temperature for the system has to be determined experimentally. Additional measures such as the control of temperature at a fixed value, using heat exchange equipment and avoiding the use of high overvoltages and stirring, which tends to reduce concentration polarisation are the desirable features for the system that could help to solve such a problem.

4.1.3 Distance between Electrodes

The third factor is that the increased distance between electrodes results in the drop in the flux. This would have a negative effect on the current efficiency. There are two ways in which the distance between electrodes would affect the copper recovery. One way is that when the distance is increased the electric field that would create the required force to drive the ions would be weak and therefore the flux of the ions would be weak resulting in the reduction in the deposition of copper on the cathode. The other way is that if the distance between electrodes is reduced the electric field would be strong and the rate of electrochemical reaction would increase due to increased energy acting on the ions in electrolyte. On the other hand the chances of creating electrical short circuits would be increased which would result in the reduction of the current density at the surface of electrodes and cause the reduction in the recovery of copper and hence the current efficiency. The distance between electrodes affects polarisation and hence capacitance between electrodes (Umino *et al.*, 2002). The formation of a film of salt complexes would result in the development of passivity, which would reduce the chemical reaction on the electrode surface. Conducting a number of experiments using different distances between electrodes at fixed values of current density and overvoltage in order to determine the value of distance that gives optimum current efficiency could solve this problem.

4.1.4 Variation of Concentration

The fourth factor is that the concentration of electrolyte drops as the deposition progresses and therefore requires either maintaining or varying at the expense of other parameters. This happens when the anode electrode is no longer able to dissolve adequate atoms of copper, which have to change the charge in order to become cations as is the case of electrorefining. In electro-winning, the problem is the depletion of cations in electrolyte, which then results in the drop in the current efficiency. The decrease in concentration is proportional to time as long as the limiting current is not exceeded ($I<I_L$). This relation can be observed in equation (4.1) where V is the volume of reactor (m^3) and the reaction is under current limited control.

$$C_0 - C = Ift / zFV \tag{4.1}$$

When the concentration drops and the current increases, the reaction becomes transport dependent and the current exceeds the limiting value ($I>I_L$). The electrolyte begins to evolve the gas of the oxidised ions and the conversion has a non-linear relationship with time as described in Pletcher and Walsh (1993:107). When both the anode and the cathode are made of the same material and the anode is soluble, the number of moles of ions deposited on the cathode is replaced by an equal number from the anode that go into solution. Over time the anode becomes depleted and the number of moles replacing the deposited ones becomes deficient. At this point the replacement comes from the electrolyte. The current and the overvoltage rise to levels exceeding the limiting values and the current efficiency decreases with time.

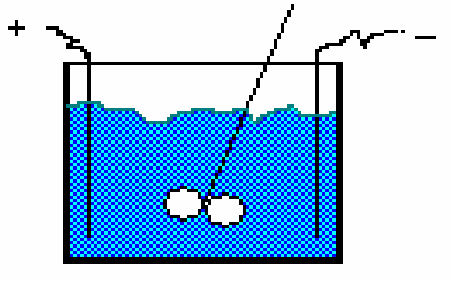


Figure 4.1: Agitated batch Reactor

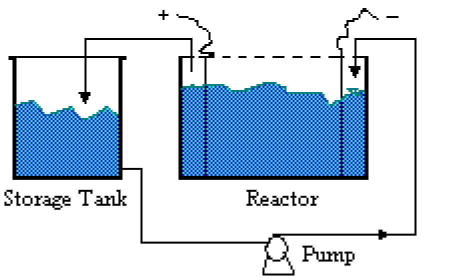


Figure 4.2: Continuous flow Reactor

In order to solve the problem, the circular reactor can be operated as either batch or steady state plug flow reactor (PFR) (Figures 4.1 and 4.2). If it is decided to operate a batch system then stirring might be necessary in order to maintain uniform concentration in the electrolyte otherwise it can also be operated without stirring. It is then easy to observe the effects of the variation of concentration with time, current and overvoltage. If on the other hand a constant concentration is to be maintained throughout the operation then a PFR will be appropriate or a large concentration of electrolyte can be used in order to observe the behaviour of the system.

If the PFR is chosen for the electrolysis, a method that most industrial applications use, then the problem can be solved by allowing the electrolyte to flow continuously through the bank of cells forming the compound reactor. The circulation of the electrolyte allows it to regulate the temperature by cooling in the heat exchanger but also maintains the concentration as the flow mixes and produces a stirring effect in the electrolyte. Extra stirring mechanisms and recirculation of electrolyte can also be incorporated and used respectively in addition to the use of flow of electrolyte as means of regulating concentration and temperature. In this study, a batch reactor was used with no stirring during the operation and therefore convective effects due to stirring were not considered.

4.1.5 Presence of Impurities

The fifth factor is the presence of dissolved impurities which presents the problem of competition between ions in solution especially when the ions have close oxidation potentials; this would result in the ions participating in the chemical reaction (Pozniak and Cole, 2007). There are two types of impurities. The first type is the chemical impurities. The metals that dissolve in electrolyte with copper such as silver (Ag), Gold (Au), Platinum (Pt), Bismuth (Bi), Iron (Fe), Nickel (Ni), Zinc (Zn), Tin (Sn), Rubidium (Rb) and Lead (Pb) may compete with copper when the conditions favour all the elements. The second type of impurity is particulate matter, which may be suspended or dissolved in nature; these impurities may interfere with the deposition of copper or may enhance the formation of nodules on the surface of the cathode. This problem can be solved when a number of experiments can be conducted in order to determine the levels of impurities that would interfere with the electrochemical process using the conditions that favour the dissolution of copper only. The metals Ag, Au, and Pt are nobler than copper and therefore do not dissolve at the conditions at which copper dissolves. The metals Sb, Bi and Sn precipitate after dissolving from the anode and end up in the slimes. The metal Pb forms an insoluble precipitate after being oxidised in the anode and will also end up in the slimes. The metals ions Fe^{2+}, Fe^{3+}, $Co^{2+}$and Co^{3+}, and metals Ni and Zn form sulphate species which remain in solution because such species are reduced at potentials that are more negative than that at which copper deposits. The conditions for copper deposition that tend to eliminate the participation of metal impurities are reported in Pletcher and Walsh (1993:231-233).

The second type of impurities, particulate matter, is brought into the electrolyte during the preparation and handling of electrolyte processes. The particulate matter may be dissolved or suspended. The particles may acquire charge and can be carried along with cations to the cathode where their deposition may result in the formation of nodules.

The deposition of copper on the nodules may be increased resulting in the development of short circuits between electrodes if the electrode separation distance is small. Since the level of particulate matter is unknown, the carrying out of a number of experiments at different levels of particulate matter can reveal the optimum level. Ideally, the zero level of particulate matter would give a high quality surface but due to the nature of operations, particularly in industry, it is not possible to attain this level due to the handling problems of storage, infiltration of particulates during pumping and particulates from the atmosphere.

4.1.6 Inadequate Electrode-active Area

The sixth factor is the electrode-active area. If the electrode-active area is inadequate then the current efficiency would decrease while the opposite is also true. For example, a small active area may carry a high current density and the current efficiency would be affected in that irregular deposition may occur which would bring about the problems of nodulation or passivity as described in Lafront *et al.* (2002). A small electrode-active area is unproductive in the sense that the quantities to be produced would be small. A large electrode-active area would result in the lowering of the current density over the electrode (Karabacak and Lu, 2006). Equation (4.2) describes the relationship between the current, the electrode-active area and concentration. The current density is dependent on the electrode active area and the overvoltage. Since the area (A) does not change during the experiment, a trial of different sizes of electrodes would give the variation of size with current. However, the variation of current with the concentration is a prominent feature in electrochemical reactions.

$$I = k_L nFCA \tag{4.2}$$

When the concentration is kept constant, the current is directly proportional to the electrode-active area (A). At the same time, the current is proportional to overvoltage at a fixed value of electrode-active area. It means therefore that any change in the geometry of the electrode-active area results in the change in the current and overvoltage levels at the electrode. The current density decreases with increasing cros-sectional area. It appears that this is not much of a problem except that large current densities realised from using small active areas, could affect the deposition due to the passivation and release of gas from the electrolyte.

4.1.7 Development of Nodules

The seventh and last factor is the development of nodules on the surface of electrodes due to inadequate separation, which creates short circuits when they grow larger. The formation of nodules may be due to factors such as current density and overvoltage. The current density encourages increased precipitation rate of copper on the cathode at the expense of crystal size (Skoog and West, 1976:433-434). It means that the size of crystals is reduced when the rate of formation is increased. Since the desired product is copper on the cathode, the smaller the size of crystals the better. However, high current densities give rise to irregular precipitates that have low strength. The concentration polarization, due to high current densities and overvoltages, and gas evolution may accompany the deposition process. The effect of this is that a spongy deposit is realised which reduces the efficiency. For example Skoog and West (1976:433-434) state that the usual offender in such situations is hydrogen-cathodic deposition.

The other factor that aids the formation of nodules is the non-effectiveness of smootheners to produce a smooth surface on the cathode. Because smootheners have different properties, their effect on the chemical reaction on the cathode would be different. The most recognisable effect would be the control of the grain size of the deposit on the surface of the cathode. Since the diffusion, migration and convection processes all take place concurrently in the electrolyte, the effect of the smoothener would be to inhibit the excessive deposition of copper ions on the cathode which would result in a smooth grain formation of copper on its surface. The inhibiting action can be achieved by the blocking action of the smoothener molecules, which are larger in size than those of copper ions and therefore produce a filtering action to the copper ions. The ions from the other compounds like sodium chloride attach to the metal cathode before electrolysis and are continuously replaced by the copper ions during the electrochemical reaction. If this action does not produce a good surface on the cathode, it means that the smoothener is not effective. The non-effectiveness of the smoothener would lead to excessive deposition of copper that would lead to the development of coarse surface and hence the current efficiency and the overall production would be reduced. The problem can be solved when moderate levels of current densities are used. Controlling cathode potentials or the addition of depolarisers could also control the evolution of gas. A number of current inhibiting actors (smootheners) have been tried in order to reduce the problem of nodulation and irregular deposition of copper (Stelter *et al.,* 2002). Thiourea has been extensively used as grain refiner (Hiskey and Cheng, 1998) but the use of K-Glue, B-Glue, and P-Glue in electrorefining of copper has not been reported in literature.

4.2 Assumptions

An assumption is a proposal that is required to be verified in the study. Although it may have been proven elsewhere by the process of search, the use of research can either confirm or disprove it. If the assumption survives the experimental testing then it becomes a theory that can be subjected to many other studies that would approve or disapprove it based on the evidence obtained. The assumption is also an expression of opinion based on incomplete evidence. The research commences with a number of questions one of which is “Is the assumption true or false?” The other questions might be: How does the parameter affect the result? How long does it take to obtain the expected result? What level of the independent produces lowest and highest results? What is the quality of the result? What is the effect of impurities, temperature, concentration and smootheners on the recovery of copper?

The assumption sets out the relation between the expected result and the output. The output is the variable that is used to produce the result. For example, if the output is overvoltage and the expected result is the deposited copper on the cathode then the output has an effect on the result. This answers the question “What is the effect of overvoltage on the recovery of copper?" If "Copper is deposited on the cathode" (is the answer), then the result is good and the level of overvoltage is appropriate. If on the other hand the result is poor then a wrong level of output is used and would require adjustment to the level so that it gives the good result. Such action is called optimisation. The aim of optimising a process is to maintain optimum values of variable parameters in order to continuously bring about the desired result. Another example, which is the further explanation of the first, is that if $Y = 2X$ where X is the independent and Y is the dependent variable, any change that is effected in X will affect the value of Y. A further explanation to this example is that the value of Y should be equal to twice that of X. If upon assigning the value of X the value of Y is not equal to twice that of X then the assumption is not true but false and therefore disproved. This explains how the Null Hypothesis can be used to confirm or disprove the assumptions. A similar approach was used in analysing the assumptions that were identified for the study.

4.2.1 Assumption 1

The first assumption is that increased overvoltage and current density increases the rate of deposition and hence affects the current efficiency. This assumption relates to the first problem where passivity is created due to excessive overvoltage or currents. In order to prove or disprove the assumption, a number of experiments were carried out using different levels of overvoltage and current densities, while keeping the distance between electrodes constant. It was expected that the efficiency close to 100% could be obtained only at the right level of the overvoltage and current density. It has already been stated that excessive overvoltages produce passivity, which reduces the deposition of copper onto the cathode. Therefore reduced overvoltage would deposit less copper.

4.2.2 Assumption 2

The second assumption is that the temperature improves the current efficiency. This relates to the second problem where the generation of heat energy by the chemical reactions in cells results in the rise in temperature. The carrying of electrolysis at different intervals of temperature would provide evidence on which to prove the effect of temperature on the current efficiency. If the increase in temperature does not increase the current efficiency then the assumption is false.

4.2.3 Assumption 3

The third assumption is that the distance between electrodes affects the current efficiency. This assumption relates to the third problem where conducting the electrochemical reaction with increasing distance between electrodes can affect the current efficiency. The decreased distance can increase the current density and the rate of electrochemical reaction. The development of nodules is attributed to the use of high overvoltages. The formation of nodules has been reported in studies conducted elsewhere (Stankovic *et al.*, 2001; Veilleaux *et al.*, 2003).

4.2.4 Assumption 4

The fourth assumption is that the concentration of electrolyte affects current efficiency. This assumption relates to the fourth problem where the concentration is a major factor in the deposition of copper. At fixed value of electrode-active area, the current efficiency is proportional to concentration as long as the limiting current is not exceeded. This is achieved when the system is operated at the current-limited control. Equation (4.3) can be used to derive the relationship.

$$\Phi = k_L zFAC / I_L \tag{4.3}$$

As soon as the limiting current is exceeded, the overvoltage increases and the current efficiency decreases. The plot of current efficiency and the concentration gives the behaviour of the system as described by equation (4.4) on which the assumption can be proven or disproven.

$$\Phi = zFV(C_o - C)/It \tag{4.4}$$

For the case of electrorefining, the current efficiency is dependent on the concentration as described in equation (4.4) where its data is indicated in Table: 4.1.

Table 4.1: Effect of concentration on the current efficiency

Concentration (mol/L)	Time (s)	Current Efficiency
C_0-C_1	t_1	F_1
C_o-C_2	t_2	F_2
C_o-C_3	t_3	F_3
C_o-C_4	t_4	F_4
C_o-C_5	t_5	F_5

4.2.5 Assumption 5

The fifth assumption is that the impurities affect the current efficiency. This relates to the fifth problem where increasing concentration of impurities would produce an effect on the current efficiency. There are a number of ways in which this assumption can be proven. The first way is that if the current efficiency exceeds 100% then it would mean that other metals other than copper have been deposited on the cathode or error has been introduced during the process of measurement. The other way is that the deposition of particulate matter on the cathode grows and causes short circuits between the anode and the cathode assuming a narrow distance of separation though it may be the optimum one, resulting in the reduction of current density at the electrodes and hence can affect the current efficiency.

4.2.6 Assumption 6

The sixth assumption is that the electrode-active area reduces the current efficiency. This relates to the sixth problem. The current density is lowered by the increase in active area at constant overvoltage. The lowering of current density would result in the lowering of the deposition rate. Regardless of the type of system, whether it is the continuous flow reactor (PFR) or batch system, the conversion as given by equation (4.5) is affected. The active area can be determined using the method described in Pletcher and Walsh (1993:85) and then evaluating the conversion from equation (4.5) where b^{11} is given by $k_L t$. If the active electrode-active area is large then the conversion would be large and vice versa and thus proving or disproving the assumption.

$$X_A = \{(1+b^{11}A_s)-1\}/(1+b^{11}A_s) \tag{4.5}$$

4.2.7 Assumption 7

The seventh assumption is that the effective inhibitors reduce the formation of nodules on the cathode. Effective inhibitors affect the current efficiency. The assumption relates to the seventh and last problem where the nodules form due to ineffective smoothening. In order for the smoothener to be effective, the right amount of its concentration is required during the operation. Therefore the right level of concentration can be determined experimentally. Smootheners may be required to achieve the desired result.

4.3 Summary

The recovery of copper from ores and wastewaters by electrolytic method is an important element in most mining and other industries. The problems that exist are associated with the quality and quantity of copper that is produced. The key factors that affect the quality and quantity of copper are the overvoltage and current density, electrode-active area, distance between electrodes, level of electrolyte concentration, smootheners and impurities, and temperature. Attempts to solve the problems of the operation of circular reactors should consider all the aspects of the process from the quality and type of electrolyte and material of electrodes to the variable parameters of the factors that can affect the current efficiency in order to prove the assumptions.

CHAPTER 5

METHODOLOGY

5.0 Introduction

The methodology sets out the materials and equipment that were assembled and operated in order to measure the various parameters or variables in the study. It provides information on the relations between the dependent and independent variables on which the conclusion can be drawn. The methodology is therefore critical as the results are determined by it. In describing the methodology for this study, it has been segmented into several sections; study design, preparation of reactors, measurements of current, temperature and voltage, the preparation of electrolytes and compositions of smootheners, measurement of impurities and data analysis. Each of these sections provides adequate information on which experiments can be carried out in order to obtain the results in a similar manner. The study design gives information on how the study was set out and how it can be accomplished in order to achieve the prescribed objectives. The methodology on preparations of electrolytes and smootheners and the measurements of current and voltage provides the conditions that are critical in order to obtain accurate results.

5.1 Study Design

The study design is an approach that is used to solve the identified problem using the predetermined methodology in order to achieve the objectives. The variables are identified and used to obtain the general behaviour of the system when the independent variables are manipulated. Sometimes the dependent variables themselves can be subjected to the treatment and the effects are observed after the treatment. The experimental study design is the most common design used for scientific and engineering projects. It is the method that leads to the achievement of the objectives while reducing the error of uncontrolled variations on the treatment or comparisons. According to Barnard and Cronje (2000:47-48), the idea is to use common sense in grouping the units into sets, and then assigning the treatments so that each one occurs once in a set. In most experimental designs, the variables are independent and dependent. It is the independent variables that are manipulated. Any change on the independent variable can either have an effect on the dependent or not. The cause is induced on the independent and the effect is observed on the dependent. By identifying a number of variables in a study it is possible to achieve the objectives. It is for this reason that a number of variables were identified for this study based on the experimental design. The most important variables identified for the study were temperature, concentration of electrolyte, current, overvoltage, distance between electrodes, electrode design or electrode-active area, smoothener concentration and the current efficiency. These variables were also identified to be the most critical variables for the study.

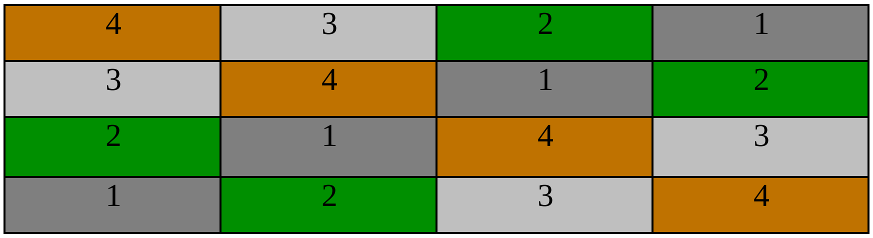
The experimental designs can use single-variable or multi-variable designs. There are three types of single-variable designs. These are; before-and-after without control, before-and-after with control and after-only with control. The before-and-after without control is the experimental method in which the test units act as their own control. According to Barnard and Cronje (2000), the method measures the dependent variable before it is exposed to the treatment and again after it has been exposed. However Barnard and Cronje (2000:49) argue that this experimental method exerts no control over the influence of outside forces. The before-and-after with control introduces another dimension to the before-and-after without control. Some of the limitations of the before-and-after without control method can be overcome by introducing the control units or groups. However, the sizes of the test and control units must be the same. For example, if a study is to be conducted with a sample size of 350, both the test and control units must have the same sample size. The after-only with control single variable design provides only two measurements to be made. A measurement can be taken on the test unit and the other on the control unit. The difference gives the effect of the treatment.

In multi-variable designs, a number of multi-level treatments can be tested using two or more variables and the researcher can also use these designs to control the effect of one or more of the extraneous factors. The common practice is to use randomised designs and advanced statistical techniques to analyse the data. There are three types of multi-variable designs; completely randomised design, randomised block design and Latin square design. These designs are used to test the effect of the variable at different levels. They can also be used to test two or more treatment variables. This is the reason why they are sometimes referred to as factorial designs. The completely randomised design is the simplest form of multi-variable design. The treatments are conducted randomly on the test units and the effect is observed by determining the variance, which shows whether there is a significant difference between the various units.

The randomised block design requires that the conditions must be the same in each of the units that is subjected to the test. For example, if it is a social economic survey, the conditions in high-income groups may not be the same as those in low-income groups. Therefore a better comparison would be low-income grouping to another low-income grouping while a high-income group should be compared to another high-income grouping in order to avoid misleading results. According to Barnard and Cronje (2000:52), the randomised block design enables the researcher to control the effect of one of the main sources of variation while measuring the effect of treatment.

The Latin square design is a design that uses the Latin square which comprises the square of four horizontal and four vertical columns. The Latin square allows the researcher to control two sources of extraneous variation provided that they do not influence each other. Each unit in the square appears once in the horizontal row and once in the vertical one. For example, Table 5.1 shows the number (1) appearing once in each of the rows and columns in the Latin square. In the Latin square method, the number of vertical variables should always be equal to the number of horizontal variables. The application of this design is in the analysis of data particularly when determining the correlations between the variables as in One and Bivariate correlations which are used to investigate the type of model that can fit the data.

Table 5.1: The Latin Square design



4	3	2	1
3	4	1	2
2	1	4	3
1	2	3	4

In the determination of the effect of current density and overvoltage on the current efficiency and rates of deposition, the distance between electrodes was set at a fixed value while the overvoltage, current, and current density were varied in order to obtain the effect on the recovery of copper on the cathode. The Latin Square method of analysing data was then possible by using four different distances in the square for data collected at the same temperature.

In the determination of the effect of distance between electrodes, the current, current density, and overvoltage were kept at constant values while the distance was varied in order to obtain the effect on the copper recovery. Again the use of the distances at the same temperature formed a Latin Square that was used in the analysis of data.

In the determination of the effect of concentration of electrolyte, the electrochemical reactors were operated at constant temperature and constant reaction volume. The concentrations were different for different samples. It is important to understand that the reactors were operated as batch reactors. The concentration of reactants changed during the chemical reaction. The limiting reactant was the copper ions while the excess reactant was the acid (H_2S0_4).

The effect of impurities on the current efficiency was studied using different levels of impurities in the electrolyte and observing the effect on the cathode surface. The values of electrode distance, current and current density and overvoltage were kept at controlled levels. The quality of surface was used as criteria for the determination of the effect of impurities on electro-deposition and the weight of the cathode was used as a guide to the efficiency for the recovery of copper by this method. The weight of the cathode was a key criterion for determining the efficiency of operation.

The effect of smootheners on current efficiency was studied using the type and concentration of smootheners. The values of the current, current density, distance between electrodes, and overvoltage were kept at fixed values. Various levels of smoothener concentration were used (one at a time of each type) during the operation of the reactors. The recovery was monitored in order to determine the effect before-and-after with control of the smootheners on the copper recovery. The weight of the cathode electrode was a key factor in the determination of the efficiency of the recovery.

The effect of temperature on current efficiency was investigated by controlling the temperature using water bath thermostat. Two methods could be used. The first method would be to immerse the heat exchanger inside the reactor and allow the cooling media to pass through it at different flow rates. The flow rate of the coolant would be used as a control of the temperature in the reactors. The second method would be to allow the electrolyte to flow through the exchanger by the forced mechanism of a pump or simply using the gravity. The recovery of copper would be measured at each of the temperatures and compared to the efficiency defined by Faraday's Law. The method used in this study was to place the circular reactors in a water bath whose temperature was controlled by the in-built setting of the thermostat.

The effect of electrode-active area on the current density and current efficiency was studied using various electrode-active areas at fixed values of distance between electrodes, current, current density, and overvoltage. The active area of electrode provided meaningful information on its variation with the current efficiency. Just as before, the key criterion for the determination of the current efficiency is the weight of the cathode at a particular value of electrode-active area.

The timing of activities was set out as is shown in Table 5.2. The proposal was developed during the period from the second month (February) of 2006 to the twelfth month (December) of the same year. The proposal was developed in order to generate the preliminary information on the project, to focus the study and to identify the hypotheses that would be used during the study. It was also meant to identify the activities and the timing of such activities. The literature review provides key information on how other authors have dealt with the subject matter, the methodologies they used and the results that were obtained. It also provides an opportunity to identify gaps, the areas that have not been tackled on the subject matter etc. It was important therefore that the literature review was covered first before the experimental work. Part of the review was carried out at the proposal development stage. This is the reason why it was set to commence in the first month of the project activities in the year 2007. Although five months were used to obtain the required literature, new developments in the field were also checked at other times during the remainder of the study. The procurement of materials was allocated two months because of the uncertainties of the availability of the same from the providers. The construction of cells was given two month. This was due to the fact that the binding of the materials and drying could take a while particular when making the rectangular reactor casings. Therefore more time was needed for this activity in order to avoid the disruption of the project. The experimental activity was allocated more time than the other activities, apart from the activity on the writing of the thesis, because this was one of the most important activity that provided results and the required correlations on the variations between overvoltage, distance between electrodes, temperature, smootheners, impurities and electrode-active area and the current efficiency. Four months were used for the investigation of the effect of smootheners and four months for the investigation of the effect of temperature on the current and current efficiency. The other activities were allocated two months each. It was anticipated that the collection of data in the laboratory would end in good time to have the results analysed, processed and have adequate time for the submission of the thesis and paper in good time. However, the analysis and writing up of the thesis was allocated six months initially but changed to accommodate the review process.

Table 5.2: Duration of project activities

Duration (years)	2006						2007						2008					
Activity/Duration (months)	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36
1 Developing the proposal	🟩	🟩	🟩	🟩	🟩	🟩												
1. Literature Review							🟩	🟩	🟩	🟩	🟩							
2. Procurement of materials							■											
3. Construction of cells								🟪										
4. Experimental																		
(i) Effect of current and voltage									🟪									
(ii) Effect of distance										🟩								
(iii) Effect of smootheners										🟩	🟩							
(iv) Effect of Concentration												■						
(v) Effect of impurities											■							
(vi) Effect of electrode area												🟪						
(vii) Effect of temperature											🟪	🟪						
5. Writing the Thesis and paper								🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦		
6. Review of Paper and Thesis																■		
7. Submission of Paper and Thesis																	■	■

5.2 Preparation of Reactor Baths

The material of the reactor baths must be that which does not react with electrolyte or does not dissolve in electrolyte. This is because the electrolyte in electrochemical cells contains sulphuric acid, which may create corrosive conditions on the reactor bath surface. It is for this reason that reactor baths may be lined with polymeric materials that are highly resistant to corrosion-action of acids. Rubber, Glass and Perspex are materials that are highly resistant to corrosion. This is why glass beakers (Pyrex) and rectangular-perspex containers were assembled and constructed respectively for the recovery of copper. The beakers were used as single pair reactors while the perspex-rectangular containers were used as multiple cell reactors at lower temperatures. The electrochemical reactions were conducted in cells each containing a specific volume of electrolyte, cathodes and anodes (Figures 5.1 and 5.2 and Appendix 8: Figures 5-6).

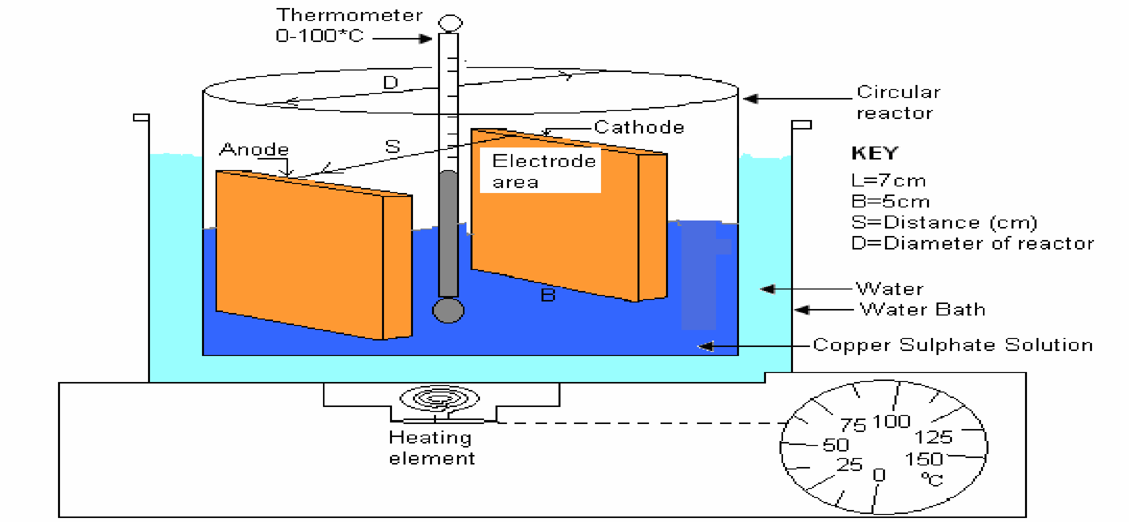


Fig. 5.1: Circular electrochemical reactor with electrodes

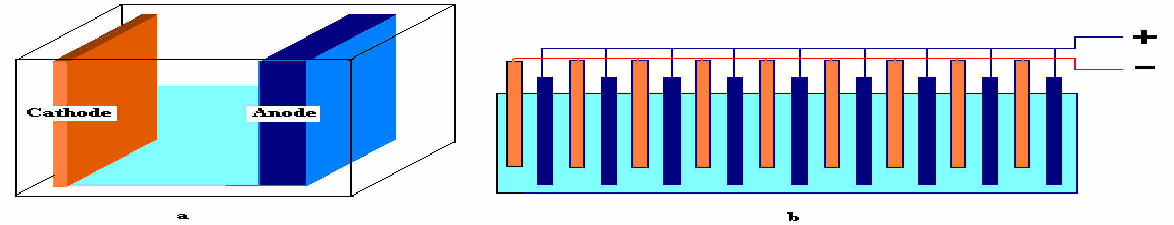


Fig. 5.2: Electrochemical reactor with (a) single cell and (b) bank of cells

The cells were supplied with external potential through anodes and cathodes and the current was distributed over the electrode surfaces. There were a number of cathodes and anodes in each battery of cells although a single electrode pair was also used. Each pair of electrodes was treated as an independent cell and therefore the analysis was based on such single cells. It was not important to consider all the cells because the electrode active areas were the same and therefore the cells were identical.

The cooling of the reactors was achieved by the use of heat exchangers (water baths) in which the reactors were immersed at a particular temperature. The temperatures were chosen from a range of 24 to 60^{o}C in order to determine the variation with the current efficiency. This range was chosen because it is the safest range that does not affect the properties of organic smootheners that were chosen for the study. The properties of plant-based smootheners (K-Glue and B-Glue) would be affected particularly their viscosities. The current, voltage and the weights of the cathode were measured at each temperature setting in order to determine the current efficiency. The water bath was fitted with an electrical heating element that was controlled by the thermostat. There was no direct contact between electrolyte and the cooling medium and the reactors were operated without stirring.

The reactors were assembled so that they could use direct current (DC). Although initially Periodic Current (PRC) was proposed, logistical problems could not allow the research to proceed with this method because the gadgets could not be found. The anode and cathodes were made from the copper starting sheets that were produced in the local mining industries and other vendors. After cutting to the required size the anodes and cathodes were dipped in the solution of copper sulphate dissolved in water. The copper sulphate is a good source of copper ions. It is also a salt that dissociates highly in water. The power was applied across the cells by connecting the negative terminal to the cathode and the positive one to the anode in order to complete the circuit. The positive terminal was connected to one side of the rheostat while the other positive was then connected to the anode. This was done in order to control the current flowing in the circuit. It was also used to set the value of the current required at a particular setting of the experiment. The arrangement was then ready for taking measurements.

5.3 Measurements

5.3.1 Electrode-active Area

The effect of electrode-active area on the current density and current efficiency was studied using various electrode-active areas at fixed values of distance between electrodes and overvoltage (V). The current density (j) was determined by the level of overvoltage and the concentration of electrolyte. Four runs were conducted at each level of overvoltage and the average values of the mass deposited and expected current density were obtained for each run in order to determine the variations with the electrode-active area. The variation of the expected current density with electrode-active area can be seen in Table: 5.3 at each set value of overvoltage.

Table 5.3: The variation of current density with electrode-active area

Active area	*10 cm^3*		*12.5 cm^3*		*17.5 cm^3*		*22.5 cm^3*		*30 cm^3*	
N^0	V Volt	j A/cm^2	V Volt	j A/cm^2	V Volt	j A/cm^2	V Volt	j A/cm^2	V Volt	j A/cm^2
1	0.1	j_1	0.1	j_1	0.1	j_1	0.1	j_1	0.1	j_1
2	0.2	j_2	0.2	j_2	0.2	j_2	0.2	j_2	0.2	j_2
3	0.3	j_3	0.3	j_3	0.3	j_3	0.3	j_3	0.3	j_3
4	0.4	j_4	0.4	j_4	0.4	j_4	0.4	j_4	0.4	j_4
n	V_n	j_n	V_n	j_n	V_n	j_n	V_n	j_n	V_n	j_n

V_n= Set value of voltage and j_n=Expected current density at the applied overvoltage

A Metre Rule was used to measure the sides of the electrodes that were dipped in electrolyte in order to determine the electrode-active area. The product of the sides gave the electrode-active area. The level of electrolyte inside the reactor was kept at constant value during the reaction by topping up the electrolyte when it dropped due to evaporation particularly at the temperature of 60°C. The evaporation process was not significant at other temperatures. Effects of evaporation were not significant in this study.

5.3.2 Effect of Current Density and Overvoltage

The measurements of current and overvoltage were carried out using the circuit shown in Figure 5.3. The circuit comprised the reactor bath with anode and cathode electrodes, the dc-voltmeter (V), dc-ammeter (A), the variable resistor (R) with a capacity of 50O and the variable power supply (E) with AC and DC ports (0-25Volts). When the power was switched on, the current was allowed to flow in the circuit. The resistor was then used to adjust the overvoltage and hence the current that was used to drive the ions in the reactor. The current was drawn from the cathode to the anode. The readings of current, concentration and overvoltage were taken periodically in order to determine the effect of current and current density on the current efficiency. The cycle of measurements for the mass that was deposited was fifteen to twenty minutes or thirty minutes. It was also possible to determine the cycle of the operation from the periodical measurements.

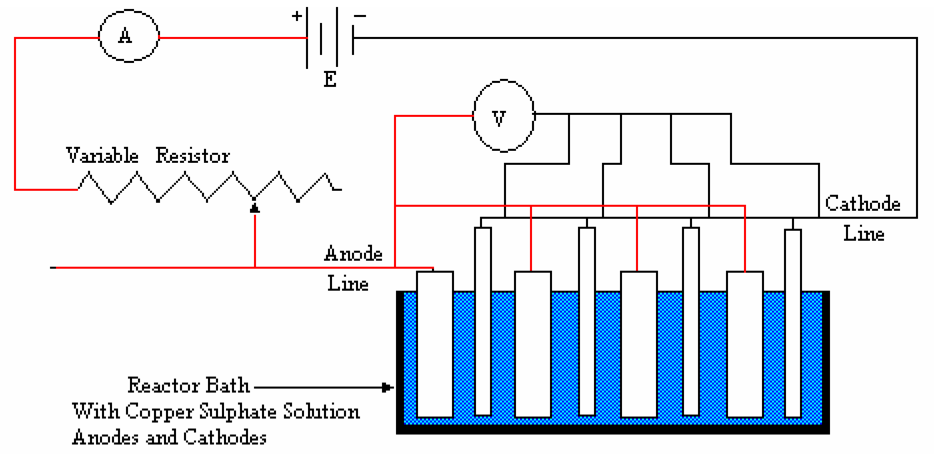


Figure 5.3: Experimental apparatus for the measurements of current and overvoltage.

The dc-ammeters and dc-voltmeters were used for the measurement of the current and voltage respectively using indicating arrows built in the meters. A variable resistor

(Rheostat) was used in order to vary the voltage and hence the current across the cell so as to compare the effect of different values on the deposition of copper. The connections were the positive of the voltmeter to the positive of power supply and negative to the negative i.e., in parallel while the ammeter was in series.

5.3.3 Smootheners and Additives

Smootheners were prepared from different materials and introduced in the solution in order to determine the best composition of smootheners that could improve the current efficiency. This process can result in the development of new types of smootheners. The materials used during the study for the making of smootheners include reagents; Glue, Thiourea, Sodium Chloride or Potassium Chloride, Gum Arabic, Ethylenediamineteraactic acid (EDTA), K-Glue, P-Glue and B-Glue and Sulphuric Acid. Each amount of the stated smootheners was weighed and dissolved in water and the volume was made up to the mark of the volumetric flask. Dilution was done in order to obtain the concentration required. A known volume of each of the smootheners was added to the samples before the electrochemical reaction was conducted. This was done in order to determine the effect on the current density and current efficiency. Any change in the combination of Glue, Ligno and Salt or use of a different type of glue produced changes in the current density and hence the current efficiency. A plot of the volume of smootheners on the independent axis, the current density and current efficiency on the dependent axis provided the correlation required for the analysis.

5.3.4 Temperature

The operation of the reactor at different temperatures provided information on the variation of temperature with current and current density as well as the current efficiency. The temperature was measured using the mercury-in-glass Thermometer (0-100^{o}C). Values of 24, 39 and 60^{o}C were chosen because this is the range in which plant based glues would not be affected by heat and therefore would give maximum application to the smoothening effect. At temperatures above and below this range the glues would break down in their properties and solidify at temperatures below this range. The periodic measurement of temperature was beneficial in order to monitor the effects on the current, current density and current efficiency. Before taking the measurements, the thermometer was checked for its latest calibration in order to ensure that the thermometer was in good order with continuous mercury inside. The thermometer was then dipped in electrolyte for thirty seconds. The reading was then recorded. Repeated readings (4) were carried out in order to ensure that the average temperature was obtained. Parallax error was eliminated by positioning the instrument at right angles to the eye.

5.3.5 Impurities

The impurities were weighed using a weighting scale and the weighed amounts were dissolved in water and made up to the calibrated volume of the volumetric flask. The impurities were then diluted to the required concentration and were introduced in five to six different samples containing the same concentration of reactant. The samples were then subjected to chemical reaction in order to determine the effect of impurities on current efficiency. This was done in order to determine the level of metals that would affect the electro-refining process. Previous studies by Lozano-Morales and Podlaha (2004), Mackinnon *et al.* (1985) and Stankovic *et al.* (2001) have also addressed the issue of metal and other factors on the electrodeposition of metals. The types of impurities used were Silver Nitrate, Bismuth Nitrate and Iron (Fe), Zinc (Zn) and Cobalt (Co).

5.3.6 Distance between Electrodes

The distance between electrodes was measured and set using a Metre Rule. The electrodes were placed at different distances (1cm, 2cm, 3cm and 4cm) in the cell, one distance at a time, in order to determine the effect of separation on the current, current density and current efficiency at constant levels of concentration. The electrochemical reaction was also conducted at different values of electrolyte concentrations and constant values of distance between electrodes, overvoltage and current densities. This was done in order to determine the effect on current efficiency. A plot of current, current density and current efficiency as dependents, against the distance between electrodes as the independent, provided the information on the behaviour of the system.

5.4 Data Analysis

The analysis of data was approached in three ways: by data mining, data exploration and final analysis. Data mining is a methodology that is used on large data sets in order to discover interesting aspects, which could further be analysed. Data exploration uses manual techniques that are used to find the way through the data set in order to bring important aspects of the data into focus for further analysis. The final analysis of data incorporates the use of reductive, mathematical and visual techniques. The reductive techniques use aggregation of facts as a basis for the analysis of data. For example the summary and simple statistical methods fall under this technique. The mathematical technique also called classical method, uses data as a whole as the basis for the analysis. The general approach of this technique is the application of the model and then testing the accuracy. If the approach does not yield the desired accuracy then a new model can be tried.

The visual analysis was used as the method in which data as a whole was used as the basis for analysis. The data was presented visually and any modelling could be done as a result of the analysis of the visuals. The models in visuals may not be mathematical but something else. The visual analysis is an important tool because it allows the researcher to use the natural abilities to analyse the data holistically by examining the patterns, trends and structures that are exposed by the attributes of data. According to Cleveland (1993), visualisation is critical to data analysis. It provides a front line attack, revealing intricate structures in data that cannot be absorbed in any other way. The analysis of data was, therefore, done under two categories. The first category is the Exploratory Data Analysis (EDA) while the second one is the Confirmatory Data

Analysis (CDA). Data mining, exploration and visual methods are grouped under this category while classical or mathematical methods fall under the second category.

The EDA is an approach or philosophy for data analysis that employs a variety of techniques mostly graphical in order to maximize insight into data set, uncover underlying structure, extract important variables, detect anomalies, test assumptions and develop models. The approach depends on the attitude of the person that analyses data and on how the data is going to be analysed. The approach is synonymous with the attitude. The philosophy of EDA, according to Tukey (1977) and Velleman and Hoaglin (1981), is not identical to statistical graphics although the two terms are used almost interchangeably. Statistical graphics is a collection of techniques that are graphically based and all focusing on one data characterization aspect. EDA encompasses a larger venue. It is an approach to data analysis that postpones the usual assumptions about what kind of model the data follow with the more direct approach of allowing the data itself to reveal its underlying structure and model (Box *et al.*, 1978). EDA is not a mere collection of techniques but is a philosophy of how the data is dissected depending on what is looked for, how it is looked for and how it is interpreted.

There are a number of ways that are used in EDA for analysing data. Some of the methods include, histogram, sequence plot, autocorrelation plot and lag plot. A histogram may be used for the purpose of summarizing the distribution of univariate data set graphically. A histogram shows graphically the centre or location of the data, spread or scale of data, skewness, presence of outliers and multiple modes in the data. The vertical axis shows the frequency while the horizontal axis the response variable. A sequence plot is an easy way to graphically summarise univariate data sets (Anscombe, 1973; Chambers *et al.*, 1983; Du Toit *et al.*, 1986). The assumption of univariate data sets is that the data behaves like random drawings with a common location, common scales from a fixed distribution. The shifts in location and scale are quite evident from sequence plots and outliers can easily be detected. The autocorrelation plots are common-used tool for checking randomness in data sets (Box and Jenkins, 1976:28-32). Autocorrelations are also used in the model identification for autoregressive, moving average time series models (Chatfield, 1989:20, 49-50). Lag plots check the randomness or not of the data sets. The random data do not exhibit identifiable structures in the plots. On the other hand, non-random structures in the plots indicate that the data is not random. A lag is fixed time displaced in the given data set.

The most techniques used in EDA include the probability plots and goodness of fit of data (Kuo and Marcia 1993:199-223). The normal probability plots are techniques for assessing whether data is normally distributed or not (Chambers *et al.*, 1983). The goodness of fit of data can be tested by the Anderson-Darling Test, which is used to test if data came from a specific distribution (Stephens, 1974). The critical values for the Anderson-Darling Test are dependent on the data distribution that is being tested. Typical values and formulae for normal, lognormal, exponential etc are described in Stephens (1974:730-737, 1976:357-369, 1977). In EDA, the data collection is followed by the analysis with a view to determining the model. In the case of Bayesian analysis, the researcher attempts to use scientific and engineering knowledge in the analysis by imposing a data-independent distribution on the parameters of the selected model. The analysis therefore consists of formally combining both the prior distribution on the parameters and the collected data in order to jointly test the assumptions about the parameters of the model. The building of a model follows the selection of the model, model fitting and validation. In the model selection, the plots of data, process knowledge and assumptions about the process are used to determine the type of model that fits the data. The selected model and the information about the data are used to select an appropriate model-fitting method that can be used to estimate the unknown parameters in the model (NIST and SEMATECH, 2006). Once the parameters have been estimated, the model is then carefully assessed to see if the assumptions of the analysis appear plausible. The checks of model fit can be framed as comparisons to replication distribution under posterior predictive distribution (Gelman, 2004). From the Bayesian stand point, the parameters; data and replicated data have a joint distribution, which is symmetrical (Meng, 1994, Gelman *et al.*, 2003). The use of data frame expands the data matrix in order to allow for more general structures (Chambers and Hastie, 1992; Billard and Diday, 2003).

The models have been developed to fit complex and realistic data, which may include the use of non-parametric and semi-parametric methods, sieve models, tree-based models and adaptive linear regression methods (Tukey and Mosteller, 1978; Hastie *et al.*, 2002). On the other hand hierachical models based on parametric and Bayesian methods capture heterogeneity and non-linearity (Carlin and Louis, 1996; Denison *et al.*, 2002). In this study, only EDA was used to analyse the data in order to determine the models that best fit the collected data. In classical analysis (CA), sometimes called mathematical method, which is similar to and the same as CDA, the data collection is followed by the imposition of a model. Models such as normality, linearity, etc. are followed by the analysis, estimation, and testing of the models which are focused on the parameters of such models. In CDA, the evidence is an important element in the analysis of data because the evidence allows the researcher to evaluate its strength and judges its merits and applicability. The evidence is also the basis for the testing of assumptions and models.

5.5 Summary

The methodology sets out the number of equipment that can be assembled and operated in order to measure the parameters or variables. It describes the study design, individual methods for assessing the variable relationships and the methods of analysing data. The study design is an approach that is used to solve the identified problem using predetermined methodology in order to achieve the objectives. The measurement of voltage, current and temperature was achieved by using voltmeters, ammeters thermometer respectively. The measurements of concentration were achieved by weighing using analytical balance and 1-Litre or 2.5-Litre volumetric flasks. Various combinations of smootheners were used in order to establish their effect on the current density and efficiency at each setting of the reactor. The data analysis was carried out using data exploration plot and bivariate correlations.

CHAPTER 6

RESULTS AND OBSERVATIONS

6.0 Introduction

The results presented in this chapter are the outcomes of numerous experiments that were conducted during the study. A number of investigations were carried out involving the effect of over-voltage, current density, and temperature, level of impurities, surface smootheners, the active area and distance between electrodes on the current efficiency. Because the high currents and voltages can cause instability in the electrochemical system, it was important to initially determine the limiting currents before evaluating the current efficiency.

6.1 Effect of Overvoltage on the Current and Curent Density

The conductivity of electrolyte depends on the type of electrolyte, the pH and the temperature. Obviously, the limiting currents would not be the same at different temperatures. The voltage and current density plots for electrochemical systems containing 5% copper sulphate electrolyte revealed different limiting currents at different temperatures for different distances of separations. At 24^{o}C, as indicated in Figure 6.1 and Appendix 5: A, the limiting current for electrode distances of 1, 2, 3 and 4cm were found to be 12, 6.0, 6.2 and 6.2 mA respectively. The highest value was for the one-centimeter distance. The limiting voltages were found to be 1, 0.6, 0.7, and 0.7Volts for the 1, 2, 3, and 4cm distance between electrodes. As can be observed from the results, the limiting values for the 1cm distance between the electrodes (both voltage and current density), are higher than the ones for the other distances. These limiting currents are too low to support the reduction of copper on the cathode-solution surface.

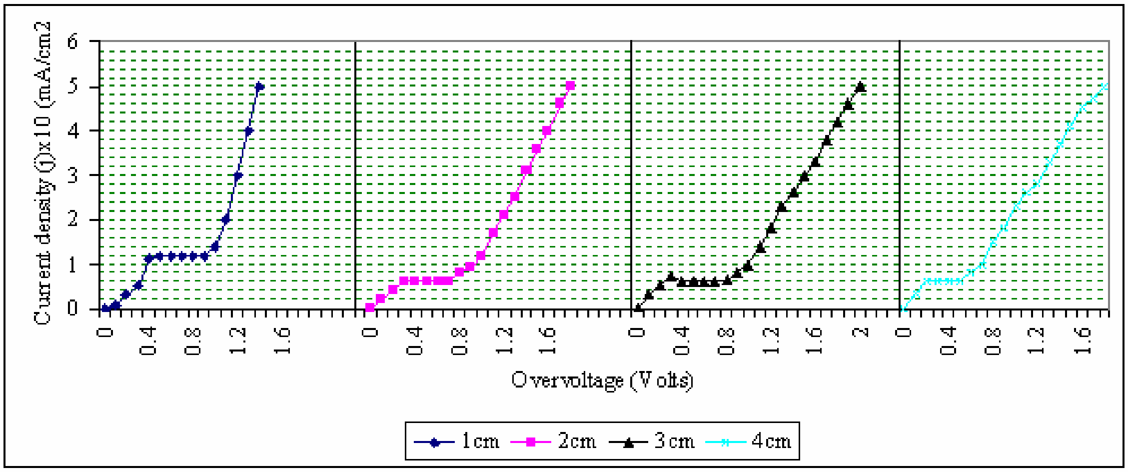


Figure 6.1: Effect of overvoltage on the current density at 24°C

At 39°C, the effect of overvoltage was investigated at distances of 1, 2, 3, and 4cm distances between electrodes. The purpose was to determine the limiting current densities in order to avoid the use of high values which could result in irregular deposition of copper on the cathode. The current densities at this temperature were observed to be different from those at 24°C. The values were found to be 40, 35, 35, and 40mA/cm^2 for the 1, 2, 3, and 4cm distances between electrodes respectively (Figure 6.2 and Appendix 5: B). The corresponding limiting voltages were 0.8, 0.7, 0.6, and 0.5 for the 1, 2, 3, and 4cm distances between electrodes respectively. These values were found to be higher than those obtained at 24°C. When compared to current density values reported by Pletcher and Walsh (1993: 75-77) for the recovery of copper (25-40mA/cm^2) these values fall within the acceptable range that would give an efficiency of 95%. It would appear from the results that the 2 and 3cm distances between electrodes would be the most appropriate at this temperature but the time for the recovery of copper would be increased. This means that the cycle time for the removal of copper from the cell would be increased. For example, one would use a period of one hour instead of 30minutes or 30minutes instead of 15minutes. This enables the system to collect more deposit on the cathode.

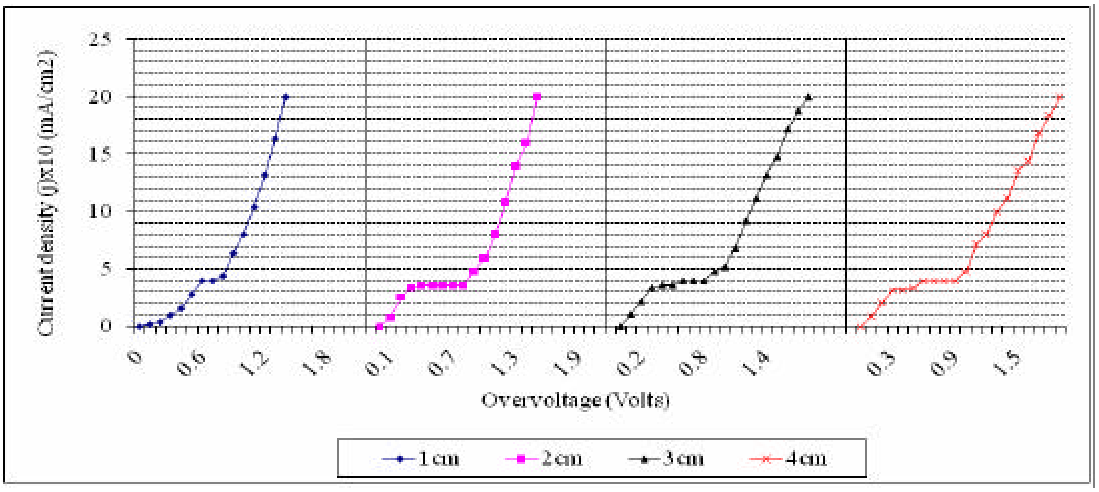


Figure 6.2: Effect of overvoltage on the current density at 39°C

The current densities of copper-sulphate electrolyte at 60°C and at different separations of electrodes were found to be higher than those at 24°C and 39°C. The limiting current densities were found to be 60, 65, 50, and 70mA/cm^2 for the 1, 2, 3, and 4cm distances between electrodes respectively (Figure 6.3 and Appendix 5: C). The corresponding limiting overvoltages were 0.8, 1, 0.9, and 1.1Volts for the 1, 2, 3, and 4cm distance between electrodes respectively. The increase in current densities can be attributed to the complete ionisation of the electorlyte due to the heat of dissociation, solvation provided by the surrrounding and that due to reaction between the acid and copper sulphate. The limiting currents at this temperature provide a wide range of choice of operating current for the reactor at all the four distances between electrodes (Cell Sizes).

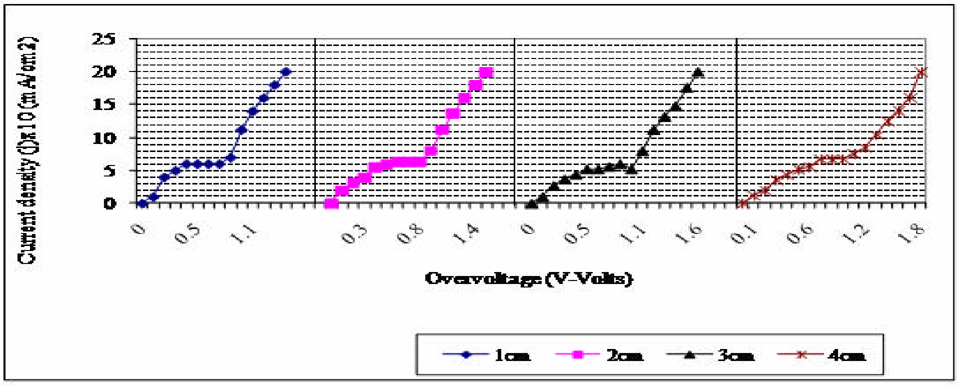


Figure 6.3: Effect of overvoltage on current density at 60°C

The general effect of the overvoltage on the current and current density was found to be that as the overvoltage increased the current and current density increased at the set temperatures. However, it was found that the distance between electrodes did not have any effect on the limiting current density. This can mean that there are other factors on which the current density is dependent. Factors such as concentration of electrolyte and the temperature could play a role in the level of limiting current density in solution.

6.2 Effect of Overvoltage on the Rate of Deposition

The investigation of voltage against the rate of deposition revealed that there was an increase in the rates of deposition for an increase in overvoltage (Figure 6.4). The increase became more intense as the overvoltage increased at all distances of electrodes. The highest value to produce rough surface was found to be 28×10^{-5}g/s for the 1cm distance, 48×10^{-5}g/s for the 2cm distance, $24\times10^{-5}$for the 3cm distance and lastly 64×10^{-5}g/s for the 4cm distance. The deposition rates are highest for the 1cm distance because the field strength, current density and applied overvoltage are high due to small size of the cell or distance between the electrodes. Since the surface of the cathode became irregular at high deposition rates and the deposited mass could not stick to cathode, the impurities could easily be deposited along with copper.

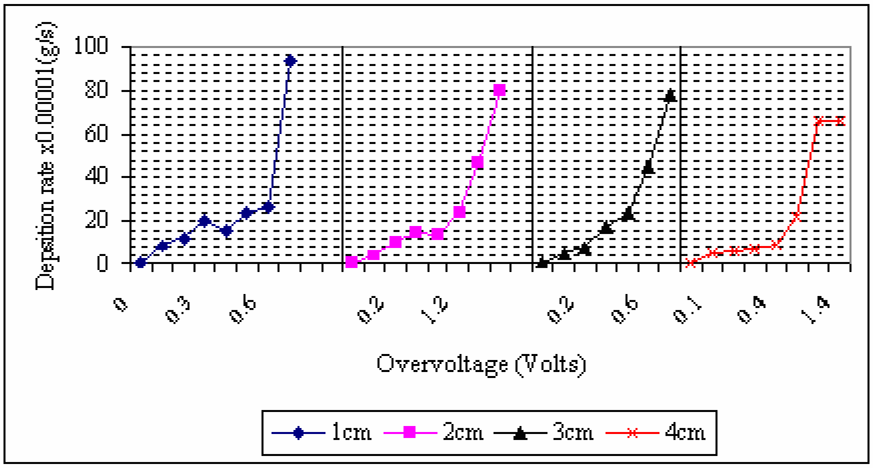


Figure 6.4: Effect of overvoltage on the rate of deposition at 24°C

The deposition-voltage curves are similar to current-voltage curves. The region where the curves are steep, after the limiting overvoltage, the system became unstable and the liberation of hydrogen produced spongy-copper deposit onto the cathode. The rate of deposition increased as the voltage increased. The rate of deposition at 0.3 Volts was lower (19.8x10^{-5}g/s) than that at 0.6Volts (27x10^{-5}g/s) for the 1cm distance. That at 0.2 Volts was lower (10x10^{-5}g/s) than that at 1.2 Volts (24x10^{-5}g/s) for the 2cm distance and that at 0.2 Volts (7.6x10^{-5}g/s) was lower than that at 0.6Volts (45x10^{-5}g/s) for the 3cm distance between electrodes (Figure 6.4). Similarly, the deposition rate at 0.4 was lower (8.5x10^{-5}g/s) than that at 1.4volts (66x10^{-5}g/s) for the 4cm distance between electrodes signifying that the applied voltage influenced the deposition of copper from solution.

It is therefore important to examine the deposition rates and such rates can also be used as means to determine the stable operating region for the reactor. For example, for the 1cm distance 0.6Volts would be the maximum operating voltage while that for the 2, 3 and 4cm distances is 0.5, 0.5 and 0.4 volts respectively because the use of voltage above these levels for the stated distances would produce irregular-loose deposit on the cathode. The results in Figure 6.5 show the effect of overvoltage on the rate of deposition at 39°C for a 5% concentration of electrolyte solution at electrode distances of 1, 2, 3, and 4cm.

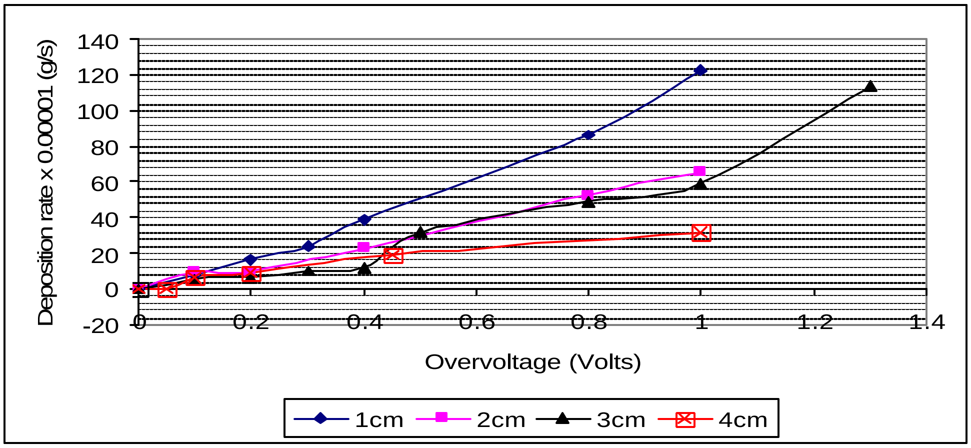


Figure 6.5: Effect of overvoltage on the rate of deposition at 39°C

The general correlation between the overvoltage and the deposition rate was that the rate increased as the overvoltage (overpotential) increased at all the distances between electrodes. The other observations were that the lowest values of deposition rates at 0.1Volts were 8.6x10^{-5}, 9.5x10^{-5}, 5x10^{-5}, and 6.3x10^{-5}g/s for the 1, 2, 3, and 4cm distances between electrode respectively while the highest values reached in the study were 123x10^{-3}at 1.0Volts for 1cm distance, 65x10^{-5}g/s at 1.0 Volts for a 2cm distance, 114x10^{-5}g/s at 1.3Volts for the 3cm distance and 32x10^{-5}g/s at 1.0Volts for the 4cm distance. At voltages above 0.8Volts a non-sticking spongy deposit was observed at the cathode. The spongy deposit made it difficult to clean the cathodes because cleaning could result in loss of the spongy deposit of copper and thus could contribute to the error in the efficiency. The deposition rates below these values for each distance produced a smooth deposit with a copper brown colour. However it was observed that the use of voltage above the limiting value resulted in an irregular, non-sticking and nodular deposit which signified an unstable system. The irregular-spongy deposit could be lost during the washing and therefore could contribute to the increase in error in the rate of deposition and hence the current efficiency as stated earlier. This is the reason why the limiting current was determined before the experiments started.

The effect of overvoltage on the rate of deposition at 60^{o}C revealed a number of patterns in correlations (Figure 6.6). There was an increase in the deposition rates for all distances between electrodes. The lowest rates were 8.8x10^{-5}g/s for 1cm distance while those of 2cm, 3, and 4cm distances were 9.2 x10^{-5}g/s, 3.8 x10^{-5}g/s and 4.1 x10^{-5}g/s respectively at 0.1Volts. The highest values of deposition rates for each distance between electrodes (1-4cm) were 170 x10^{-5}g/s at 1Volt, 150 x10^{-5}g/s at 1.6 Volt, 132 x10^{-5}g/s at 1.6 Volts and 119 x10^{-5}g/s at 1.8 Volts respectively. If we can examine the deposition rate for the same overvoltage and each size of the cell we can see that the values are decreasing as the size of the cell increases. For example, at 1Volt the deposition rate is 170 x10^{-5}g/s for the 1cm size, 80 x10^{-5}g/s for the 2cm size, 78 x10^{-5}g/s for the 3cm size and 48 x10^{-5}g/s for the 4cm size. In general, the deposition rate was found to decrease with the increase in distance. Whilst there was an increase in rates of deposition with the increase in overvoltage, there was also a corresponding decrease in concentration of copper sulphate solution. It is important to note also that the rates of deposition were found to be much higher when the voltages exceeded the limiting values. The increased rates meant that even the elements that have reduction potentials higher to that of copper could be deposited also. The weight of the deposit would thus be increased and the current efficiency would be affected especially for efficiencies greater than 100%.

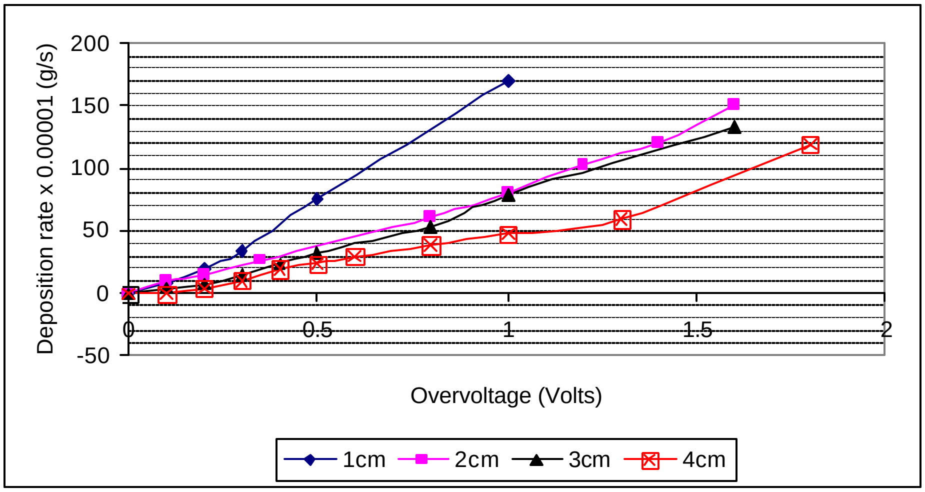


Figure 6.6: Effect of overvoltage on the rate of deposition at 60^{o}C

6.3 Effect of Temperature on Current Density and Efficiency

It has been observed that the temperature enhances the conductivity of ions in solution. Increased temperatures increase the conductivity of solutions. The increased temperatures enhance the dissolution of electrolyte into the solvent thereby increasing the number of ions and at the same time increasing the conductivity. These effects were found to contribute to the levels of current density and efficiency. The limiting overvoltages were found to be in the same range (0.5-1.1Volts) but these produced the lowest values of current densities at 24^{o}C, increased values at 39^{o}C and the highest values were at 60^{o}C. This explains why the choice of operation temperature for the process had to be 60^{o}C. The results in Figure 6.7 further shows that increasing the temperature resulted in the increase in the limiting current density. This phenomenon was observed for all distances between electrodes.

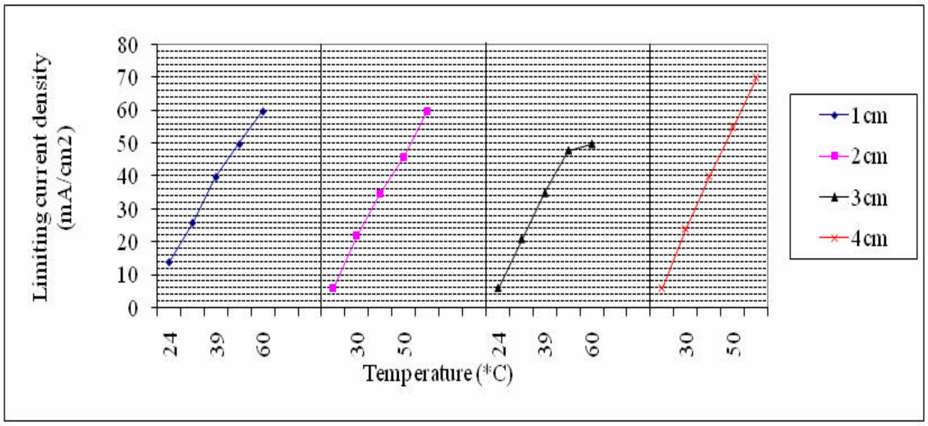


Figure 6.7: Effect of temperature on the limiting current densities

The effect of temperature on the current efficiency, without adding the additives, as shown in Figure 6.8 revealed the most stable and highest efficiencies at distances between electrodes of 2 and 3cm at 24, 39 and 60°C. The lowering of current efficiency due to distance was observed at 4cm at 60°C. This implies that the temperature had little effect on the current efficiency. The choice of the 2cm distance that was used in further experiments was based on the results from experiments conducted so far. Unacceptable values of efficiencies were observed in the case of 1cm distance between electrodes where the efficiency higher than 100%, which is the maximum, was observed at 60°C. This was due to inadequate distance between electrodes which resulted in excessive overvoltage and current density to develop across the reactor.

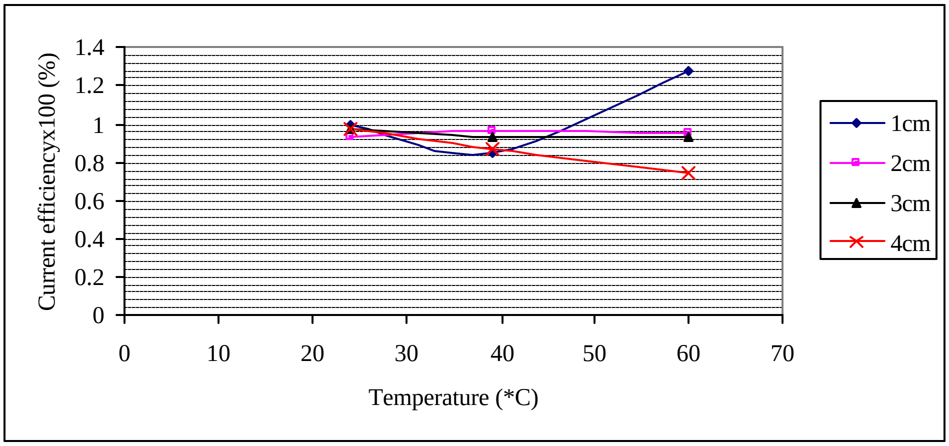


Figure 6.8: Effect of temperature on the current efficiency at 0.3Volts

Generally, the temperature did not have any effect on the current efficiency as is observed in Figure 6.8 for values at 24^{o}C and 39^{o}C for all distances between electrodes and values for the 2, 3 and 4cm distances between electrodes. The decline of values for the 4cm distance might be due to effects of concentration and separation distance. At 4cm electrode distance, the values of efficiencies fell below the maximum value (100%) and therefore were not acceptable. Since high efficiencies (68<CE<100%) could be obtained at all the temperatures, effects of temperature could only be considered in the temperature–concentration of electrolyte system where, as alluded earlier, the temperature aids the dissociation process of electrolyte. The efficiency at 60^{o}C for the 1cm distance between electrodes indicates a distance effect rather than temperature effect and its high value (120%) can be due to increased current density developed at the electrodes, as a result of inadequate distance, that resulted in irregular depositions to be obtained at values of overvoltage from 0.4Volts and above which resulted in unacceptable current efficiency to be obtained.

The fact that the 1cm distance is small, high current density could easily be achieved when 0.3Volts was applied while a low current density could easily be achieved at the 4cm distance due to the increase in distance between electrodes. This is due to the fact that as the distance between electrodes increases, the field strength that produces the current density weakens due to the weakened potential affected by increased resistance due to water molecules in solution. Although the conductivity is increased at higher temperatures, the efficiency can be reduced when the current density is lowered by lowering the temperature which induces the dissociation of electrolyte in solution. This means that temperatures below 24^{o}C would produce fewer ions in solution and hence the efficiency would be unstable because the system would starve for ions sooner than the chosen normal period of electrorefining. In the same token, the temperatures above 60^{o}C would allow the water in the solution to evaporate quicker than expected due to excess heat at such high temperatures. Most organic smootheners would break down particularly those from cellulose material. It is for this reason that the temperatures between 24<T<60^{o}C were chosen for the study. The 60^{o}C was particularly chosen for the later parts of the study because it would allow the copper sulphate to release adequate ions in solution as indicated by the increase in current density with the increase in temperature.

6.4 Effect of Current Density on Current Efficiency

The effect of current density on the current efficiency was investigated at temperatures of 24°C, 39°C and 60°C and distances between electrodes of 1, 2, 3, and 4cm as shown by Figures 6.9, 6.10, 6.11 and Appendices 1, 2, and 3 using data exploration method of analysis. The results for the 1cm and 4cm distances showed efficiencies above 100% at current densities greater than 74mA/cm^2 at 24°C while the efficiencies for the 2 and 3cm distances were found to be normal (80<CE<100%) (Figure 6.9).

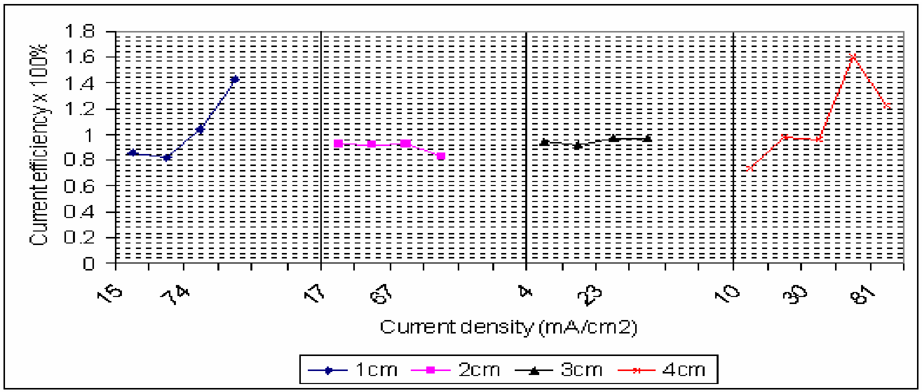


Figure 6.9: Effect of current density on the current efficiency at 24°C

At 39°C, the results for the 1cm distance between electrodes showed a similar pattern as those for the 1cm distance at 24°C (Figure 6.10). The values for the 2cm distance showed some values of efficiencies to be above 100% for current densities above 50mA/cm^2. For the case of the 3cm distance, increased values of efficiencies at current densities above 73mA/cm^2 were observed whilst the efficiencies above 100% were also observed above 30mA/cm^2 for the 4cm distance between electrodes. It can be concluded from the results that stable efficiencies can be obtained for the 2 and 3cm distances between electrodes at the current densities below the 50 and 73mA/cm^2 respectively. It can also be concluded that efficiencies above 100% mean that erroneous readings, error in weighing and parallel reactions may have occurred.

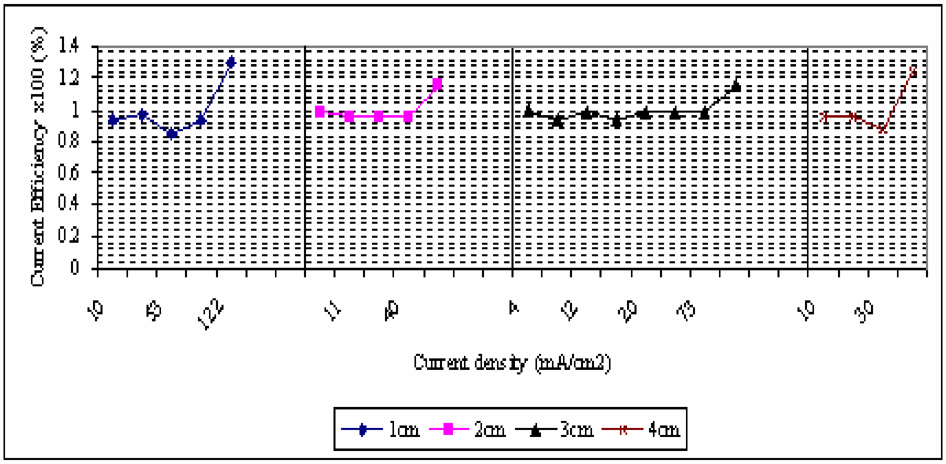


Figure 6.10: Effect of current density on the current efficiency at 39°C

The results for the 1cm distance show that the increase in the current density increased the current efficiency 60°C (Figure 6.11). Efficiency above 100% was observed for the 2cm distance between electrodes for values of current density above 63mA/cm^2. The overall trend of efficiency for this distance was that any increase on the current density produced an increase in efficiency. Erroneous efficiencies for the 3cm distance between electrodes were observed for current densities above 122mA/cm^2 while the overall trend was similar to the one observed in the 1 and 2cm distances. In the case of the 4cm distance between electrodes, the current efficiency ranged from 80 to 90 and 100% for current densities of 14, 37, 59 and 88mA/cm^2 up to 167mA/ cm^2 giving a similar trend to the ones in the 1 and 2cm distances.

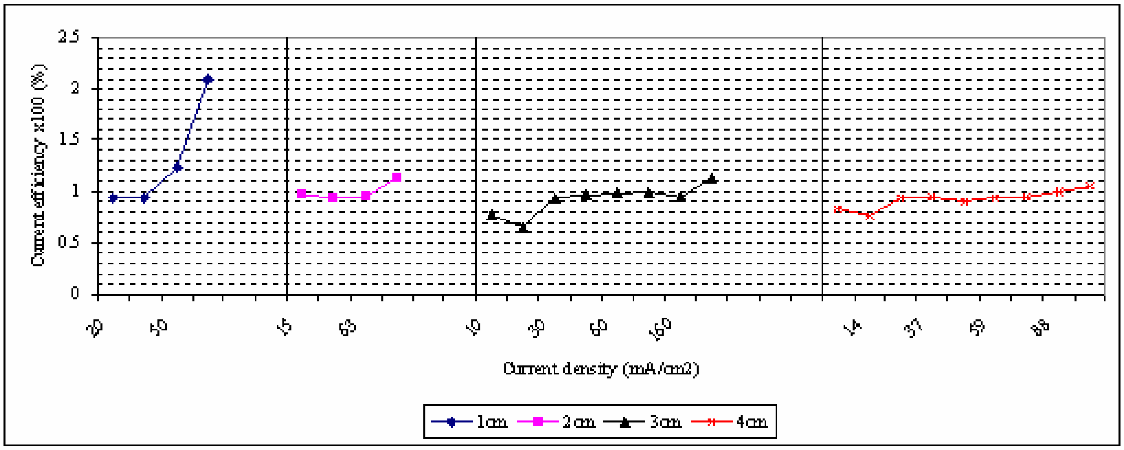


Figure 6.11: Effect of current density on the current efficiency at 60°C

6.5 Effect of Distance between Electrodes

The effect of distance between electrodes was investigated against the current in the circuit for a fixed voltage at three different temperatures (24, 39 and 60°C). The results showed that the 1cm distance between electrodes had the highest currents for all the three temperatures with values of 0.5, 0.5 and 0.6Amps respectively (Figure 6.12). For the 2cm distance the highest and lowest values of current were 0.5Amps and 0.3Amps respectively while in the case of 3cm distance, the highest value of current was 0.3Amps at 60°C (T60) and the lowest was 0.2Amps at 24°C (T24) and 39°C (T39). In the case of the 4cm distance between electrodes, the highest and lowest values of current at 60°C were 0.14 and 0.08 Amps respectively. The results mean that increasing the distance between electrodes increases the resistance across the cell and therefore reduces the current strength and the current density on the active areas of the electrodes. The reduced current density can increase the time for the deposition due to decreased deposition rate that follows at lowered values of current density.

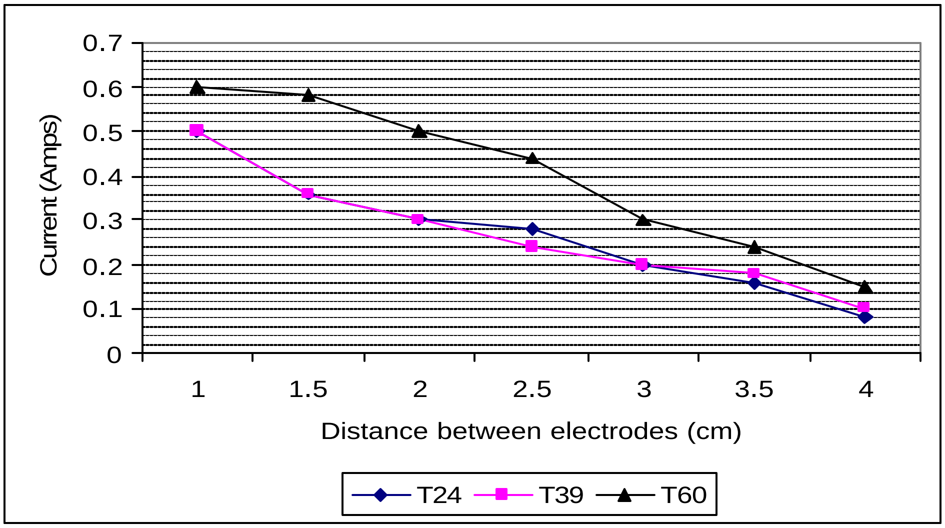


Figure 6.12: Effect of distance between electrodes on the current

It is therefore important to determine the appropriate current for the deposition before the actual operation of the reactors. The practice is to carry out a quick assessment of the current using voltamograph for a particular system which is determined by the concentration of electrolyte and the cell overvoltage.

The effect of distance between electrodes was investigated, also, in terms of the variability between the rate of deposition and the separation of electrodes at the same current. The results showed that at 24^{o}C the highest deposition rate was at 9.2x10^{-4}g/s at 2cm distance while the lowest rate was found to be 2.8x10^{-4}g/s at 4cm distance. The deposition rates at 39^{o}C showed the highest rate was 9.6x10^{-4}g/s at 1cm distance while the lowest rate was 1.2x10^{-4}g/s for the 4cm distance. In the case of 60^{o}C temperature, the highest deposition rate (R_r) was 10.8x10^{-4}g/s while the lowest value was for the 4cm distance at 2.4x10^{-4}g/s (Figure 6.13). At T24 the rate of deposition decreased as the current decreased. A similar pattern was observed at temperatures T39 and T60. It means therefore that increasing the distance between electrodes decreases the current and current density and therefore decreases the rate of deposition due to decreased electric field strength on the electrode-active area.

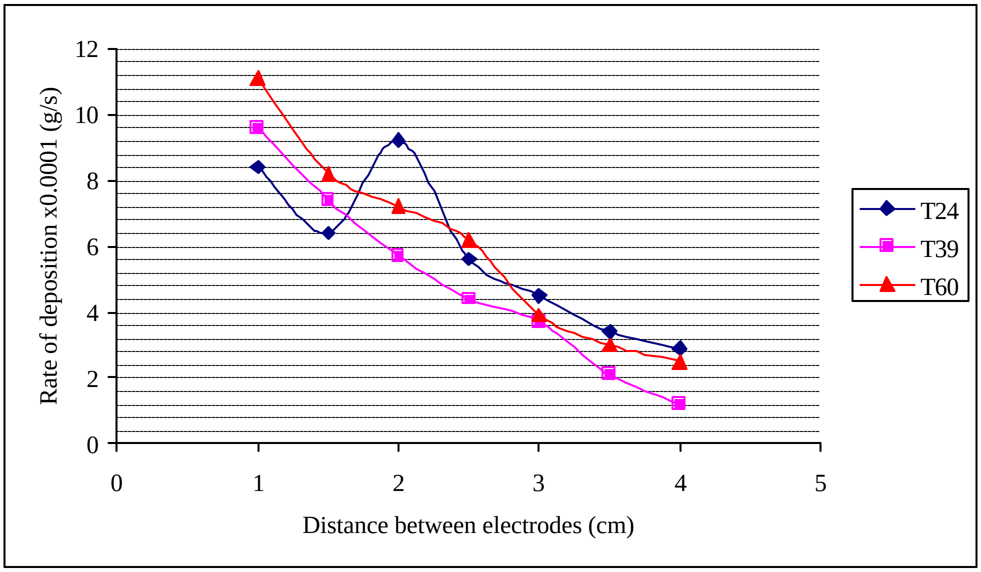


Figure 6.13: Effect of distance between electrodes on the rates of deposition

The effect of distance between electrodes on the current efficiency was investigated at the same fixed voltage (0.3V) at three different temperatures (24, 39 and 60^{o}C). The results showed that the 1cm distance between electrodes indicated the current efficiencies of 100%, 85% and 128% for the 24, 39 and 60°C respectively while the values for the 4-cm distance were 98, 87 and 75% at 24, 39 and 60°C respectively (Figure 6.14). The acceptable level of current efficiency is between 80 to 100%. It appears from the results obtained that the distance between electrodes produced little effect on the current efficiency. This can be seen in Figure 6.14 for the results of CE24 and CE39. Altough some variation can be observed in values for CE60 the current efficiency must be dependent on the charge passed and not on the distance between electrodes. Under the conditions of the experiments, the 2 and 3cm distances between electrodes provided the right level of current density at the range of applied overvoltages (0<V<1.3Volts). It was therefore imperative that the 2 and 3cm distances between electrodes be taken as the best choice for the size of the reactor. It is for this reason that the 2cm distance between electrodes was chosen for the investigation of the rest of the parameters during the study. Although the temperature is important in electrorefining process because it helps the ionisation process of electrolyte, the current density is also important to the efficient electrorefining process.

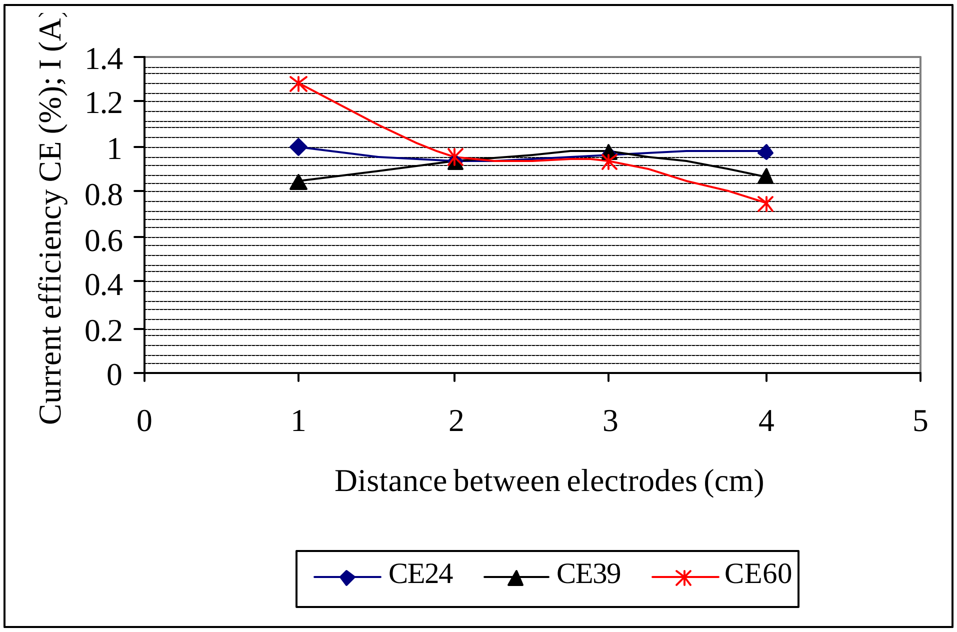


Figure 6.14: Effect of distance between electrodes on the current efficiency at 0.3V

Apart from choosing the correct distance between electrodes and the temperature, the factors such as electrode-active area and concentration of electrolyte could contribute to the efficient operation of electrorefining. The designer of the reactors should ensure that the electrodes provide adequate electrode-active area to allow the smooth recovery of copper from solutions.

6.6 Effect of Concentration on Current Density and Current Efficiency

The solution of electrolyte was prepared in varying concentrations from 1.5g/L to 74g/L. The individual concentrations were 1.5, 3, 6, 8.9, 14.8, 29.6, 59.2 and 74g/L. Other details can be seen in Appendix 4. A voltamogram was taken for each solution in order to determine the limiting currents (Figures 6.15a and 6.15b). The results of the voltamogram showed low values of limiting currents for solutions with low concentration, and high values for solutions with high concentration. A solution with 1.5g/L concentration, which was the least, gave a limiting current density of 1.5mA/cm^2 while the solution with a concentration of 74g/L, which was the highest, gave a limiting current of 70mA/cm^2. The limiting currents for 3, 6, 8.9, 29.6 and 59.2 were found to be 3, 6, 7, 16, 32, and 60mA/cm^2. It can be observed from these findings that the values of limiting currents are equal to the concentration of the solutions in the case of very low concentrations or dilute solutions only.

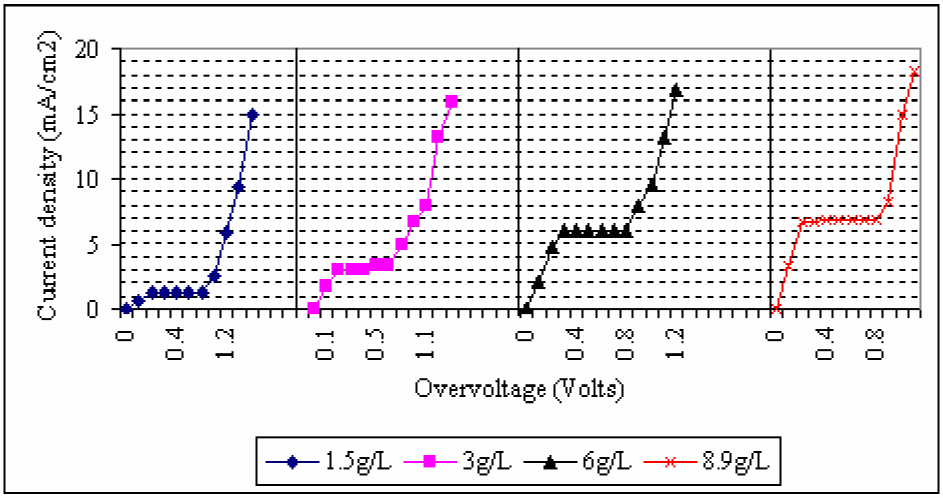


Figure 6.15a: Effect of electrolyte concentration on the limiting current at 60^{o}C

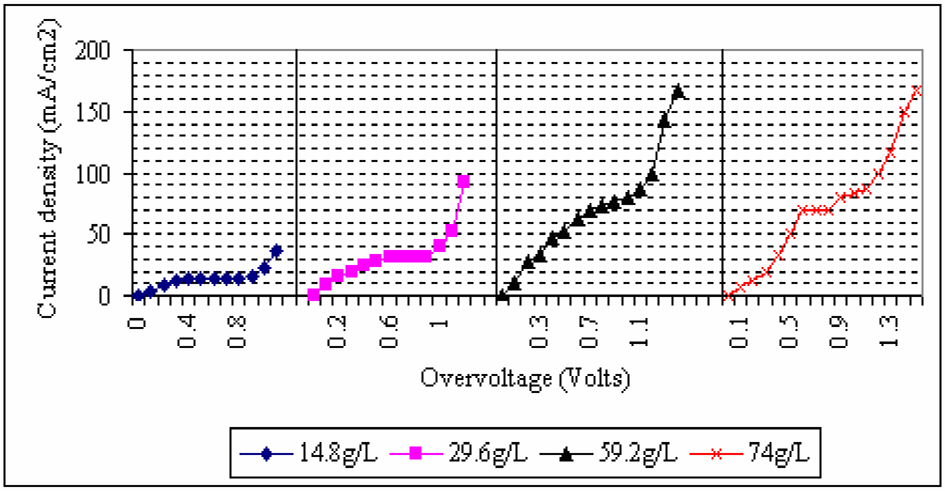


Figure 6.15b: Effect of electrolyte concentration on the limiting current at 60°C

For example, the concentrations of the first three solutions, from the lowest, produced limiting currents equal to their concentration while other solutions did not show a similar pattern.

The results in Figure 6.16 show three distinct regions. The first region is that below the 5g/L concentration, the second one is that between 5 to 15g/L and the third one is that above 15g/L concentration of electrolyte. The first region showed a lot of bubbles on the cathode meaning that the gas was released as by-product of electrodeposition of copper. The gas release accompanied the unstable deposition of copper, which could not stick to the cathode. It means that the potential was above the limiting value and would cause the deposition of metals other than copper. It, therefore, is not advisable to operate the reactor with potentials that fall in this region, as the cathode would be passivated in a short period of time (15 minutes) and the impurities would distort the values of current efficiency. The second region is the transition region. The conditions for operating the reactor within this region would be at the concentration of 10g/L with a potential below 0.4Volts and above 0.1Volts. The third region was found to be the most stable region for concentrations above 10g/L. The minimum concentration for operating the reactor with stable conditions was 10g/L for all ranges of currents from 0.1 to 0.5Amps.

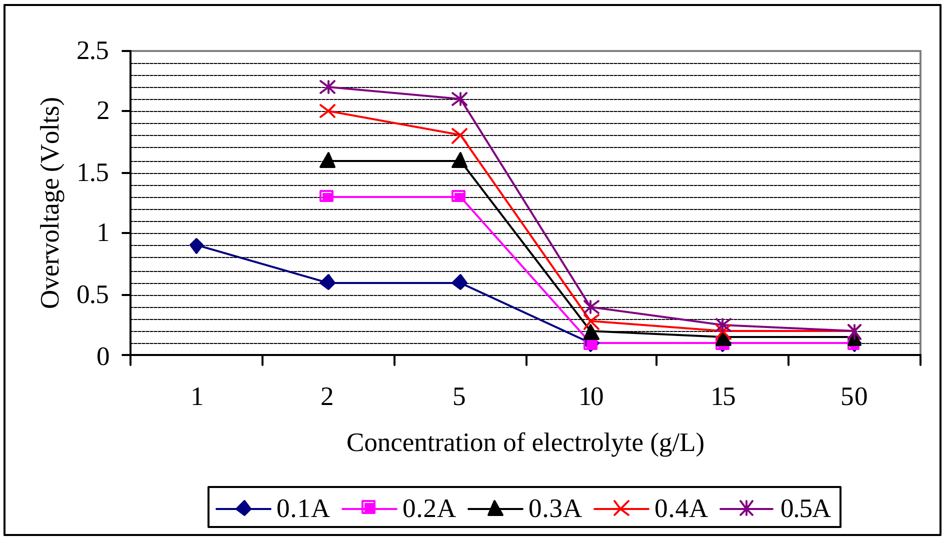


Figure 6.16: Effect of concentration on the cell overpotential

The current efficiency is usually affected when the deposition process is unstable. The instability is caused by the use of high potential which drives the ions hurriedly to the cathode. The cathode releases the gas instead of the anode. The result is that the reduced ions do not have enough time to embed themselves onto the cathode and therefore remain attached to the cathode loosely creating a loose layer, which eventually passivates the cathode and the reaction stops within 10 to 30 minutes. One of the conditions that create high potentials in the electrolytic reactors is the use of low concentrations. It can be observed in Figure 6.16 that the potentials created by concentrations below 5g/L are all within the unstable region and therefore the current efficiencies would be greatly affected. The other condition is the use of high current or current densities that produce current efficiencies greater than 100%. This has already been discussed in the above sections where it was established that high levels of current or current densities produce increased rates of deposition of copper on the cathode, which may lead to the formation of nodules that can cause short circuits. Conversely low potentials and currents produced low deposition rates. However concentrations greater than 10g/L produced stable conditions and provided adequate ions necessary for electrodeposition of copper on the cathode.

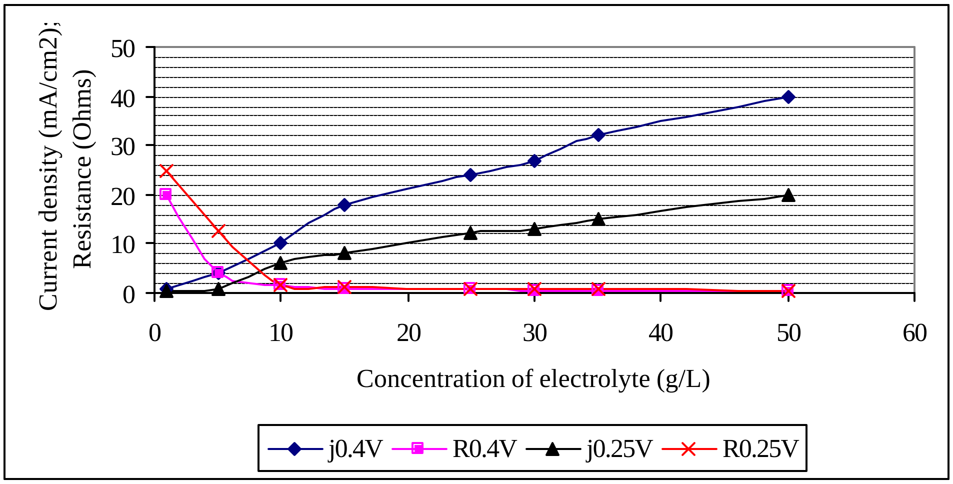


Figure 6.17: Effect of concentration on resistance, current density and potentials

The investigation of electrolyte concentration and current density and resistance revealed two key observations. The cell resistance increased with decreased level of concentration and conversely the resistance decreased with the increase in concentration. The current density decreased with the decrease in concentration and conversely the current density increased with the increase in concentration of electrolyte (Figure 6.17). The highest resistance was in 1g/L at 25 and 20O for the 0.25Volts (R0.25V) and 0.4Volts (R0.4V) respectively while the lowest was in 50g/L concentration of electrolyte. The highest concentration in the study was 50g/L while the lowest was 1g/L of copper sulphate. This translates to 19.9g/L and 0.398g/L of copper respectively. The highest concentration of electrolyte produced the highest current densities of 40mA/cm^2 at 0.4Volts (j0.4V) and 20mA/cm^2 at 0.25V (j0.25V) while the lowest concentration produced the lowest current densities of 2mA/cm^2 at 0.4Volts and 1mA/cm^2) at 0.25Volts. These results mean that the conditions favour the recovery of copper at concentrations above 10g/L; the best starting point being 15g/L. The use of the voltage range of 0.25 to 0.4Volts did not present any problem to the circular reactor. Any potential within this range would be suitable for the recovery of copper at concentrations above 15g/L of copper-sulphate solutions. However, the use of low concentrations below the 15g/L more so below 10g/L, has the disadvantage of high resistance to the flow of ions or current between electrodes in the reactor. The reason is that the molecules of water would exceed molecules of the electrolyte. This makes it difficult for the current to flow. It means that the voltage has to rise in order to produce a significant level of current. The results in Figure 6.17 also show that the resistance is high for concentrations below the 15g/L value as compared to the ones above the same level. It also means that if one has to operate the reactor effectively, one has to choose concentrations above the 15g/L level. Obviously, the current efficiency would be affected; increasing for concentrations above 15g/L level and decreasing for concentrations below the same level.

The effect of concentration on the current efficiency can be seen in Figure 6.18. The limiting current density (Lj) increased with the increase in concentration showing a stable increase at concentrations above 10.8g/L. For concentrations below the 10.8g/L the limiting current density was unstable and so was the current efficiency (CE) indicating a decrease in this region but a stable efficiency above this concentration. The current density (j) increased up to the 10.8g/L level and remained constant for values above it. The limiting current increased as the concentration of electrolyte increased. It is therefore not recommended that the reactor operates at concentrations below 10.8g/L as unstable values of current efficiency would be obtained making the operation inefficient. The current efficiency for this region was found to be between 65 to 115%.

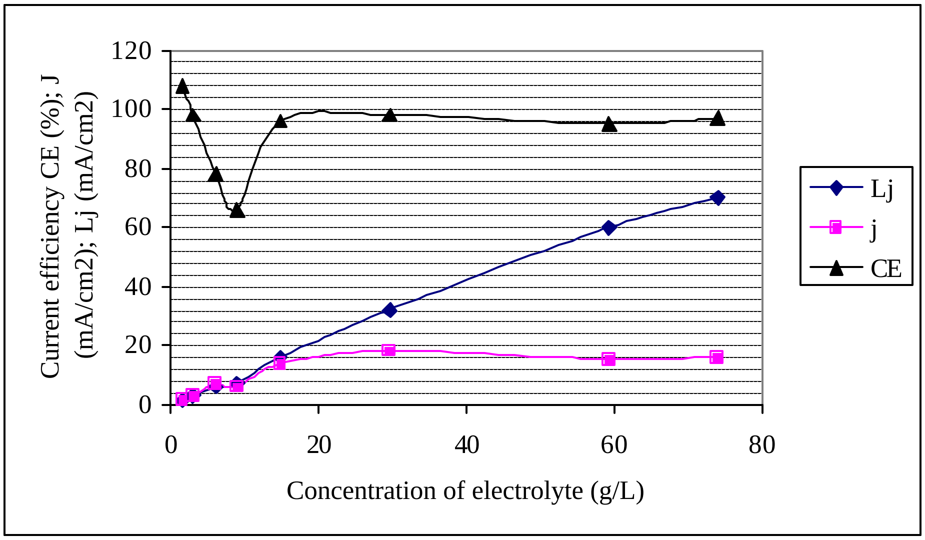


Figure 6.18: Effect of concentration on current density and efficiency at 60°C

The efficiency of 115% is unacceptable as the maximum efficiency is 100%. The high result could be due to low concentration which produced an unstable system. The voltage could drive other metals along with copper to the cathode.

6.7 Effect of Impurities on the Current and Current Efficiency

The information in Figure 6.19 and Appendix 7:A shows the voltamographs that were determined in order to establish the operating current density for the system (50g/L $CuSO_4$ + 90g H_2SO_4) in the presence of different levels of concentrations of impurity (Ni + Fe + C0) prepared as 1000ppm of solution. The results showed that for the impurity concentrations of 1ppm, 6ppm, 12ppm and 20ppm the limiting currents were 0.91, 1, 1.1 and 1.2amps respectively. The results mean that a choice of current of up to 0.91amps can be made for the safe operation of the reactor in order to observe any effect of impurities on the current efficiency. The choice of current of 0.5amps which represents a current density of $25mA/cm^2$ for an overvoltage of 0.2 volts were used to establish the effect of impurities on the efficiency. It was observed that the combined impurity (Fe + Co + Ni) had no effect on the current efficiency at concentration levels of 1 to >100ppm (Appendix 7: B).

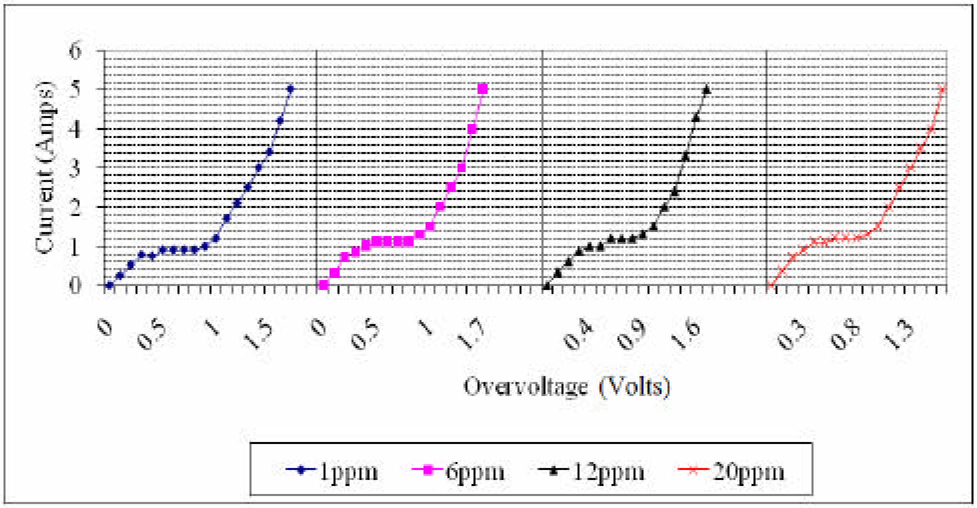


Figure 6.19: Effect of metals with highly negative oxidation potentials

The reason for this was that the concentration of copper sulphate is higher than that of the impurity and therefore if there was any competition, it could not be significant to produce any effect on the deposition of copper on the cathode since the reduction potential for copper (0.34V) is lower than that of the metal ions of Iron (III) (0.77V) but much higher than Zinc (II) (-0.76V) Nickel (II) (-0.25V) and Cobalt (II) (-0.28V). Other systems of impurities, particularly systems that will have impurities that have the same reduction potentials or close to the reduction potential of copper were investigated.

The systems of impurities using silver nitrate and bismuth nitrate were used as study cases. The silver nitrate solution (0.1M) was prepared by dissolving 16.99g of the electrolyte in distilled water and the volume was made up to one Litre. Volumes of 1, 2, 5, 10, and 20ml of silver nitrate ($AgNO_3$), molecular mass of 169.9g/mol, were added to samples 1, 2, 3, 4, 5 of copper sulphate solution (50g/L) and the volume was made up to 250ml respectively. The concentration of silver nitrate in samples 1, 2, 3, 4, and 5 were 0.03, 0.06, 0.14, 0.3, and 0.6g/L respectively. The control sample did not contain silver nitrate. The results of the voltamograph in Figure 6.20 show that the silver nitrate as impurity affected the limiting current. The control sample with 0g/L of silver nitrate shows clearly that the limiting current density is at the level of 50mA/cm^2 and that of 0.03g/L of silver nitrate attained 70mA/cm^2 level.

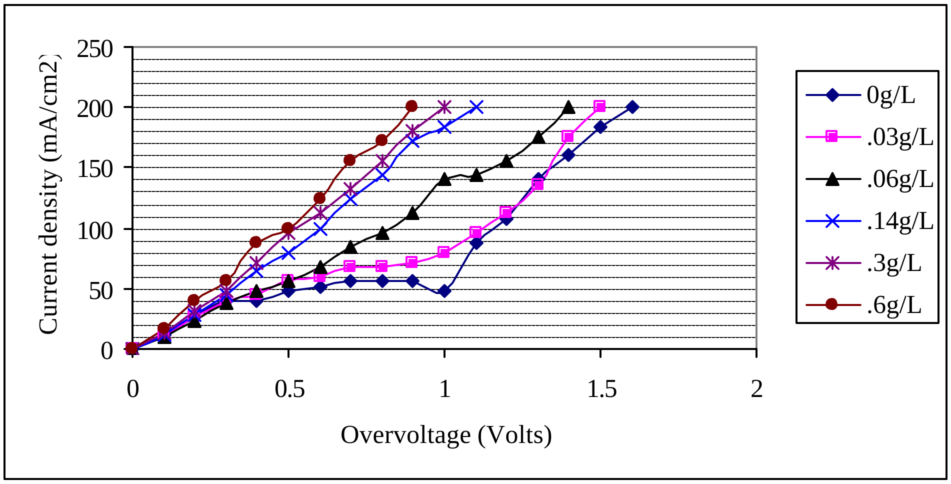


Figure 6.20: Effect of silver nitrate on the limiting current density

The concentrations from 0.06 to 0.6g/L of silver nitrate interfered with the limiting current density formation and the voltamographs are almost linear. The normal voltamograph is that of the sample with no impurity (control sample), which shows a linear ascent up to the limiting value and stays horizontal from 0.4 to 1Volts after which the ascent is linear again but does not carry on with linearity (confirmation may be required). For the purposes of this study the measurements went up to 200mA/cm^2 (5Amps) for the dependent variable and 1.6Volts maximum for the independent variable. The significance of these results is that they can be used to determine the presence of impurities that have the same reduction potentials as copper. It would be difficult, however, to determine the limiting current for samples that contain high levels of impurities, as the voltamographs would be linear in such cases. Perhaps the trial and error method would lead to the determination of such values. The results of the effect of silver nitrate on the current efficiency at constant current (I) revealed two patterns; a steep decline of the efficiency curve and a slow slanting curve. The steep-decline curve from the current efficiencies (CE) of 101% to 30% indicates that there was a slow inhibition of the deposition of copper (m) to the cathode (Figure 6.21). No visible deposits of silver metal were obtained on the surface. One would say that the inhibition was due to the competition between the metals copper and silver.

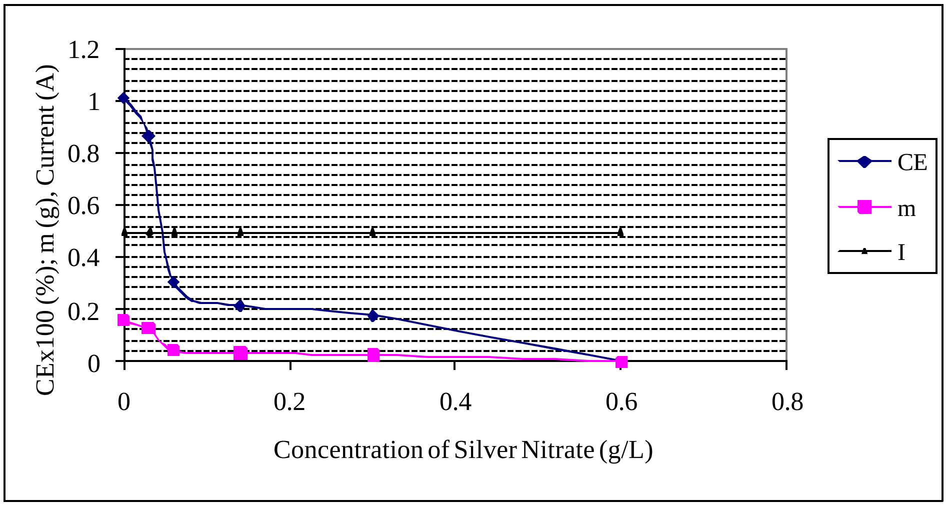


Figure 6.21: Effect of silver nitrate on the current efficiency

In the case of the slow-decline curve, there was a strong inhibition on the deposition of copper to the cathode. This was demonstrated by the formation of visible layer of silver on the surface of both the cathode and anode. One notable feature was that even when the current was not allowed to pass through the circuit, silver was observed to surround the electrodes completely within a one-minute period. The inhibition continued until the concentration of 0.6g/L of silver nitrate produced no deposit on the cathode. The mass deposited in the fifteen-minute duration was zero for a current of 0.5Amps and a potential of 0.15Volts and therefore the rate of deposition (g/s) was also zero at this concentration level of impurity. This is a total inhibition of copper but silver metal was seen to deposit on the layer that covered the electrodes. The highest efficiency was that of the control sample while the lowest current efficiency was that of the sample with 0.6g/L of silver nitrate solution. Therefore the presence of silver nitrate, as impurity, produced a negative effect on the current efficiency because the current efficiency decreased with the increase in the concentration of impurity.

The system with bismuth nitrate ($Bi(NO_3)_3.5H_2O$), molecular mass of 484.98g/mol, as impurity was investigated in the circular batch reactor at 60^oC. Five samples were used in the investigation; a control sample with 0% concentration of bismuth nitrate and four samples each with 0.05, 0.22, 0.5 and 1.48% concentration of Bismuth Nitrate in reactor electrolyte. A voltamograph provides an idea as to whether impurities are present if the voltamograph of electrolytes containing impurities deviate from the characteristics of that of the control sample. A check on the current density for an active area of $25cm^2$ revealed two deviations from normal. The current density was lowered for voltage values greater than 1.1Volts i. e., just above the normal limiting current density for the control sample. This was exhibited in all the samples more so in samples with 0.22 and 0.5% concentration of bismuth nitrate (Figure 6.22). The other notable feature of the voltamographs is that the voltamograph of electrolyte with 1.48% concentration of bismuth nitrate, revealed a highest value of limiting current density ($120mA/cm^2$) while the rest of electrolytes with impurities exhibited the lowest current density ($50mA/cm^2$). The advantage with bismuth nitrate is that it precipitates into white crystals when the electrochemical reaction proceeds. It also precipitates readily in the presence of chlorides to bismuth chloride, which are white crystals. The addition of chloride compound to electrolytes introduces this benefit of removing bismuth in the bulk of electrolyte to the bottom of the reactor. This is why most copper refineries introduce either sodium chloride or potassium chloride in the electrolyte at some point in the refinery or direct into the reactors before or during the recovery of copper.

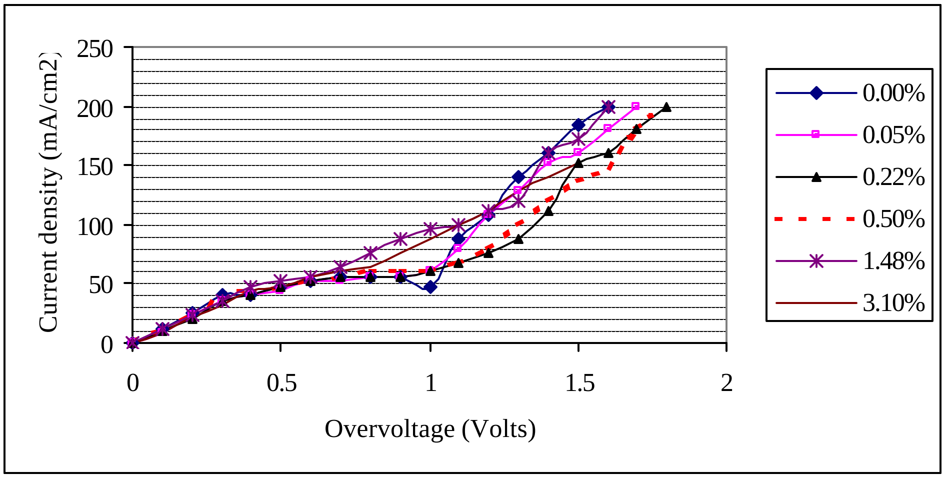


Figure 6.22: Effect of bismuth nitrate on current density

It can be concluded therefore that bismuth nitrate affected the current density more so at values above the limiting current density of the control sample. The limiting value deviated especially when the concentration of bismuth nitrate was 1.48% and above. The graphs for the 1.48% and 3.1% exhibited linearity. These levels of concentration cannot be used as criterion for the estimation of the limiting current. It can also be estimated that the resistance remains constant at these levels of impurities.

The current efficiency was investigated at the same levels as those at which the voltamographs were taken using two different currents and current densities. The results were recorded at 0.5 and 0.8Amp currents and 0.2 and 0.3V overvoltage respectively. The results in Figure 6.23 and Appendix 7C revealed a decrease in current efficiency as the level of bismuth nitrate increased. The control sample produced the highest current efficiency at both the 20mA/cm^2 (0.5A, 25cm^2) current density and 0.2V and 40mA/cm^2 current density (0.8A, 25cm^2) and 0.3V. The 3.1% concentration of bismuth nitrate produced the lowest current efficiency at both the 0.5A and 0.2V and 0.8A and 0.3V respectively. Even though the effect is less than that of silver nitrate, the current efficiency need not be lowered at any time. Electrode potential for bismuth (III) is 0.32V which is close to that of copper (Appendix 7D). However it could not deposit on cathode but formed a white precipitate that could retard the deposition process.

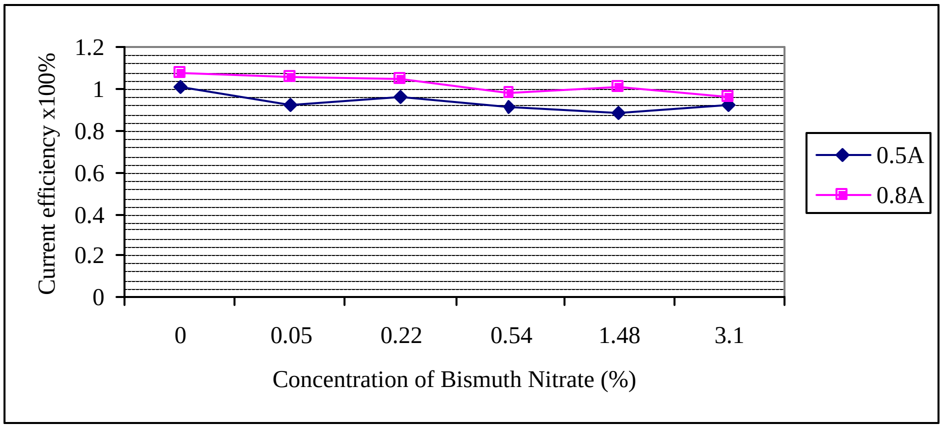


Figure 6.23: Effect of bismuth nitrate on current efficiency

6.8 Effect of Electrode-active Area on the Current Efficiency

The active area of the electrode affected the limiting current as indicated in Figure 6.24 and Appendix 6: A and B. Five different distances were used during the investigation (10, 12.5, 17.5, 22.5 and 30cm^2). The results show that the limiting current for a small active area (10cm^2) was lower (60mA/cm^2) when compared to those of the other active areas. The highest active area (30cm^2) exhibited the highest limiting current (80mA/cm^2). The values for the 2cm and 3cm distances were found to be 65 and 70mA/cm^2 respectively. This means that the active area produces some effect on the limiting current density because changes in the limiting current density as indicated by the range of 60-80mA/cm^2 can produce changes in the behaviour of the cell. The rate of reaction and therefore the rate of deposition of copper can be affected. If there is a drop of current density by 20mA/cm^2, there is a corresponding drop of mass deposited at the cathode.

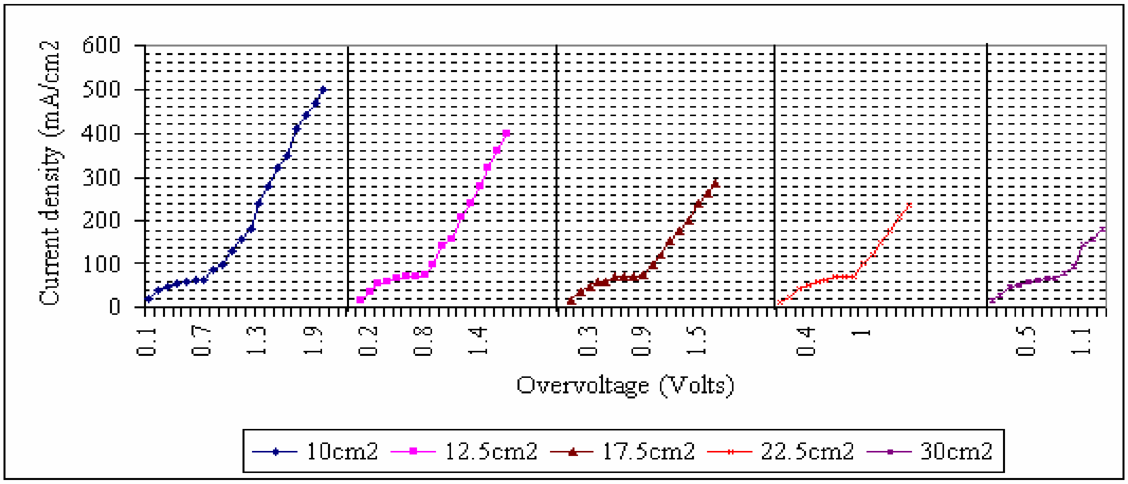


Figure 6.24: Effect of active area on limiting current density for a distance of 2cm

The determination of the limiting current by carrying out a voltametric investigation, allows the researcher to choose the correct level of operating current because the use of currents above the limiting value results in accelerated deposits, which could lead to poor deposition on the surface. The effect of active area on the current density can be observed in Table 6.1 in which the increase in electrode active area produces a decrease in the current density. It can be observed that the voltage across the cell decreases as the active area increases. The decrease in the current density produces a decrease in the deposition of copper from solution at fixed time and current.

Table 6.1: The effect of electrode active area on the current density

Time *(min.)*	*Area* *(cm^2)*	*h* *(V)*	*I* *(A)*	*j* *(A/cm^2)*	*M* *(g)*	*Temp* *(^oC)*	*Distance* *(cm)*
15	10	0.3	0.5	0.050	0.1746	60	2
15	12.5	0.3	0.5	0.040	0.1455	60	2
15	17.5	0.2	0.5	0.030	0.1397	60	2
15	22.5	0.15	0.5	0.022	0.113	60	2
15	30	0.15	0.5	0.017	0.0924	60	2

The study of the circular reactor in order to establish the effect of active area on the current efficiency revealed that an increase in active area from 10 to 30cm^2 produced a decrease in the current efficiency from 118 to 62% for a decrease in current density of from 0.05 to 0.017A/cm^2. The results also showed that the decrease in current density produced a decrease in the mass deposited per time (Figure 6.25). In the duration of 15minutes, the 10cm^2 active area deposited 0.1746g at a current density of 0.113g/s of copper respectively.

The current efficiency (CE) was found to decrease as the electrode-active area increased (Figure 6.25). The mass (m) deposited decreased as the electrode-active area increased. The correlation of the current density (j) with electrode-active area indicated a decrease of current density with increasing electrode-active area. The mass deposited decreased as the electrode-active area increased

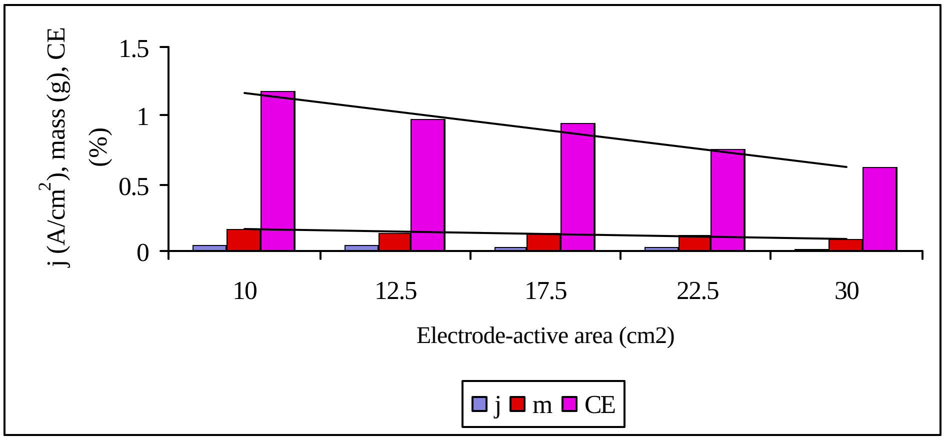


Figure 6.25: Effect of electrode-active area on the current efficiency in 15 minutes

6.9 Effect of Smootheners on the Current Density and Current Efficiency

The sodium chloride, a chemical that is frequently used as an additive in electrorefining processes, was weighed and added to samples and the volume of the samples were made up to 250ml. It is an inorganic compound that readily dissociates in water. It forms sodium sulphate when ions of sodium and sulphate react. The concentrations of sodium chloride in the samples ranged from 0 to 0.21%. The control sample had a concentration of 0%, which was the lowest concentration, while the highest concentration was in the sample with 0.21% sodium chloride. The effect of sodium chloride on the current density was investigated in order to determine whether it played a role in the shift of the limiting current from that of the control sample to something else. The results in Figure 6.26 show that the current density increased with the increase in voltage up to the current density of 50mA/cm^2 and voltage of 0.4Volts. From this point, the current density increased with a very small gradient up to 80mA/cm^2 giving a change in voltage (?V) of 0.86Volts.

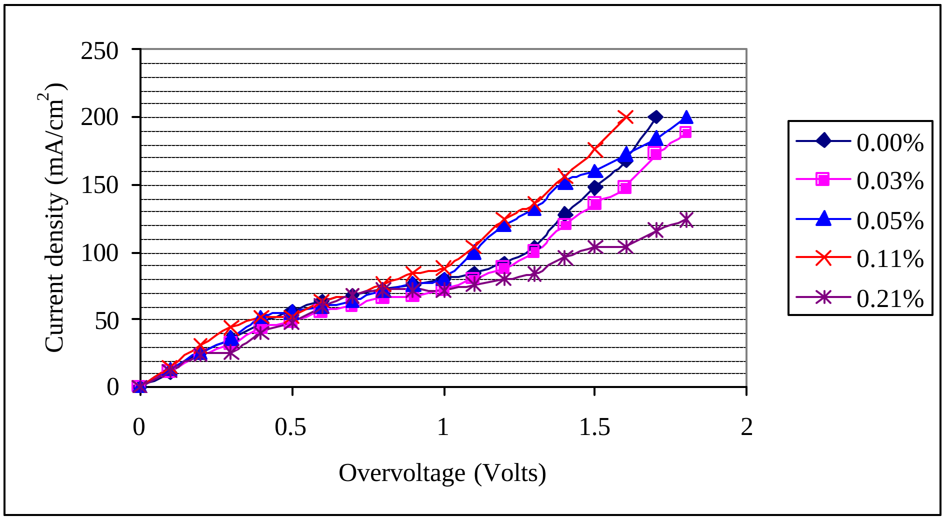


Figure 6.26: Effect of sodium chloride on the current density

During this period, the electrolyte provided increased resistance to the flow of electrons and hence the flux. When the voltage equal to ?V was reached, the resistance, which can be estimated from $V = RI$, was then overcome and the current density began to flow linearly with the applied potential. The region covered by the voltage (?V) is the limiting current density region. When the system was operated at current densities below this value, no abnormal nucleation was observed on the surface at the desired concentration of electrolyte (50g/L). But the operation of the system above the limiting current density region revealed abnormal nucleation of copper and gas bubbles on the surface of the cathode simultaneously. The curves for the 0.03% and 0.05% samples were above the curve for the control sample above the limiting current density region while those of the 0.11% and 0.21% concentrations were below that of the control sample. This means that concentrations of sodium chloride above 0.05% lower the current density and those below 0.05% concentration increase the current density at levels above the limiting value. Therefore sodium chloride as an additive did not affect the current density when the reactor was operated at current densities below the limiting value since the results, at all concentrations of sodium chloride, showed no deviation from normal.

Thiourea, an organic compound, was used as one of the additives. The others are chloride and glues of different types. Thiourea was used in order to establish the effect on the current density and hence the current efficiency. Concentrations of 0 to 300ppm were added to 250ml reactor samples by dissolving appropriate amounts of the compound in electrolyte and making up the volume to 250ml. It is interesting to note from the results in Figure 6.27 that a strong inhibition was produced by increased concentration of thiourea particularly at concentrations of 200 and 300ppm.

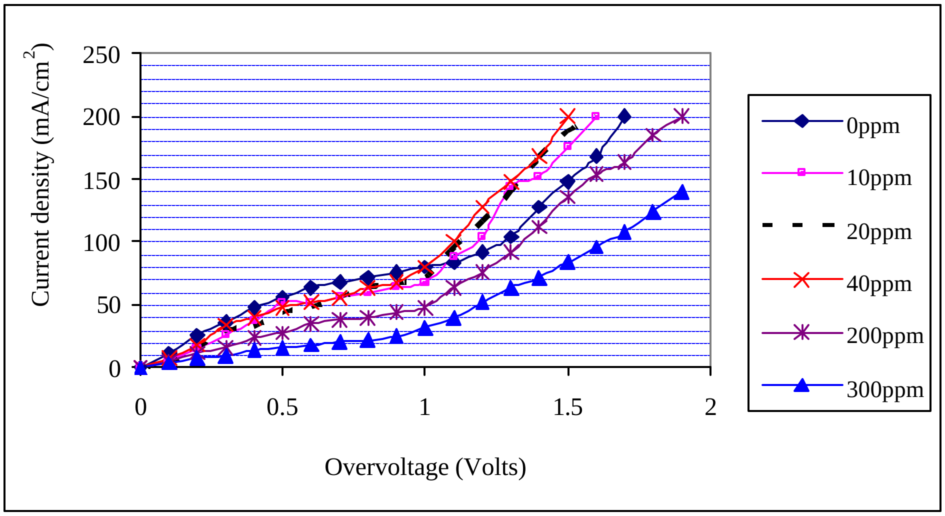


Figure 6.27: Effect of thiourea on the current density

At these levels of concentration, thiourea lowered the level of the limiting current from 60mA/cm^2 to 40mA/cm^2 at 200ppm concentration level and 20mA/cm^2 at 300ppm concentration level indicating a strong inhibition of the flow of current of ions in the system. On the other hand, the concentration levels of thiourea from 40ppm and below produced a lowering of limiting current density of 10mA/cm^2 at 0.5Volts potential.

The inhibition of current requires a careful examination of the behaviour of the additives in the system. The interaction between Tu and copper sulphate and that of glue and NaCl might require further examination. The complexing nature of copper with additives was seen to produce a green colour that is characteristic of Cu (I) ions. The results also revealed that the potential required to overcome resistance in the systems was 0.5Volts for all the cases of the concentrations of thiourea, which represents a range of 0.5 to 1Volt potential. The 1-Volt potential is also the point where all the concentrations of Thiourea below the 40ppm mark failed to inhibit the current density. Therefore, at concentrations below the 40ppm level, thiourea was able to inhibit the limiting current density below the 1-Volt potential while above this potential it did not. The inhibition was overcome by increased overvoltage. At concentrations above 40ppm, thiourea inhibited the limiting current density up to the 1-Volt potential and continued to slow down the current density above this potential. Therefore increased overvoltage did not have any effect on the inhibition process of thiourea at concentrations above 40ppm. The effect of thiourea on the current efficiency can be seen in Figure 6.28. The amount of copper deposited in fifteen minutes was used in evaluating the efficiency. The results show that the current efficiency decreased as the concentration of thiourea increased. The current efficiency of the control sample (0ppm) was found to be the highest (106%) and that of the highest concentration of thiourea (1600ppm) the lowest (40%) in this study. In terms of resistance, the concentrations from 800ppm and above produced increased resistances while those below 800ppm produced resistances proportionate to the concentration. The lowest resistance was 0.52? at 0ppm concentration of thiourea, which is the resistance of the control sample.

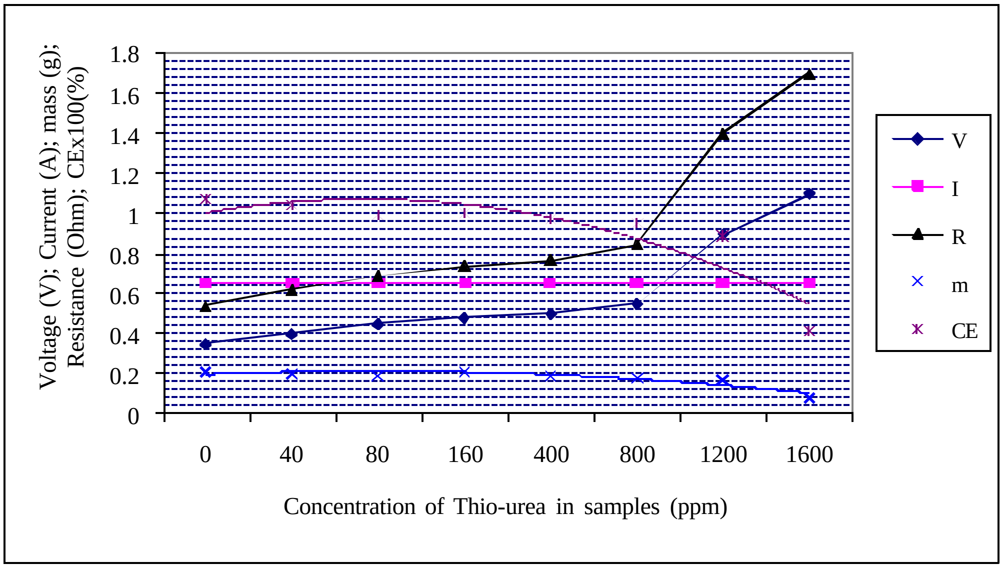


Figure 6.28: Effect of thiourea on the current efficiency (CE)

The behaviour of resistance with respect to thiourea was that as the concentration increased the resistance increased. This explains why thiourea is a strong inhibitor of current and current density. Whilst the current remained constant throughout the study, the voltage varied from 0.35Volts at 0ppm, being the least value, to 1.1Volts at 1600ppm concentration of thiourea being the highest value reached in the study. It was observed, also, that the rate of deposition decreased with the increase in the concentration of thiourea. The rate of deposition being the lowest at 1600ppm and the highest being that in the control sample at 0ppm. In terms of smoothening effect, the surface of the cathode exhibited a bright and smooth colour of copper deposit on the cathode indicating that thiourea was effective in smoothening the surface of the cathode. However, the smoothening effect was observed to be effective at concentrations up to 580ppm. At this concentration level, the resistance curve crosses the current efficiency curve. The general correlation between resistance, current efficiency and concentration of thiourea is that the concentration of thiourea is function of current efficiency and resistance. It further means that the current efficiency is inversely proportional to the concentration of thiourea and inversely proportional to the electrolyte resistance. But the concentration of thiourea is directly proportional to the resistance. As the concentration increases the resistance increases. A model can thus be developed from the above-stated relationships, which is indicated in equation (6.1) where f_1 (mol/L?) is a constant, C (mol/L) is the concentration of thiourea, F is the current efficiency (%) and R (?) is the resistance. At the point where the resistance meets the current efficiency, the value of the efficiency will be equal to the value of the resistance but the units will be different.

$$dC = (f_1 / \Phi)dR \tag{6.1}$$

Similarly, as the voltage increases the resistance increases and the current efficiency decrease. This means, also, that the current efficiency is inversely proportional to the voltage and the model for such correlation is that indicated in equation (6.2). Where f_2 (V/?) is a constant and therefore the term f_2/? becomes a constant representing the current I (Amps), which reduces equation (6.2) to equation (6.3).

$$dV = (f_2 / \Phi)dR \tag{6.2}$$

$$dV = IdR \tag{6.3}$$

In the investigation of the effect of glue, different types of glue were tried in order to produce some effect on the current efficiency. Paper glues K-glue, P-glue and B-glue were tried in the study. The P-glue is the paper glue manufactured by Penguins Plc. The density of glue was measured by weighing, using the analytical balance, a known volume of the glue. The mass divided by the volume gave the density of glue having unknown density. The average density of most glue was found to be 1.0312g/ml, which was approximated to 1g/ml. The volumes of glue measuring 0ml, 1ml, 5ml, 10ml, and 20ml were added to samples in order to produce concentrations of 0, 4, 20, 40 and 80ppm of glue that was added to the control sample, and samples 1, 2, 3 and 4 respectively. The volumes of the samples were then increased to reach the 250ml mark through the addition of more electrolytes. The results in Figure 6.29 indicated that glue did not have any effect on the limiting current density in the potential range of 0-1Volts.

However, it increased the current densities at potentials above 1Volt for all the concentrations of glue except that of the control sample. The paper glues did not produce any inhibition on the current density, which remained in the region of 50mA/cm^2 for a voltage range of 0.5 to 1 Volt for all the investigations.

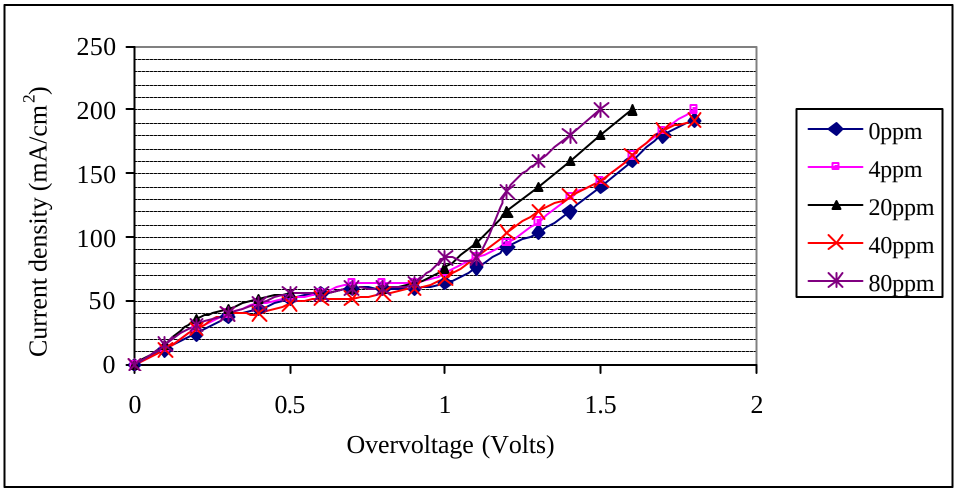


Figure 6.29: Effect of K-glue on the current density

The effect of K-glue, NaCl and Thiourea as a combined additive on the current density and current efficiency was studied. Stock solutions of K-glue (1000ppm), thiourea (2000ppm) and NaCl (2000ppm) were prepared from which volumes of 1, 5, 10, 20, 40, 100 and 150ml were measured and added to different but equal electrolyte samples. Since the concentrations of the additives were different, the volume of each additive was used as the variable in the analysis of the results. The volume was thus used in the determination of the concentration of each additive in the samples. The total volumes of the samples, after the addition of the additives, were 253, 265, 280, 310, 370, 550, and 700ml. Then 250ml from each of these samples was measured and placed in the reactor for the electro-deposition of copper. This methodology was used for all other investigations in the determination of the effect of smootheners on the current efficiency. Smootheners such as Gum Arabic (G-Arabic), Ethylenediaminetetraactic acid (EDTA) and Bostick glue (B-glue) were investigated using the same methodology. Equal volumes of each of the smootheners, with different concentrations, were used during the study in order to determine their effect on the deposition of copper on the cathode.

The results in Figure 6.30 show the effect of K-glue, NaCl and thiourea on the current density. Since K-glue did not produce significant changes in the limiting current density, it therefore was not expected to produce any significant changes in the current density in the presence of thiourea and sodium chloride. Similarly, sodium chloride did not produce significant changes in the limiting current density and therefore was also not expected to produce any changes in the limiting current densities. Therefore the changes in the limiting current densities that can be observed in Figure 6.30 must be due to the inhibition effect produced by thiourea. The inhibition on the electrodes resulted in the lowering of the limiting current densities.

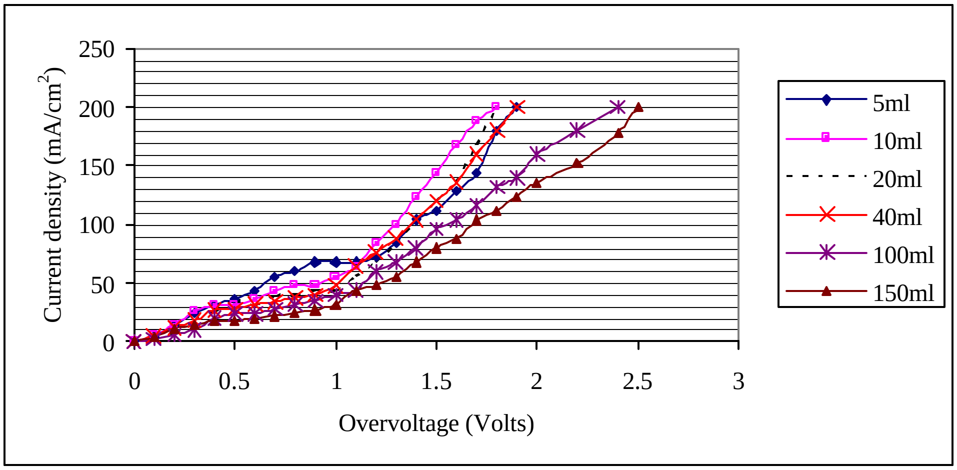


Figure 6.30: Effect of K-glue, thiourea and NaCl on the current density

The inhibition effect by thiourea in the presence of K-glue and NaCl can be determined by the lowering of the limiting current from 60mA/cm^2 to 50, 40, 30, 25 and 20mA/cm^2 for the 10, 20, 40, 100 and 150ml representing concentrations of 0.071, 0.129, 0.216, 0.364 and 0.429g/L respectively. The 5ml volume of thiourea, representing a concentration of 0.04g/L, did not produce any effect on the limiting current density. One obvious factor contributing to the lowering of the limiting current density must be due to the fact that thiourea has negative sites, which enable it to migrate to the anode, surrounds it and prevents the free flow of ions from the anode to the electrolyte. This process lowers the flow of current in the circuit as the resistance increases across the cell reactor. The effect of K-glue above the limiting current is to increase the current densities so that if one attempts to operate the reactor at high current densities, the K-glue attempts to stabilise the flow of current in the reactor and therefore assists in the smooth deposition of copper during electro-refining thereby producing normal grain size of copper atoms on the surface of the cathode.

Gum Arabic, as one of the surface smootheners, was used during the electrorefining process. Gum Arabic is a product extracted from trees (Acacia). Its action, during electrorefining, was similar to that of K-glue. Since the effect of glues was to improve the current efficiency, the limiting current was not affected by G-Arabic. It means that it did not inhibit the current density. However, G-Arabic was found to produce the smoothening effect on the grains that were deposited on the cathode. Like K-glue, G-Arabic was found to increase the current density above the limiting value. The results in Figure 6.31 indicate that the lowering of the limiting current density and the general lowering of the current density can be attributed to thiourea and not G-Arabic and NaCl.

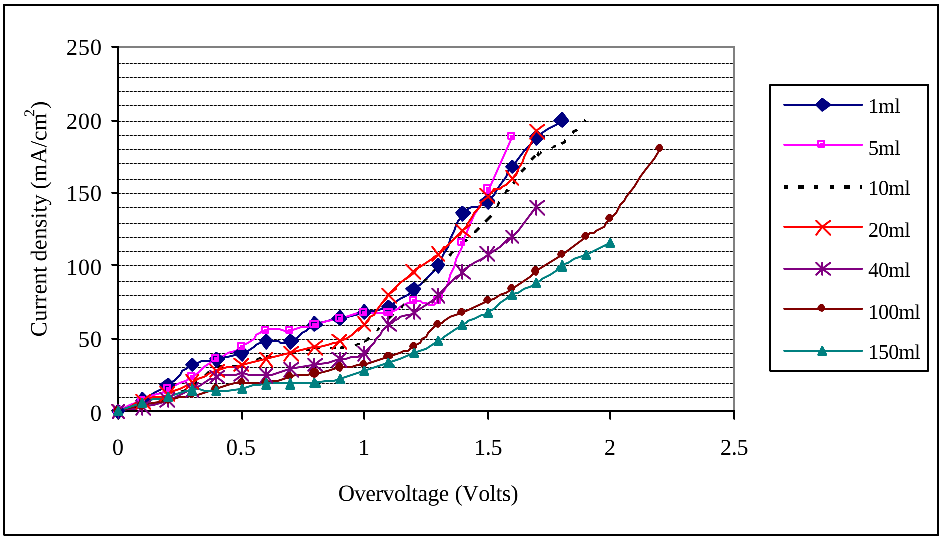


Figure 6.31: Effect of G-Arabic, thiourea and NaCl on the current density

The results show that the limiting current density was lowered from 65mA/cm^2 for the 1 and 5ml volumes of thiourea representing concentrations of 0.008g/L and 0.038g/L respectively to 40mA/cm^2 for the 10 and 20ml representing concentrations of 0.071 and 0.129g/L, 25, 20, and 15mA/cm^2 for the 40, 100 and 150ml representing concentrations of 0.216, 0.364 and 0.429g/L respectively.

Thiourea maintains its superiority as a strong inhibitor at volumes above 40ml than at volumes below 20ml, i.e., by maintaining low current densities above the limiting values when compared to those at volumes below 20ml. Thiourea produces increased resistance to the flow of electrons and hence the flow of ions in solution resulting in reduced deposition on the cathode.

The effect of K-glue and G-Arabic on the current efficiency was studied at constant current (I) with varying potential (V) and resistance (R) as indicated in Figure 6.32 (1) and (2) respectively. The resistance increased as the concentration of additives increased and so was the voltage. The K-glue stabilised the current efficiency and therefore maintained it to levels above 95% for values of volume of 20ml representing a concentration of 0.0645g/L and above

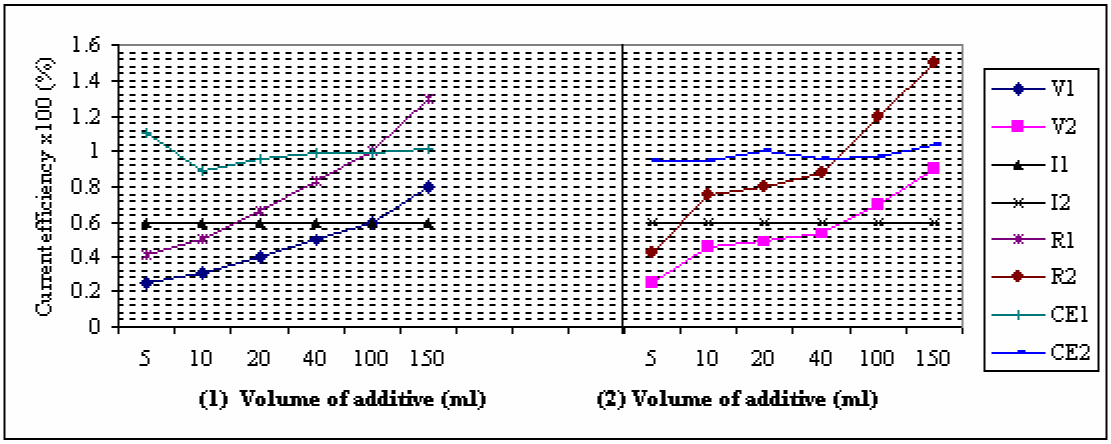


Figure 6.32: Effect of (1) K-glue and (2) G-Arabic on the current efficiency

The current efficiency was unstable for concentrations below 0.0645g/L, i.e., 0.0356g/L for a volume of 10ml and 0.0188g/L for a volume of 5ml of K-glue. This means that the region below the 10ml volume was unstable and that above 100ml was also unstable. The stable region was found to be between the 10ml and the 100ml volume of K-glue additive with the current efficiency (CE) values ranging from 95 to 100%. The lowest value of current efficiency was found to be in the unstable region at 10ml volume of K-glue with an efficiency of 88% while the highest was also found to be in the unstable region with a value of 112%. However, the quality of the surface, i.e., the grain size was not affected. It can also be pointed out here that whilst the Thiourea lowered the current efficiency as its volume increased, the K-glue reversed the trend to normal levels up to the end of the stable region. At and after 100ml volume of K-glue added, the glue failed to maintain the normal characteristics of the cathode surface though the efficiency increased further. The surface became dark in colour at this point upwards and the deposits of thiourea were observed at the cathode. This means that the concentration of thiourea dominated in producing the instability in electro-deposition of copper on the cathode.

The advantage of K-glue can be seen in the correlation results in Table: 6.2 where K-glue-thiourea produced a weak-positive correlation coefficient of 0.142 with the current efficiency. This value represents a weak effect of thiourea on the current efficiency. The weakened effect is due to the presence of K-glue which provides extra sites on which thiourea ions are temporarily attached thus allowing the smooth passage of copper (I) and copper (II) ions through the film to the cathode surface. This is confirmed by the weak-negative correlations between current efficiency and K-glue-thiourea concentration, voltage (-0.009) and resistance (-0.025). The strong-negative effect of thiourea on the current efficiency is removed by the strong-positive effect of K-glue resulting in improved current efficiency. The correlation coefficients of K-glue-thiourea concentration with the voltage and the resistance were very high (0.971 and 0.967). These values give a significance of 0.01 level (2-tailed). This means that it is true; when the concentration increases the resistance increases and the voltage of the system increases.

Table: 6.2 Correlations of K-glue-thiourea concentration (concn) with CE

		Concn	*CE*	*Voltage*	*Resistance*	*Current*
Concn	Pearson Correlation	1	.142	.971[**]	.967[**]	.[a]
	Sig. (2-tailed)	.	.788	.001	.002	.
	N	6	6	6	6	6
CE	Pearson Correlation	.142	1	-.009	-.025	.[a]
	Sig. (2-tailed)	.788	.	.986	.963	.
	N	6	6	6	6	6
Voltage	Pearson Correlation	.971[**]	-.009	1	1.000[**]	.[a]
	Sig. (2-tailed)	.001	.986	.	.000	.
	N	6	6	6	6	6
Resistance	Pearson Correlation	.967[**]	-.025	1.000[**]	1	.[a]
	Sig. (2-tailed)	.002	.963	.000	.	.
	N	6	6	6	6	6
Current	Pearson Correlation	.[a]	.[a]	.[a]	.[a]	1
	Sig. (2-tailed)	.	.	.	.	.
	N	6	6	6	6	6

[**]. Correlation is significant at the 0.01 level (2-tailed).

a. Cannot be computed because at least one of the variables is constant.

Thiourea alone produced strong-positive correlation coefficients with voltage and resistance and strong-negative correlation with the current efficiency. The Pearson Correlation analyses in Table 6.3 show negative correlation coefficients for the current efficiency with voltage (-0.995), resistance (-0.994) and thiourea concentration (-0.946). This means that increasing these factors does not increase the current efficiency. Therefore, the removal of copper from solutions can best be done at fixed values of voltage and concentration of thiourea. It can also be observed, however, that correlation coefficients for thiourea concentration with voltage and resistance were positive (0.965; 0.965). This means that increasing the concentration of thiourea would increase the voltage and resistance in the reactor.

Table: 6.3   Correlations of thiourea with the current efficiency

		Thiourea	CE	Voltage	Resistance	Current
Thiourea Concn	Pearson Correlation	1	-.946**	.965**	.965**	.[a]
	Sig. (2-tailed)	.	.000	.000	.000	.
	N	8	8	8	8	8
CE	Pearson Correlation	-.946**	1	-.995**	-.994**	.[a]
	Sig. (2-tailed)	.000	.	.000	.000	.
	N	8	8	8	8	8
Voltage	Pearson Correlation	.965**	-.995**	1	1.000**	.[a]
	Sig. (2-tailed)	.000	.000	.	.000	.
	N	8	8	8	8	8
Resistance	Pearson Correlation	.965**	-.994**	1.000**	1	.[a]
	Sig. (2-tailed)	.000	.000	.000	.	.
	N	8	8	8	8	8
Current	Pearson Correlation	.[a]	.[a]	.[a]	.[a]	.[a]
	Sig. (2-tailed)	.	.	.	.	.
	N	8	8	8	8	8

**. Correlation is significant at the 0.01 level (2-tailed).
a. Could not be computed because at least one of the variables was constant.

This agrees well with Ohm's Law (V=IR). In both the cases of CE and thiourea correlations the siginificance was at 0.01 level (2-tailed). This means that the results are 99.99% true. This is the reason why glues are added to the electrorefining processes in order to improve the efficiency

Ten grams of G-Arabic were weighed and dissolved in water to make a solution with a concentration of (10,000ppm) from which concentrations of 0.0395, 0.189, 0.357, 0.645, 1.081, 1.818 and 2.142g/L were produced in the reactor by adding volumes of 1, 5, 10, 20, 40, 100, and 150ml respectively. The effect of G-Arabic, in the presence of Thiourea (2000ppm) and NaCl (2000ppm), on the reactor electrolyte was to stabilise the system so that it could be operated at stable current efficiencies thereby producing a smooth surface particularly in the most stable regions below the 50ml and above the 10ml volumes representing concentrations of 1.25 and 0.357g/L respectively. In addition, the effect of G-Arabic was to stabilise the current in order to produce a smooth deposit on the cathode. As can be observed in Figure 6.32 (2), stable current efficiencies were obtained. The variation of resistance in solution was due to thiourea (Tu) and not K-glue and G-Arabic. The effect of G-Arabic was to reverse the reductive trend produced by Tu to levels of 100% and below. The system required increased values of overvoltage as the concentration of the additives increased in order to maintain the current efficiency at the 100% and below levels. The surface on the cathode for the voltage range (0.25-0.55V) exhibited good colour, normal grain and no thiourea deposit as can be seen in Figure 6.33. Whereas, it was difficult to produce smooth surface on the cathode without smoothener at high voltage and current density as is shown in Figures 6.34-6.36, the smoothener plays an important role in producing a high quality surface and hence high quality copper cathode. The anode did not also show any deposit of thiourea in this region. But at potentials above 0.55V the surface began to change from copper colour to dark-black colour and some deposit of thiourea could be observed on the cathode that could produce an increase in current efficiency above normal values as shown in Figures 6.34-6.36 above. At the point when the solution began to produce gas bubbles, the deposition was found to be irregular.

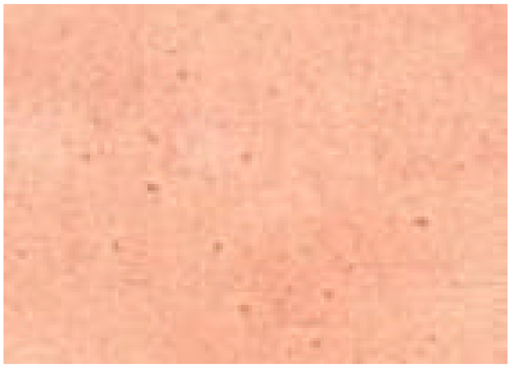


Figure 6.33: Copper deposit at 0.1-0.4V and 0.25-0.8A with smoothener

Figure 6.34: Non-sticking copper at 0.9V and 0.8-1.5A without smoothener

Figure 6.35 Non-sticking copper at 0.5V and 1.1A at 60^{o}C without smoothener

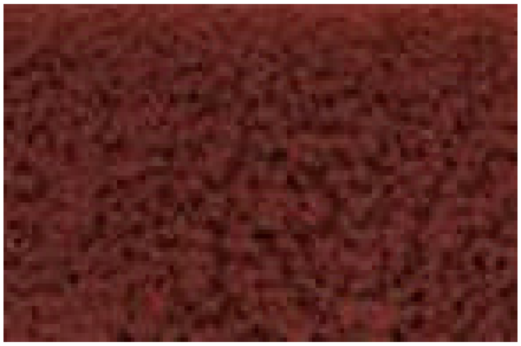


Figure 6.36: Non-sticking copper at 0.75V and 1.65A at 60^{o}C without smoothener

The bubbles were found to contribute to the irregularity of the deposited mass. The attachment of such a deposit was found to be weak on the cathode and could therefore be washed easily. The surface of the cathode was observed to become darker and darker as the potential was increased and so was the current density signifying that the conditions were not conducive for normal copper recovery from solution.

The effect of Ethylenediaminetetraacetic acid (EDTA) (20,000ppm) as an inhibitor to the process of electrochemical reaction was studied in the presence of NaCl (2,000ppm or 2g/L) and Bostick Glue (B-Glue) with a concentration of 18800ppm. The concentrations of EDTA in the samples were 0.377, 0.714, 1.29, 2.16, 3.64 and 4.29g/L for volumes of 5, 10, 20, 40, 100 and 150ml respectively. The results in Figure 6.37 show that the increased concentration of EDTA produced inhibition on the current in the reactor resulting in the lowering of current. The lowering of the current was due to increased resistance created in solution by the ions from EDTA. EDTA is a poor conducting electrolyte, like Tu, but forms complex ions with copper which results in an easy release of ions to be deposited on the cathode. Copper (I) ions tend to react faster than Copper (II) ions hence the additives facilitate the process of reducing copper to lower valence level. The results also show that the lowest value of current (0.15A) for I1 was observed at the highest EDTA concentration of 4.29g/L while the highest value (0.3A) was observed at the lowest EDTA concentration of 0.377g/L.

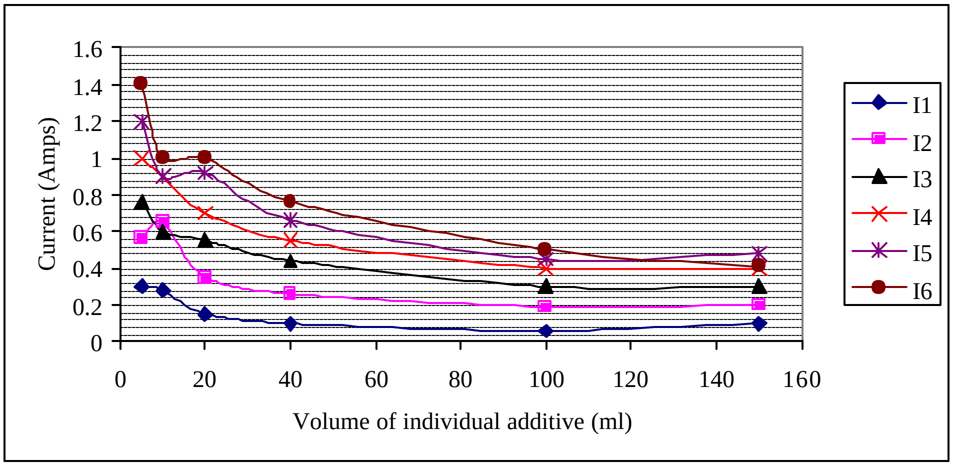


Figure 6.37: Effect of EDTA, NaCl and B-glue on the reactor current

Similarly, the highest levels of currents for I2 (0.65A), I3 (0.76A), I4 (1A), I5 (1.2A) and I6 (1.4A) were observed at EDTA concentration of 0.377g/L while the lowest values were at I2 (0.08A), I3 (0.3A), I4 (0.4A), I5 (0.45A at 100ml) and I6 (0.41A) at EDTA concentration of 4.29g/L. The lowering effect of current by the inhibitors results in the lowering of the current density and particularly, the limiting current density. The plot of current density versus overvoltage for a system using EDTA as inhibitor in the presence of smootheners NaCl and B-glue revealed that EDTA is a superior inhibitor when compared to B-glue and sodium chloride. The EDTA was found to be equally a strong inhibitor as thiourea as is indicated by the results in Figure 6.38.

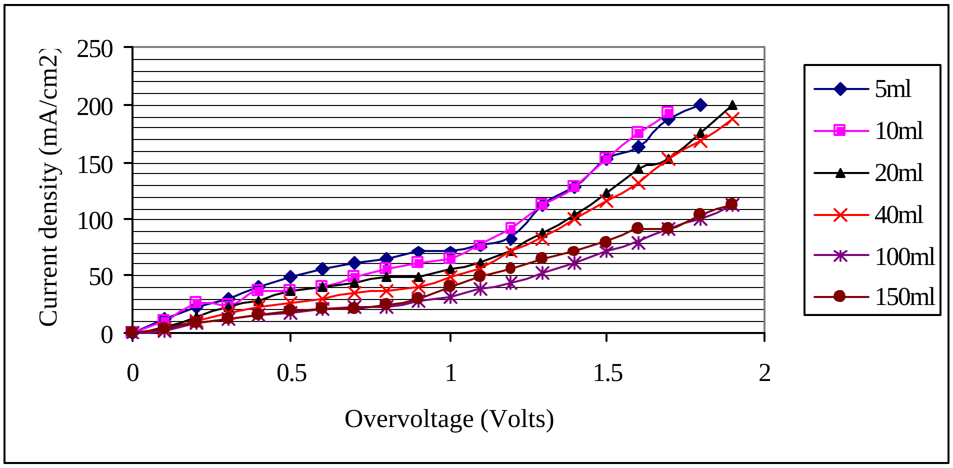


Figure 6.38: Effect of EDTA, NaCl and B-glue on current density

The usual action of such inhibitors is to lower the current density and hence the limiting current density. The limiting current densities were therefore lowered from 70mA/cm^2 for the 5ml (0.377g/L) to 20mA/cm^2 for the 100 and 150ml (3.64 and 4.29g/L) volumes of EDTA. If the concentrations of additives are properly chosen, it is possible to strike a balance between the attainment of increased current efficiency and good surface properties of the cathode and anode during the chemical reaction. One can, therefore, operate the reactor at high values of current densities in the presence of smootheners without compromising the current efficiency and quality of copper on the cathode. For example, if the system is operated at 50mA/cm^2, it will be operating at the limiting current level at a concentration level of EDTA of 1.29g/L or 20ml volume. The problems of irregular granulation on the surface due to high levels of current densities can be minimized as the presence of B-glue and NaCl stabilizes the system. However, if it is operated at the current density above this value then the system may overheat and cause the electrolyte to boil thereby releasing a great deal of gas bubbles on the cathode which then results in irregular deposition of copper on the cathode.

The release of gas bubbles was found to be the major contributor to the formation of rough surface. The advantage of using the surface smootheners is that the system can be operated at high current density that does not exceed the limiting value and still obtain high current efficiencies because the smootheners provide conducive conditions for the deposition of copper.

The EDTA was found to produce a greater stability in the values of current efficiency when compared to thiourea at all levels of concentration, when the reactor was operated at constant current (I) and current density. The potential across the reactor increased as the resistance (R) increased. The resistance increased due to the increase in concentration of EDTA (Figure 6.39). This means that it was possible to operate the reactor at high values of overpotential without affecting the chemical reaction. The potential across the reactor varied with the volume of additive and therefore varied with the concentration of the additive. The current efficiency was more stable as the concentration of additives increased. The resistance increased as the concentration of additive increased. The region of stability however, narrowed from 10 to 20ml representing concentration difference of 0.576g/L, i.e., from 0.714 to 1.29g/L. But the system could still be operated with good surface properties up to the 50ml level. The surface properties above the 50ml volume representing a concentration of 2.5g/L were found to be poor.

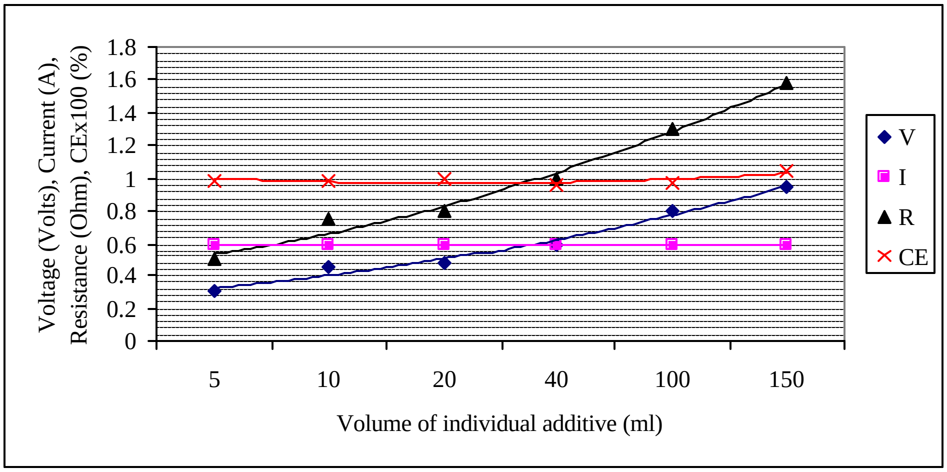


Figure 6.39: Effect of EDTA, NaCl and B-glue on the current efficiency

The increased resistance with the highest value at 150ml of 1.5O and lowest at 5ml of 0.48O resulted in the variation of potential across the reactor but the current efficiency was maintained above the 90% level by the use of B-glue and NaCl along with EDTA.

The effect of smootheners on the surface of the cathode was further investigated in terms of the strength of the colour of the surface of the electrode. At the same time, the formation of nodules was also investigated. The formation of large nodules was not observed during the entire range of the additive volume variation which is relative to the variation of concentration. Only fine nodules were observed at volumes above 100ml. These nodules did not stick to the cathode and could easily be washed with water leaving the dark colour of the deposit on the cathode. The results in Figure 6.40 show that as the volume of the smootheners increased the Tinctorial Power increased. Tinctorial Power is the strength of colour as perceived by the eye and was measured using a standard Caramel Colours Chart as given in Figure 6.40. The results mean that as the Tinctorial Power increased the bright colour of copper deposit decreased in both the cases of Tu and EDTA application. However the values of Tinctorial Power for the application of EDTA were found to be lower than those for the Thiourea until the maximum diminishing colour was reached at the Tinctorial Power of 0.56. A further examination of the occurrence of the change of colour was found to begin at the volume of 50ml and the colour diminished at volumes above 100ml.

It therefore means that the higher the Tinctorial Power the darker the colour and the lower the power the brighter the colour. The colour of copper without additive was found to be less bright while that with 5ml of Tu and EDTA were found to be the brightest. The Tinctorial Power of 0.56 produced the darkest colour on the cathode. It must be borne in mind therefore that the appropriate level of the additive produces the best results and this must be determined from tests before the operation of the plant if such data is not available. With this test, it is possible to determine the effectiveness of the additive or smoothener because the side-by-side comparison of colour demonstrates the relative colour strength of Caramel Colours.

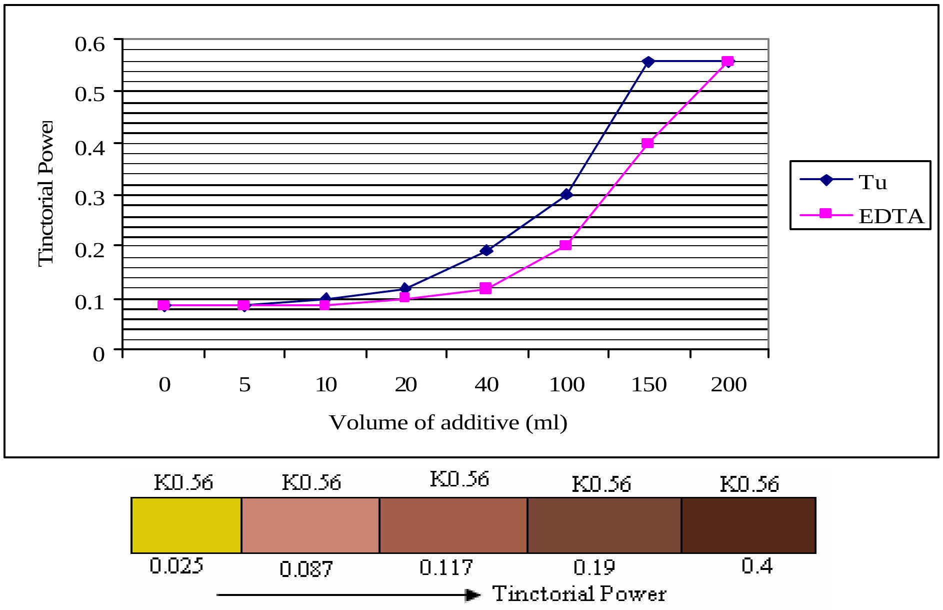


Figure 6.40: Effect of smootheners on the colour quality of the copper cathode

The colour strength is quantified by a measurement called Tinctorial Power ($K_{0.560}$). The higher the Tinctorial Power ($K_{0.560}$) the darker is the Caramel Colour. Tinctorial Power, $K_{0.560}$ (TP, $K_{0.560}$) is also defined as the absorbance of a 0.1% weight/volume solution measured through a 1 cm light path at a wavelength of 560 nanometers using a high quality spectrophotometer (2 nm or less bandpass). The determinations of the colours in this study were side-by-side comparison of colours.

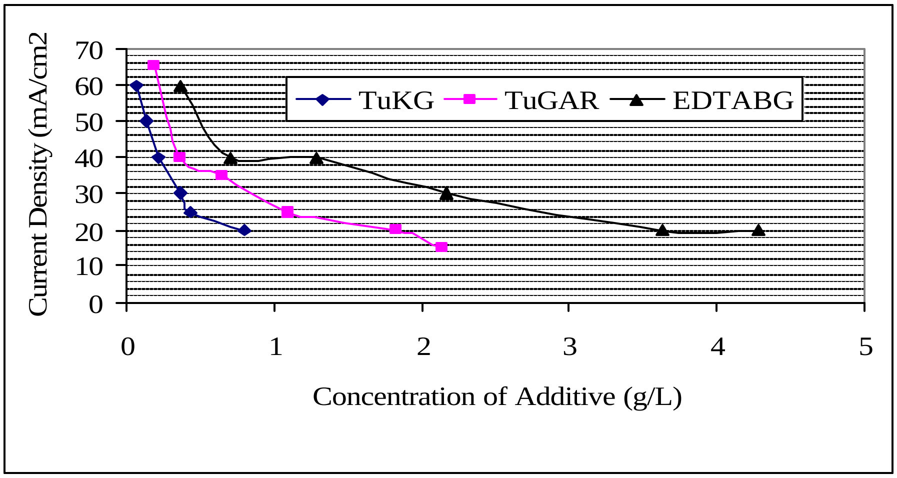


Figure 6.41: Comparison of current density reductions with level of additives

If this test appears to be difficult particularly to colour-blind personnel, then the comparison given in Figure 6.41 is indicative of how the best range of concentration of additives can be determined. The combination of Thiourea and K-Glue produced a better surface quality for a good range of concentration volume of 5-100 ml for K-Glue when compared to that of Thiourea and Gum Arabic of 5-40 ml and that of EDTA and B-Glue of 10-50 ml. This makes K-Glue a better choice for the operation.

6.10 Summary

The current density and overvoltage were important variables to drive the chemical reaction in the circular reactors. The metal impurities with more negative oxidation potentials did not affect the electrodeposition of copper whilst metals with oxidation potentials close to that of copper reduced the current efficiency. The current density increased with the increase in temperature, overvoltage and concentration of electrolyte.

The increase in overvoltage and current density above limiting values produced increased rates of deposition. The increase in concentration of electrolyte produced an increase in limiting current density. The increase in electrode-active area produced a decrease in the current efficiency. The sodium chloride, as an additive, did not affect the current density.

The use of smootheners; thiourea, EDTA reduced the limiting current density and hence the current efficiency. This effect was counteracted by using glue which enabled the process to attain normal efficiency level. The process can therefore be operated at high values of overvoltage and current densities as long as the limiting current is within the range that the process is able to operate efficiently. The current efficiency was found to be inversely proportional to the voltage. This leads to the lowering of current efficiency at high values of overvoltage. If the reactor has to be operated at high level (V>0.9volts) of overvoltage adequate inhibitor must be added in order to lower the limiting current and hence the operating current density that would produce normal current efficiency (90<CE<100%). Therefore the use of K-glue, B-glue in conjunction with each of EDTA or thiourea and NaCl improved the current efficiency.

The results have generally shown that as the volume, which is a direct function of concentration, of smootheners increased the Tinctorial Power increased. Tinctorial Power is the strength of colour as perceived by the eye and was measured using standard Caramel Colours Chart. The quality of the surface was also an indicator that the quality of copper deposited was of good quality and that the process operated at optimum conditions. If the colour of the surface was copper brown, with no dark spots but with regular granulation, then the quality of copper deposited was good. If the surface showed any abnormal deposition it means that the conditions under which the reactor was operated were not optimum.

CHAPTER 7

DISCUSSION, CONCLUSION AND RECOMMENDATIONS

7.0 Introduction

This chapter presents the discussions, conclusions and recommendations based on the data and results that were obtained during the study. It also examines whether the objectives and assumptions have been achieved and proven respectively. The key issues under the discussion are the effects of the key variables that received the treatment in order to produce the effect on the dependents. The key variables were the temperature, current density and overvoltage, electrode-active area, concentration of electrolyte, impurities and smootheners and distance between electrodes. The key dependent was the current efficiency as the main focus of the study.

7.1 Discussion

7.1.1 Effect of Overvoltage and Current Density on the current efficiency

The current density and overvoltage are among the key critical parameters in the electrodeposition processes. It has already been observed that the increase in overvoltage results in the increase in current and hence the current density for a particular active area and distance between electrodes. The current density is also affected by temperature and concentration of electrolyte (Kang-gen *et al.*, 2000). Because the current density increases with temperature, electrorefining can only be conducted at constant temperature in order to obtain optimum results. A careful choice of current density is important because if it is outside the limiting value the process ceases to provide efficient results. High values of current densities bring about erroneously high efficiencies. The objective was to evaluate the effect of overvoltage and current density on the current efficiency in order to determine the optimum values.

The optimum values are values that produce the efficiency required for the production of good quality copper. Since it was observed that increasing the overvoltage resulted in the increase in current and current density, the increase in overvoltage resulted in the increase in the rate of deposition. Similarly, the increase in the current density resulted in the increase of the rate of deposition. The assumption for the problem that the increased overvoltage and current density increases the rate of deposition was achieved. It is also an obvious matter that the assumption; increasing the deposition rate increases the current efficiency which obeys the Law of Faraday was proven. This assumption related to the problem of passivity that develops due to excessive overvoltage or current density.

7.1.2 Effect of Temperature

The rate of chemical reaction is an exponential function of temperature as alluded to earlier in the literature survey and review of electrochemical engineering. It is observed from the rate equations therefore that there is a reduction in chemical reaction when the temperature is lowered and an increase in chemical reaction when it is increased. Obviously, conducting the chemical reaction at temperatures below room temperature would give yield at increased periods of time and hence would not be beneficial to the productivity. It would also increase the cost of maintaining the temperature as ice would be required to reduce and maintain the temperature below room conditions. It was also decided not to use the temperatures above 60^oC because evaporation and boiling would have been a problem. The level of electrolyte would be lowered before the time for the chemical reaction would lapse. It is for this reason that the temperatures for the study were chosen from room conditions with increments of 15 and 21^oC as 24, 39 and 60^oC respectively. The properties of organic compounds could be affected at temperatures near and above the boiling point. The effect of temperature on electrodeposition of copper has been studied elsewhere (Kang-gen *et al.*, 2000). It has now been further confirmed that the temperature affects the limiting currents. This was shown in the results in Figure 6.7 where it is indicated that the limiting current for the 1cm distance between electrodes at 0.8volts at 24^oC was lowest ($11mA/cm^2$) when compared to those at 39°C (40mA/cm^2) and 60°C (60mA/cm^2). Similarly, the limiting current was highest at 60°C and lowest at 24°C for the 2, 3 and 4cm distances between electrodes respectively. If the temperature affects the limiting currents it means, therefore, that the current efficiency would equally be affected.

It can be observed also that the temperature enhances the conductivity of ions in solution thereby increasing the conductivity of the solution. This is achieved by the increase in temperature which enhances the dissolution of electrolyte into the solvent thereby increasing the number of ions and at the same time increasing the conductivity. In another study, the temperature was found to increase the electrodeposition of cuprous oxide (Rakhsheni and Varghese, 2006). It is therefore not surprising to have obtained increased values of masses at 60°C than those at 24 and 39°C. This explains why it was decided to choose the operation temperature for the process to be 60°C. The rate of deposition increased as the temperature increased meaning that the reaction was favoured at 60°C than at temperatures below it. The increase in the rate was attributed to the increase in temperature, which increased the temperature-dependent conductivity of ions. The reaction was therefore endothermic. Since the efficiency depends on the current and the mass deposited at a particular temperature, Faraday's Law would apply at every other temperature as given by $\Phi = mzF / MItx60$. The rate of deposition is suggestive of the rate of reaction. The two should be equal if the efficiency is one hundred percent. If the temperature is changed the rate of deposition would change and therefore the rate of reaction at each of the electrodes would change as well. Similarly the rate constant would change as it is dependent on the temperature. The Faraday's Law is not violated regardless of temperature since it depends on the charge passed per time. Since the objective was to establish the effect of temperature on the current efficiency, the increased rates of deposition and increased levels of efficiencies signifies that the temperature plays a significant role in improving the efficiency since the values of limiting currents increased with the increase in temperature. The rates of deposition increased also with the increase in temperature.

7.1.3 Effect of Distance Between Electrodes

The way in which the distance between electrodes affected the current efficiency was by lowering the rate of deposition when the distance increased due to the reduction in strength of current density. The rates of deposition were lowered at higher distances between electrodes at 24°C. Similarly, the rates of deposition were lowered at 39°C for the 2cm and 3cm distances but high for the 1cm distance. In the case of operating the system at 60°C, the rates were favoured at distances of 1cm and 2cm and low for the 3 and 4cm distances between electrodes. The rates would be increased at 4cm distance if the current density is increased for the same active area and lowering the current density for the 1cm distance would reduce the deposition rates. The operating variables of current density and overvoltage can be chosen from a voltamogragh, which gives the limiting current density, or if the limiting current is known then a choice of the operating current and current density and overvoltage can be made. The objective was to determine the effect of distance between electrodes on the current efficiency in order to establish the optimum distance. The assumption related to this objective was that the distance between electrodes affects the current efficiency. This assumption related to the problem where conducting electrolysis with increasing distance between electrodes can affect the current efficiency. It has been proven beyond reasonable doubt that the increase in the distance between electrodes lowers the current and hence the current density, overvoltage and the current efficiency but increases the resistance of the system.

7.1.4 Effect of Electrolyte Concentration

The concentration of electrolyte has been observed to contribute to the increase in current density (Kang-gen *et al.*, 2000). In another study, the concentration was used to investigate the effect on the current efficiency where it was found that the efficiencies were different for different distances of electrode beds (Ruotolo and Gubulin, 2002). In this study the current-efficiency results were also different for different values of concentrations particularly in the region of low concentration. In order to obtain good results it is important therefore that the concentration is maintained at a value above 10.8g/L. At lower concentrations the resistance increases because the pH is reduced due to the presence of more water molecules than those of sulphuric acid, which aids the ionisation of the electrolyte solid to remain dissolved in solution. The relationship developed in this study between the current efficiency and concentration can help the plant operators and other engineering related areas to have information on what level of efficiency they would expect at a particular concentration. It means therefore that increasing the concentration provides more stable conditions for the process to deposit copper on the cathode at higher concentrations than lower ones. It can be observed therefore that the objective; to examine the effect of electrolyte concentration on the current and production efficiencies in order to establish the level that provides adequate recovery was achieved. It can also be observed that the assumption (Fourth Assumption) related to this objective that the concentration of electrolyte affects the current efficiency was proven. This assumption related to the fourth problem where the concentration of copper (II) sulphate is a major factor in the deposition of copper.

7.1.5 Effect of Impurities

The concentration was used in the investigation of the effect of impurities on the current efficiency. Since it was found that increased concentration affects the efficiency more, it would be prudent on the plant operators to ensure that impurities are checked before the electrolyte is delivered to the reactors for the recovery of copper. Impurities such as silver and bismuth nitrates can easily be controlled by introducing sodium chloride or potassium chloride which precipitates such impurities in their chloride forms. For example, silver ions precipitate out as silver chloride, immediately the salt is added, before the current is passed through electrolyte as given by the overall reaction $Ag_2NO_3(l) + 2NaCl(l) = 2AgCl(s) + Na_2NO_3(l)$. However, the precipitation of bismuth is delayed until when the current is passed into solution. When the current is passed, The bismuth chloride begins to precipitate out of the solution as white crystals as given by the reaction $Bi_2NO_3(l) + 2NaCl(l) = 2BiCl(s) + Na_2NO_3(l)$. Silver ions were observed to be more reactive than copper (II) ions for obvious reasons. Silver is higher up in the electrochemical series than copper and therefore is classified as being more reactive than copper (II). This is the reason why silver ions reacted immediately with the electrode surfaces forming a layer (1-2mm) on the cathode and anode within one minute of their introduction into the electrolyte. As the current was passed more silver ions were deposited on the coating making it difficult for copper (II) ions to deposit themselves on the cathode. This resulted in the lowering of the current efficiency. In the case of bismuth, a little layer formed but most of it remained floating in the bulk electrolyte as bismuth chloride. It is important to note that the oxidation potentials of these impurities are similar to that of copper (II) hence the reason why they were able to compete with copper ions.

It was a different scenario in the case of the impurities that have oxidation potentials higher or more negative than that of copper. A combined impurity made of three metal ions (Fe + Ni + Co) was found to have little effect on the current efficiency because the oxidation potentials of these metals are more negative than that of copper. If we examine the assumption that was developed for the effect of impurities on the current efficiency in Chapter 4, we can observe that the presence of impurities in electrolyte affects the current efficiency and therefore the assumption was proven. The increase in concentration of impurities was found to produce a further decline in current efficiency. It can therefore be concluded that the presence of impurities produces a negative effect on the current efficiency. The effect is proportional to the level of its concentration. If the concentration of impurities increases the lowering of the current efficiency is increased and vice versa. A negative slope could be obtained which would give an inverse relationship in the model. Thus the objective, to determine the effect of metal and other impurities on the current efficiency was achieved.

7.1.6 Effect of Electrode-active Area

The effect of active area can be obtained in terms of changes in current efficiency as was given by the trend models or as is given by $d\Phi = wdA$ where the value of the constant (w) is equal to the slope, which is negative and the relationship is linear. If we go to the results in Chapter 6, we observe that the mathematical models for the relationship provide the effect of the active area on the current efficiency. The active area must be proportionate to the current density required for the operation as increased active areas reduce levels of current densities and hence the current efficiencies. Let us examine the objective and the assumption that were developed for the problem. The objective was to determine the effect of electrode area on current efficiency in order to establish the optimum electrode area in relation to the current density and efficiency. The assumption was that the electrode-active area reduces the current efficiency. What was observed during the study was that the current density was lowered by the increase in electrode-active area at constant overvoltage or current density. The results therefore had shown that the electrode-active area affected the current density and the current efficiency as demonstrated by the results in Chapter 6. The assumption had been proven because the current density was lowered as the electrode-active area increased at constant values of current density and overvoltage.

7.1.7 Effect of Smootheners

In the use of smootheners, the concentration was a critical factor in establishing the effect on the current efficiency and the smoothness of the cathode surface. The smootheners used in this study were thiourea, EDTA, G-Arabic, K-glue, B-glue and P-glue as stated earlier. The resistance of the solution was observed to increase as the concentration of the smootheners increased. In another study, it was found that the measured resistivities increased as thiourea concentration increased from 10^{-6} to 10^{-3} M as the current density increased from 1-50 mA/cm^2 (Donepudi *et al.*, 2001). This explains why there is need for higher potential application when the concentration of the smootheners is increased. The effect of G-Arabic, in the presence of Thiourea on the reactor electrolyte was to stabilise the system so that it could be operated to attain stable current efficiencies thereby producing a smooth surface particularly in the most stable regions below the 50ml and above the 10ml volumes representing concentrations of 1.25 and 0.357g/L respectively. However a tarnishing reaction takes place at the surface of copper electrode where it reacts with thiourea (Llopis *et al.*, 1962). The tarnishing reaction results in the lowering of the brightness of copper colour to a tarnished one. The presence of thiourea in the deposit at the electrode is suggestive of the fact that the reaction $H_2NCSNH_2 + 2H^+ + 2e^- \xrightarrow{T} NH_4CN + H_2S$ occurs at the surface of the electrode or at the electrolyte-electrode interface (Donepudi *et al.*, 2001). It is this reaction that produces the tarnished colour of the surface at the cathode when high levels of concentration of thiourea are used.

In the bulk solution, thiourea forms an intermediate complex with copper ions which reluctantly gives up the copper ion to the cathode. Thus two parallel reactions take place. The first reaction is the main one that converts directly the copper ions into copper solid as given by $Cu^{2+} + 2e \xrightarrow{T} Cu$ where the letter T stands for the temperature at which the reactor is operated. This reaction takes place when there is low concentration of thiourea. When adequate thiourea is added, the solution changes colour from blue to light green signifying the complexing nature of thiourea. The reaction is as given by $Cu^{2+} + Ch_4N_2S^{4-} \xrightarrow{T} Cu(SN_2Ch_4)^{2-}$. In addition, the effect of G-Arabic was to stabilise the current density in order to produce a smooth deposit on the cathode at higher levels of current densities until the critical point was reached when the surface began to burn out as a result of the imbalance in the system due to increased concentration of thiourea (Tu). The effect of addition of thiourea on the kinetics of anodic dissolution and cathodic reaction on copper in acidic sulfate solutions has been studied using potentiodynamic polarization measurements which showed that it has a very strong influence on the kinetics of discharge processes at different metals and produced decreasing exchange current densities and changes of Tafel slopes (Stankovic and Vukovic, 1996). According to Doona and Stanbury (1996), In excess Cu(II), the complex ion $[\mathrm{Cu(Tu)}]^{2+}$ has a stability constant $b_1 = 2.3 \pm 0.1 M^{-1}$. The fast reduction of Cu(II) in excess Thiourea obeys the rate law as is given by the expression $-d\{Cu^{2+}\}/dt = k^1\{Cu^{2+}\}^2[Tu]^7$. The rate law means that the reduction of copper (II) is second order with respect to copper concentration, seventh order with respect to Tu concentration and ninth order overall. It also means that when Tu is limiting the reduction of copper would be affected and the extent to which the reaction can go depends on the amount of Tu in solution.

The EDTA is a more efficient and widely tested chelating agent (Huang *et al.,* 1997; Wu *et al.,* 1999; Grcman *et al.,* 2003). In electrorefining, EDTA forms a tetra-sodium EDTA salt which remains ionised in solution. If the EDTA salt is used in electrorefining, then it behaves like other salts, i.e., ionise when dissolved in water. The EDTA ion chelates with copper to give an intermediate complex ion as is given by the intermediate reaction $Cu^{2+} + (EDTA)^{4-} \xrightarrow{T} Cu(EDTA)^{2-}$. The associated ions of sulphate and sodium from copper sulphate and tetrasodium-EDTA ($(Na)_4EDTA$) respectively form Sodium Sulphate salt which precipitates out in solution when the current (I) is passed at a given temperature (T) as is given by the reaction $4Na^{+} + 2SO_4{}^{2-} \xrightarrow{I(T)} 2Na_2SO_4$. The most likely path way of the reaction between the ions of copper and EDTA is the formation of copper (I) complex ion as is given by the chemical reaction $2Cu^{2+} + (EDTA)^{4-} \xrightarrow{T} Cu_2(EDTA)^{2-}$. The reaction of the intermediate ion thus requires less current density in order to release the copper ion and deposit it onto the cathode. This would be one explanation of the process of inhibition by EDTA. It means therefore that there would be a saving of electrical energy. The lowering of current usage means that the operator can be able to use high current density without disturbing the electro-deposition process and thus can realise high yields at high current densities in short periods of time.

The effect of Gum Arabic on the chemical reaction is to provide stability when the deposition proceeds. It is a stabilizer. It is an organic compound and therefore has properties similar to K-glue and B-glue. The common ground for these glues is that all are manufactured from plants. Gum Arabic is extracted from Acacia trees mainly in countries in North Africa. Gum Arabic is prepared from an exudates from the stems and branches of sub-Saharan *Acacia senegal* and *Acacia seyal* (Leguminosae) trees and produced naturally as large nodules during a process called gummosis to seal wounds in the bark of the tree (Verbeken *et al.,* 2003). Gum Arabic consists of a mixture of lower molecular weight polysaccharide which is the major component and higher molecular weight hydroxyproline-rich glycoprotein with values of Molecular Weights of 0.25×10^6 and 2.5×10^6 respectively (Goodrum *et al.,* 2000). It is a complex and variable mixture of arabinogalactan oligosaccharides, polysaccharides and glycoproteins. Depending on the source, the glycan components contain a greater proportion of L-arabinose relative to D-galactose (*Acacia seyal*) or D-galactose relative to L-arabinose (*Acacia Senegal).* The gum from *Acacia seyal* also contains significantly more 4-O-methyl-D-glucuronic acid but less L-rhamnose and unsubstituted D-glucuronic acid than that from *Acacia Senegal* (Phillips *et al.,* 2008). It is therefore a hydrocolloid that is useful in promoting physiological effects (Williams and Phillips, 2008). Because of its long chain and large molecular weight, it is suitable for the stabilization and emulsification processes. Its presence in electrorefining of copper helps to stabilize the movement of copper ions from the anode to the solution and from the solution to the cathode. We can see therefore that this is how the smootheners affect the deposition and the quality of the surface of the cathode.

7.2 Environmental Considerations

The environmental considerations should be directed at the effluents from the electrorefining process. The gases from the cells, the spent solutions and the dust from thiourea and also EDTA all can be suspected to produce different levels of impacts on the workers. In handling solid thiourea, the workers may inhale dusts that have been found to produce hypothyroidism in workers in a thiourea plant (WHO, 2003). Thiourea (CH_4N_2S) occurs in two tautomeric forms: and thus has three functional groups: amino, imino, and thiol (BUA, 1995). The first form has all the hydrogens bonded to nitrogen and the nitrogens are bonded to carbon while sulphur is also bonded to carbon. In the second form one nitrogen is bonded to two hydrogens while each of the other hydrogens are bonded to the other nitrogen and sulphur. Thiourea is soluble in water (137 g/litre at 20 °C), soluble in polar protic and aprotic organic solvents, and insoluble in non-polar solvents (BUA, 1995, Mertschenk *et al.*, 1995: 803–815.). The effects of thiourea can thus be discussed in two dimensions: the effects on the environment and the effects on humans. A number of effects have been determined in numerous studies.

The effects on the environment have been documented in a report by WHO (WHO, 2003). A few are highlighted here. The available experimental data on the environmental bioaccumulation as well as the measured *n*-octanol/water partition coefficients indicated no bioaccumulation potential for thiourea in aquatic organisms. The administration of thiourea to laboratory animals caused a reduction in weight gain and enlargement of the thyroid gland resulting in symptoms of hypothyroidism to appear. However no reports of carcinogenicity have been attributed to thiourea exposure in humans. Glazer and Orion (1984) investigated the effects of thiourea on the development of nematodes. Excised tomato roots, growing on basal medium and inoculated with eggs of *Meloidogyne javanica*, were exposed to thiourea concentrations in the range of 6–46 mg/litre. After 96 hours of exposure, thiourea concentrations of 12 mg/litre inhibited nematode development. Only 36% matured to adults (in the untreated control: 90%) after an observation period of 4 weeks

Different fungi were found to be relatively insensitive to thiourea exposure. But complete growth inhibition was observed for *Penicillium rugulosum* after a 7-day exposure to 2000 mg thiourea/litre (Lashen and Starkey, 1970). According to Lashen and Starkey (1970), terrestrial plants proved to be generally more sensitive. Whereas thiourea concentrations below 12 mg/litre increased the growth of excised tomato roots (*Lycopersicum esculentum*) within 4 weeks of exposure in a defined basal medium, 18, 23, and 46 mg/litre reduced growth by about 45%, 60%, and 30%, respectively (Glazer & Orion, 1984).

The effects of thiourea on humans include the following: The side-effects of thiourea have been described from observations of the former therapeutic use of thiourea in the 1940s as a thyroid depressant (MAK, 1988). Cases of contact dermatitis have been described in thiourea production workers; the contact dermatitis disappeared rapidly after the workers had been transferred to another workplace (Speranski *et al.,* 1969).

The concentrations of thyroid hormones T4 and T3 were significantly lower in the exposed workers than in the controls (T4: 78.0 ± 5.2 versus 109.4 ± 2.0 nmol/litre, $P < 0.05$; T3: 1.2 ± 0.1 versus 3.8 ± 0.1 nmol/litre, $P < 0.001$) (Talakin *et al.*, 1985).

Products such as wet suits, swimming goggles, orthopaedic devices, protective gloves, and shoes containing these compounds have been shown to produce allergic contact dermatitis (Kanerva *et al*., 1994; McCleskey and Swerlick, 2001). In an early study with hyperthyroid patients ($n = 12$), it was shown that a dose of 15 mg (about 0.2 mg/kg body weight per day for a 70-kg person) daily for 10–12 weeks was insufficient to depress thyroid activity, as judged by the concentrations of serum precipitable iodine, while a dose of 70 mg daily (1.0 mg/kg body weight per day) in conjunction with iodine solution produced a remission in hyperthyroidism (Winkler *et al.*, 1947). It is therefore necessary that thiourea be removed from effluents by the addition of hydrogen peroxide (H_2O_2) after the determination of its concentration using the method developed elsewhere (Krzewska *et al*., 1984).

EDTA salts are used as a component in food products, pharmaceuticals and formulated consumer products, such as soaps, shampoos and detergents, so there is great potential for consumer exposure. For example, EDTA salts are used for surface preparation, metal cleaning and plating in metal work. They are used as personal care products to increase effectiveness and improve stability of solid soaps, creams, oils, ointments shampoos and hair preparation. They are used in agriculture to provide micronutrients to fertilizers, in photography as bleach in film processing and in textiles for dyeing colour stripping. In water treatment, EDTA salts are used to control hardness and scale formation due to calcium and magnesium. Most of the chelating agents are used as components in chemical processes. The pulp and paper, cleaning, chemical processing, agriculture and water treatment take up about 80% of the world consumption (SRI, 2003). Although EDTA salts have been found to be non-toxic to fish, ingestion of salts with high pH or low pH can cause ulceration and burns of the mouth and throat. High pH tetrasodium EDTA have been found to produce severe eye irritation and can impair the vision (Dow, 2004:3-7). According to the Detergent Ingredient Review Committee

(DIRC, 1995), "The salts of EDTA are soluble in water and therefore form ions of sodium and EDTA but there is no evidence of bio-accumulation in most of the aquatic organisms". Conclusions from the Institute for Health and Consumer Protection (IHCP) European Union Risk Assessment Report of EDTA show that there is no risk to the environment (IHCP, 2004).

The World Health Organization (WHO) and the United States Food and Drug Administration (USFDA) have independently assessed the health safety of EDTA and have set the acceptable daily intake of EDTA at 2.5 mg/kg/person/day or roughly 150 mg/day for the calcium disodium salt. Human consumption of EDTA at levels observed in drinking water combined with that amount of EDTA consumed as part of average daily food intake, are well within WHO and FDA acceptable daily intake guidelines.

It is acceptably clear that EDTA is safe and does not accumulate in the environment, EDTA would be the best choice for electrorefining process because it would not produce adverse effects on the workers. However, the main disadvantage is that the cost of EDTA in the recovery of metals from soils has been reported to be high (Nogueira *et al.,* 2007). The other chemical that would be of great concern to the environment is the acid in the electrolytes of electrorefining processes. The sulphuric acid is highly soluble in water and has a half life of 2-20 days. The entry into the environment is through industrial effluents. It has high potency to provide hydrogen ions in solution. Increasing hydrogen ions in solution increases the acidity. If the acid is not adequately neutralised, a great deal of damage to the environment would take place; instant damage at high levels of hydrogen concentration and gradual at lower levels of concentrations. The damage to environment can be classified into two categories. The short term category produces acute effects. The acute-ecological effects include death of animals, fish, and birds which can be observed in 2-4days after exposure. The long term category is the chronic phase in which the chronic effects include short life span, lower fertility, changes in the behaviour of animals (Vincoli, 1997:2813). It is therefore important that adequate neutralisation using lime would be necessary before the discharge of effluents from electrorefining plant in order to protect the life of plants, aquatic life, and the prevention of lowering of the quality of surface and underground waters.

7.3 Economic Benefits

Many organisations in Zambia would find the results useful in the initiation of efforts to establish small-scale plants. The mining sector of Zambia or the Government of the Republic of Zambia would find the information useful in the efforts to meet the challenge of technology advancement and mining sector copper improvement strategies. The academic fraternity and particularly students will find the information useful as one of their reference sources in the process of carrying out their project reviews. Other business entities particularly those that are into copper recovery may want to use the study as an opportunity to decide to venture into the copper recovery using electrorefining method.

The major benefit that the study will provide is the use of new smootheners, which are available and are not currently exploited. Employment generation and sustainable development goes hand in hand with such innovations. If the study can be adopted then it would provide an opportunity to many and therefore sustain lives in the informal sector as the demand for copper in the informal sector for repairing equipment both in electrical and automotive small scale industries is increasing. The study would therefore provide an easy way to purify copper from ore or scrap metals.

Wastewater treatment is experiencing a number of problems. The removal of heavy metals and the metals higher up in the chemical series is becoming increasingly difficult as the pollution events are increasing due to faulty equipment and lax management systems. Electrorefining is one of the methods that can easily be adapted and applied in this area at a large scale to treat wastewaters, removing metals, before they are released into the environments. It is also a good method to remove precious metals such as gold and silver.

Electroplating using electrochemical process is used in many countries in the world and therefore this is an already existing benefit that human kind is enjoying. However there are many new areas of applications that could benefit from this methodology. The use of smootheners such as K-glue and B-glue which can help to reduce the nodulation problem would provide a great benefit to the electrochemical industry. It can be observed in Table 7.1 that the price of the smootheners could be a factor that could increase the cost of the recovery of copper from solutions.

Table 7.1: The current prices of some smootheners and inhibitors

No	Item	Cost/kg ($)	Cost/tonne ($)
1	Paper Glue (Beacon Zip); solid	13.3	13 300
2	Paper Glue (Krazy Glue); gel	7.5	7 500
3	Paper Glue (Craft Glue); gel	24.3	24 300
4	Paper Glue (Bostik Glue Stick); solid	21.0	21 000
5	Bone Glue; granules	1.5	1 500
6	Gum Arabic (Acacia Senegal); granules	5.0	5 000
7	EDTA; granules	2.0	2 000

At 7.5$/kg K-glue would introduce a lower cost to the recovery than B-glue whose price per kilogram, 21$, is on the high side. Even the cost of some other smootheners such as Beacon Zip (solid), Craft glue (gel) at 13.3 and 24.3$/kg respectively can be considered to be on the high side when compared to K-glue. Although bone glue is the cheapest at 1.5$/kg it may not be the effective smoothener at the current levels that K-glue and B-glue have proven to be in this study. Gum Arabic has proven to be equally effective as K-glue in this study and its price per tonne is 33.3% lower than that of K-glue. It would provide a better leverage in terms of cost.

7.4 Conclusion

The study drew a number of conclusions. The increase in electrode active area decreased the current and the current density and hence the current efficiency. It requires the adjustment of overvoltage in order to maintain the same deposition rate at the desired electrode active area. The increase in overvoltage and current density increased the deposition rate, which resulted in irregular deposits on the cathode particularly at current densities exceeding the limiting value. The increase in temperature of the reactor favoured the current efficiency more so at temperatures above 40^{o}C and temperatures less than 70^{o}C for the 2 and 3cm distances between electrodes. The increase in distance between electrodes produced a decrease in the rate of deposition on the cathode. Therefore adjustment to the overvoltage and current density was required in order to maintain the same level of rate of deposition and current efficiency. The concentration of electrolyte was a principal factor to the level of the limiting current and the smooth operation of the circular reactors. Concentrations above 10.8g/L produced stable current efficiencies. The metal impurities that have reduction potentials greater than that of copper were found to have no effect on the electrolytic process while those with similar decomposition potentials like Silver and bismuth nitrates produced strong inhibition on the electrochemical reaction and hence lowered the current efficiencies. The use of K-glue, B-glue, G-Arabic, thiourea and EDTA produced varying smoothening effects on the cathode. Therefore the limiting current, current density, active area, temperature, and concentration of electrolyte and smootheners are useful parameters in the evaluation of copper recovery from solutions.

7.5 Recommendations

In making recommendations one has to have the operating factors that affect the electrorefining process in mind. It is also important to note that the copper recovery by the electrochemical method is widely used in the world but the problems that enchroach the process during operation have been a challenge to many that operate such processes. Often times the staff that operate such processes are semi skilled as is the case in most third world countries and therefore it is common that employees can ignore important parameters that are required to produce quality copper. In such cases the industry may spend huge sums of money on the correction of such problems. The recommendations that are given below are inter-linked with the fact that the current efficiency is a critical parameter in ensuring that the yield is at the level that can bring about profitability to industries.

The increase in electrode active area decreases the current and the current density and hence the current efficiency. It is therefore recommended that the reactors be operated at right level of current density determined from chromatogram studies. This requires the adjustment of overvoltage in order to obtain the current that can produce the desired current density in order to maintain a high current efficiency. The key in determining such is the limiting current density. The increase in overvoltage and current density increases the deposition rate, which results in irregular deposits to form on the cathode particularly at current densities exceeding the limiting value. The problem can be solved through the determination of the value of the limiting current density and then, as stated earlier, adjusting the overvoltage to the level that attains the current density to the level below the limiting value. The increase in temperature of the reactor favoured the current efficiency more so at temperatures above 30^{o}C and temperatures less than 70^{o}C. Although the current efficiencies were high in some cases at temperatures lower than the stated range, the instability can make the operation difficult as most ions of the electrolyte are not released into solution. It is therefore recommended that the operation of the reactors be at temperatures above 30^{o}C (39 to 70^{o}C) as temperatures above 70^{o}C can damage the plant based smootheners K-glue and B-glue.

The increase in distance between electrodes produced a decrease in the rate of deposition on the cathode. Therefore adjustment to the overvoltage and current density is required in order to maintain the same level of rate of deposition and current efficiency. The concentration of electrolyte is a principal factor in the operation of electrorefining process. The level of the limiting current and the smooth operation of the circular reactors depended on the concentration. It is important therefore that the concentration in reactors be maintained at levels above 10g/L and below 100g/L. This range produced high levels of current efficiencies. The other reason is that at concentrations lower than 10g/L the resistance in the solution increases and therefore the current density is affected. Electrowinning may be very useful at concentrations below this range.

The metal impurities that have oxidation potentials more negative than that of copper were found to have no effect on the electrolytic process. Users of electrorefining process should not worry about these. However, elements that have the same oxidation potentials as that of copper, examples being bismuth and silver or their nitrates, which were found to compete with copper during the electrochemical reactions need to be eliminated before the process begins or during the process by adding an eliminator such as sodium chloride which can precipitate out such metals as bismuth and silver as chlorides. Such compounds do not ionise easily in the electrolyte at the operating temperature.

Smootheners have been found to refine the grain of the cathode surface and hence help to improve production efficiency. Smootheners such as thiourea and Bone glue are extensively used in industry to produce commercial grade copper. Sodium Chloride and potassium chloride are also used. The use of G-Arabic is reported in other studies as indicated in the report. However the use of K-glue, B-glue and P-glue in electrorefining is not reported in literature. These compounds were found to be effective in the smoothening of cathode surfaces. The users of electrorefining processes should try K-glue and B-glue in order to reduce the costs of production. Thiourea and EDTA should not be used alone because these chemicals are strong current density inhibitors and impact on the current efficiency highly. Both these chemicals were found to lower the current efficiency. Therefore it is recommended that each of thiourea and EDTA be used in conjunction with either K-glue or P-glue or B-glue or G-Arabic in the presence of sodium chloride.

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APPENDICES

Appendix 1: Effect of overvoltage and current density at 24^{o}C

1A: Effect of overvoltage and current density on the current efficiency at 24^{o}C for 1cm

I	*V*	*A*	*j*	*t*	*T*	M_1	M_2	*m*	*F*	*Distance*
A	V	cm^2	A/cm^2	min	^{o}C	g	g	g	x100	cm
0.25	0.1	13.5	0.015	15	24	23.8902	23.9607	0.0705	0.95	1
0.38	0.2	13.5	0.028	15	24	23.9607	24.0697	0.1090	0.97	1
0.60	0.3	13.5	0.044	15	24	24.0697	24.2482	0.1785	1.00	1
0.70	0.50	13.5	0.052	15	24	19.0732	19.1752	0.2887	0.97	1
0.80	0.60	13.5	0.059	15	24	19.1752	19.6619	0.4867	0.82	1
1.00	1.00	13.5	0.074	15	24	19.6619	20.2782	0.6163	1.04	1
2.00	2.00	13.5	0.148	15	24	20.2782	21.9687	1.6905	1.42	1

1B: Effect of overvoltage and current density on the current efficiency at 24°C for 2cm

I	V	A	j	t	T	M_1	M_2	m	F	*Distance*
A	V	cm^2	A/cm^2	min	°C	g	g	g	x100	cm
0.10	0.10	12	0.008	15	24	24.2482	24.2792	0.0310	1.00	2
0.30	0.20	12	0.025	15	24	24.2792	24.3700	0.0908	1.02	2
0.35	0.30	12	0.029	30	24	32.1369	32.4145	0.2776	0.93	2
0.40	0.80	12	0.033	30	24	32.4145	32.6586	0.2441	1.03	2
0.80	1.20	12	0.067	30	24	32.6586	33.0950	0.4364	0.92	2
1.70	1.80	12	0.142	30	24	33.0950	33.9335	0.8385	0.83	2

1C: Effect of overvoltage and current density on the current efficiency at 24°C for 3cm

I	V	A	j	t	T	M_1	M_2	m	F	*Distance*
A	V	cm^2	A/cm^2	min	°C	g	g	g	x100	cm
0.14	0.10	22.5	0.004	15	24	23.2934	23.3326	0.0392	0.94	3
0.25	0.20	22.5	0.010	15	24	23.3326	23.4007	0.0681	0.92	3
0.55	0.30	22.5	0.023	15	24	23.4007	23.5593	0.1586	0.97	3
0.66	0.40	22.5	0.030	15	24	23.5593	23.7493	0.1900	0.97	3

1D: Effect of overvoltage and current density on the current efficiency at 24°C for 4cm

I	*V*	*A*	*j*	*t*	*T*	M_1	M_2	*m*	*F*	*Distance*
A	V	cm^2	A/cm^2	min	°C	g	g	g	x100	cm
0.14	0.1	20.3	0.010	15	24	24.3700	24.4090	0.0390	0.94	4
0.20	0.2	20.3	0.010	15	24	24.4090	24.4610	0.0520	0.88	4
0.40	0.30	20.3	0.020	30	24	31.3160	31.4318	0.1158	0.98	4
0.50	0.40	20.3	0.025	30	24	31.4318	31.5860	0.1542	1.00	4
0.80	0.70	20.3	0.039	30	24	31.4170	31.8050	0.3880	0.82	4
1.25	1.11	20.3	0.062	30	24	31.8050	32.9908	1.1858	1.60	4
1.65	1.40	20.3	0.081	30	24	32.9908	34.1867	1.1959	1.22	4

Appendix 2: Effect of overvoltage and current density at 39°C

2A: Effect of overvoltage and current density on current efficiency for 1cm distance

I	*V*	*A*	*j*	*t*	*T*	M_1	M_2	*m*	*F*	*Distance*
A	V	cm^2	A/cm^2	min	^oC	g	g	g	x100	cm
0.28	0.1	16	0.010	15	39	13.7640	13.8414	0.0774	0.93	1
0.50	0.2	16	0.028	15	39	13.8414	13.9856	0.1442	0.97	1
0.85	0.3	16	0.053	15	39	13.9856	14.2023	0.2177	0.85	1
1.25	0.4	16	0.078	15	39	14.2033	14.5580	0.3547	0.93	1
2.00	0.8	16	0.122	15	39	14.5580	15.3320	0.7740	1.30	1

2B: Effect of overvoltage and current density on current efficiency for 2cm distance

I	*V*	*A*	*j*	*t*	*T*	M_1	M_2	*m*	*F*	*Distance*
A	V	cm^2	A/cm^2	min	^oC	g	g	g	x100	cm
0.30	0.10	27.5	0.010	15	39	27.2559	27.3412	0.0853	0.96	2
0.40	0.20	27.5	0.020	15	39	27.3412	27.4325	0.0913	0.96	2
0.80	0.40	27.5	0.030	15	39	27.4325	27.6390	0.2065	0.87	2
1.30	0.80	27.5	0.050	30	39	27.6390	28.1173	0.4783	1.24	2

2C: Effect of overvoltage and current density on current efficiency for 3cm distance

I	*V*	*A*	*j*	*t*	*T*	M_1	M_2	*m*	*F*	*Distance*
A	V	cm^2	A/cm^2	min	°C	g	g	g	x100	cm
0.15	0.10	24.8	0.004	16	39	18.3652	18.4132	0.0480	1.00	3
0.20	0.20	24.8	0.008	15	39	18.4132	18.4687	0.0555	0.93	3
0.32	0.30	24.8	0.012	15	39	18.4687	18.5617	0.0930	0.98	3
0.70	0.40	24.8	0.016	15	39	18.5617	18.7712	0.1095	0.93	3
1.00	0.50	24.8	0.020	15	39	18.7712	19.0583	0.2871	0.98	3
1.52	0.80	24.8	0.061	15	39	19.0583	19.5022	0.4439	0.98	3
1.80	1.00	24.8	0.073	21	39	19.5022	20.2454	0.7432	0.98	3
3.00	1.30	24.8	0.121	15	39	20.2454	21.2688	1.0234	1.15	3

2D: Effect of overvoltage and current density on current efficiency for 4cm distance

I	*V*	*A*	*j*	*t*	*T*	M_1	M_2	*m*	*F*	*Distance*
A	V	cm^2	A/cm^2	min	°C	g	g	g	x100	cm
0.10	0.05	14	0.010	15	39	15.5205	15.5205	0.0000	0.00	2
0.20	0.10	14	0.011	15	39	15.5205	15.5773	0.0568	0.96	2
0.30	0.20	14	0.020	15	39	15.5773	15.6357	0.0854	0.96	2
0.60	0.45	14	0.040	15	39	15.6357	15.8063	0.1706	0.96	2
0.85	1.00	14	0.061	15	39	15.8063	16.4094	0.2909	1.15	2

Appendix 3: Effect of overvoltage and current density at 60^oC

3A: Effect of overvoltage and current density on current efficiency for 1cm distance (Dist)

I	V	A	j	t	T	M_1	M_2	m	F	*Dist*
A	V	cm^2	A/cm^2	min	^oC	g	g	g	x100	cm
0.29	0.10	16	0.020	15	60	16.5770	16.6564	0.0794	0.93	1
0.60	0.20	16	0.034	15	60	16.6564	16.8236	0.1672	0.94	1
0.80	0.30	16	0.050	15	60	16.8236	17.1252	0.3016	1.28	1
1.10	0.50	16	0.070	15	60	17.1252	17.8055	0.6803	2.09	1
1.50	1.00	16	0.090	30	60	-	-	1.0440	1.06	1
2.00	1.20	16	0.125	23	60	-	-	1.4400	0.96	1

3B: Effect of overvoltage and current density on current efficiency for 2cm distance

I	V	A	j	t	T	M_1	M_2	m	F	$Dist$
A	V	cm^2	A/cm^2	min	^oC	g	g	g	x100	cm
0.29	0.10	13.5	0.015	15	60	22.7720	22.8550	0.0830	0.97	2
0.50	0.20	13.5	0.037	15	60	22.8550	22.9920	0.1370	0.93	2
0.85	0.35	13.5	0.063	15	60	22.9920	23.2325	0.2405	0.95	2
1.65	0.80	13.5	0.122	15	60	23.2325	25.1320	0.5525	1.13	2
1.80	1.0	13.5	0.133	15	60	-	-	0.7200	0.82	2
2.2	1.2	13.5	0.163	15	60	-	-	0.9270	0.86	2
3.0	1.4	13.5	0.222	12	60	-	-	1.0800	0.92	2
3.8	1.6	13.5	0.281	12	60	-	-	1.3500	0.91	2

3C: Effect of overvoltage and current density on current efficiency for 3cm distance

I	V	A	j	t	T	M_1	M_2	m	F	$Dist$
A	V	cm^2	A/cm^2	min	°C	g	g	g	x100	cm
0.15	0.10	16	0.01	15	60	23.5590	23.5932	0.0342	0.77	3
0.30	0.20	16	0.02	15	60	23.5932	23.6513	0.0581	0.65	3
0.50	0.30	16	0.03	15	60	23.6513	23.7895	0.1382	0.93	3
0.75	0.40	16	0.04	17	60	23.7895	24.0321	0.2426	0.96	3
1.00	0.50	16	0.06	15	60	24.0321	24.3186	0.2865	0.98	3
1.65	0.80	16	0.10	15	60	24.3186	24.8036	0.4850	0.99	3
2.52	1.00	16	0.16	15	60	23.9243	24.6292	0.7049	0.95	3
3.60	1.60	16	0.23	15	60	24.6292	25.8208	1.1916	1.13	3

3D: Effect of overvoltage and current density on current efficiency for 4cm distance

I	*V*	*A*	*j*	*t*	*T*	M_1	M_2	*m*	*F*	*Dist*
A	V	cm^2	A/cm^2	min	^oC	g	g	g	x100	cm
0.10	0.10	20.3	0.005	15	60	22.8441	22.8307	0.0000	0.00	4
0.15	0.20	20.3	0.010	15	60	22.8307	22.8676	0.0369	0.83	4
0.28	0.30	20.3	0.014	15	60	22.8676	22.9608	0.0932	0.75	4
0.60	0.40	20.3	0.025	15	60	22.9608	23.1263	0.1655	0.94	4
0.75	0.50	20.3	0.037	15	60	23.1263	23.3395	0.2132	0.95	4
1.00	0.60	20.3	0.049	15	60	23.3395	23.6092	0.2697	0.90	4
1.30	0.80	20.3	0.059	18	60	23.6092	24.0366	0.4274	0.93	4
1.55	1.00	20.3	0.076	37	60	24.0366	25.1176	1.0810	0.95	4
1.80	1.30	20.3	0.088	15	60	25.1176	25.6515	0.5339	1.00	4
3.40	1.80	20.3	0.167	15	60	25.6515	26.7246	1.0731	1.05	4

3E: Effect of voltage on the deposition rate at 24°C

1cm		2cm		3cm		4cm	
Voltage (Volts)	**Rate x10^{-5} (g/s)**	**Voltage (Volts)**	**Rate x10^{-5} (g/s)**	**Voltage (Volts)**	**Rate x10^{-5} (g/s)**	**Voltage (Volts)**	**Rate x10^{-5} (g/s)**
0	0	0	0	0	0	0	0
0.1	7.8	0.1	3.4	0.1	4.3	0.1	4.3
0.2	12	0.2	10	0.2	7.6	0.2	5.8
0.3	19.8	0.3	15	0.3	17.6	0.3	6.4
0.4	16	0.8	14	0.4	24	0.4	8.5
0.5	24	1.2	24.2	-	-	0.7	21.6
0.6	27	1.7	46.6	-	-	1.11	66
2	94	-	-	-	-	1.4	66

Appendix 4: Effect of concentration on the current efficiency

The effect of electrolyte concentration on current efficiency

Item	***Cn***	*h*	***I***	***Area***	***j***	M_a	M_c	***m***	***t***	***Efficiency***
Units	g/L	V	A	cm^2	A/cm^2	g	g	g	min	X100%
1	1.50	0.50	0.05	30.25	0.00165	25.6217	25.6377	0.0160	15	1.08
2	3.00	0.30	0.09	30.25	0.00300	25.6377	25.6638	0.0261	15	0.98
3	6.00	0.50	0.21	30.25	0.00694	25.6638	25.7122	0.0484	15	0.78
4	8.90	0.40	0.15	25.00	0.00600	23.2670	23.3060	0.0390	15	0.66
5	14.8	0.40	0.38	27.50	0.01382	23.4736	23.5816	0.1080	15	0.96
6	29.6	0.35	0.50	27.50	0.01818	23.5816	23.7268	0.1452	15	0.98
7	59.2	0.35	0.50	32.50	0.01538	23.7268	23.8670	0.1402	15	0.95

Appendix 5: Effect of temperature

5A: Effect of overvoltage on the current at 24°C for various distances between electrodes

1cm	V	0	0.10.	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1.1	1.2	1.3	1.4	-	-	-	-
	I	0	0.08	0.32	0.5	1.11	1.2	1.2	1.2	1.2	1.2	1.4	2	3	4	5	-	-	-	-
2cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8
	I	0	0.2	0.42	0.6	0.6	0.6	0.6	0.6	0.8	0.9	1.2	1.7	2.1	2.5	3.1	3.6	4	4.6	5
3cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8
	I	0	0.3	0.5	0.7	0.6	0.62	0.62	0.62	0.63	0.8	1	1.4	1.8	2.3	2.6	3	3.3	3.8	4.2
4cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	-
	I	0	0.33	0.6	0.62	0.62	0.62	0.8	1	1.5	1.8	2.3	2.6	2.8	3.3	3.7	4.1	4.5	4.7	5

5B: Effect of overvoltage on current density at 39^{o}C for various distances between electrodes

1cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.10	1.20	1.30	1.4	-	-	-	-	-
	jx10	0	0.2	0.4	1.0	1.6	2.8	4.0	4.0	4.4	6.4	8.0	10.4	13.2	16.4	20	-	-	-	-	-
2cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.10	1.20	1.30	1.4	-	-	-	-	-
	jx10	0	0.8	2.6	3.4	3.6	3.6	3.6	3.6	4.8	6.0	8.0	10.8	14.0	16.0	20	-	-	-	-	-
3cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.10	1.20	1.30	1.4	1.50	1.60	1.70	1.80	-
	jx10	0	1.1	2.2	3.4	3.6	3.6	4.0	4.0	4.0	4.8	5.2	6.80	9.20	11.2	13	14.8	17.2	18.8	20.0	-
4cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.10	1.20	1.30	1.4	1.50	1.60	1.70	1.80	1.9
	jx10	0	0.9	2.1	3.2	3.2	3.4	4.0	4.0	4.0	4.0	4.8	7.20	8.00	10.0	11	13.6	14.4	16.8	18.4	20

5C: Effect of overvoltage on the current density at 60°C for various distances between electrodes

1cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1.0	1.1	1.2	1.3	1.4	-	-
	jx10	0	1.0	4.0	5.0	6.0	6.0	6.0	6.0	7.0	11.2	14	16	18	20	-	-
2cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	-
	jx10	0	2.0	3.2	4.0	5.6	6.0	6.4	6.4	6.4	8.0	11.2	13.6	16	18	20	-
3cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5
	jx10	0	1.0	2.7	3.7	4.4	5.2	5.2	5.6	6.0	5.2	8.0	11.2	13.2	14.8	17.6	20
4cm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5
	jx10	0	1.2	2.0	3.6	4.4	5.2	6.8	6.8	6.8	7.6	8.4	10.4	12.4	14	16	20

Appendix 6: Effect of electrode active area

6A: Effect of active area on current density for 5% concentration of electrolyte

10.0cm^2	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
	j	0	20	38	48	54	58	60	60	86	98	130	160	180	240	280	320	350	410	440	470	500
12.5cm^2	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	-	-	-
	j	0	16	36	56	57	64	68	68	72	96	144	160	208	240	280	320	360	400	-	-	-
17.5cm^2	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	-	-	-
	j	0	14	33	46	57	57	69	69	69	74	97	120	154	177	200	240	263	286	-	-	-
22.5cm^2	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	-	-	-	-	-
	j	0	11	24	41	49	58	62	71	71	71	102	120	147	178	209	236	-	-	-	-	-
30cm^2	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	-	-	-	-	-	-	-
	j	0	15	29	49	50	57	60	67	67	77	93	143	157	183	-	-	-	-	-	-	-

6B: Effect of electrode active area on current efficiency for a 5% concentration of electrolyte

Time (min.)	Area (cm^2)	η (V)	I (A)	j (A/cm^2)	M_{ic} (g)	M_{fc} (g)	M (g)	Temp (^oC)	Distance (cm)	F x100%
15	10	0.3	0.5	0.050	22.5294	22.7040	0.1746	60	2	1.18
15	12.5	0.3	0.5	0.040	22.7040	22.8495	0.1455	60	2	0.98
15	17.5	0.2	0.5	0.030	22.8495	22.9892	0.1397	60	2	0.94
15	22.5	0.15	0.5	0.022	22.9892	23.1022	0.113	60	2	0.76
15	30	0.15	0.5	0.017	23.1722	23.2646	0.0924	60	2	0.62

Appendix 7: Effect of impurities

7A: Voltametric readings for electrolyte with dissolved impurities (Fe + Co + Ni)

1ppm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.7	1.9
	I	0	0.25	0.52	0.78	0.75	0.91	0.91	0.91	0.91	1.0	1.2	1.7	2.1	2.5	3.0	3.4	4.2	5.0
6ppm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.5	1.7	-	-
	I	0	0.31	0.7	0.85	1.0	1.1	1.1	1.1	1.1	1.3	1.5	2.0	2.5	3.0	4.0	5.0	-	-
12ppm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.4	1.6	1.8	-	-
	I	0	0.34	0.6	0.88	1.0	1.0	1.2	1.2	1.2	1.3	1.5	2.0	2.4	3.3	4.3	5.0	-	-
20ppm	V	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.7	-
	I	0	0.38	0.72	0.92	1.1	1.1	1.2	1.2	1.2	1.3	1.5	2.0	2.5	3.0	3.5	4.0	5.0	-

(a) Distance between electrodes=2cm, concentration of reactant=50g/L, temperature=$60^{o}C$

7B: Effect of combined impurities (Fe +Co + Ni) on current efficiency at 25mA/cm^2)

I	V	t	M_1	M_2	m	F	t_{cum}	m_{cum}	F_{cum}	Imp
A	V	min	g	g	g	x100	min	g	%	ppm
0.5	0.2	15	24.4925	24.6375	0.1450	0.98	15	0.1450	98.0	1
0.5	0.2	15	24.6375	24.7810	0.1435	0.97	30	0.2885	97.4	6
0.5	0.2	15	24.7810	24.9263	0.1453	0.98	45	0.4338	97.7	12
0.5	0.2	15	24.9263	25.0728	0.1465	0.99	60	0.5803	98.0	20
0.5	0.2	15	25.0728	25.2290	0.1562	1.05	75	0.7365	99.5	40
0.5	0.2	15	25.2290	25.3790	0.1502	1.05	90	0.8867	99.8	60
0.5	0.2	15	25.3790	25.5303	0.1513	1.02	105	1.0380	100.0	>100

(a) Distance between electrodes is 2cm, concentration is 50g/L and temperature is 60°C

7C Effect of Bismuth on current efficiency for fifteen-minute duration

Impurity	*Voltage*	*Current*	*m*	*CE*	*Voltage*	*Current*	*m*	*CE*
wt%	V	A	g	x100%	V	A	g	x100%
0	0.2	0.5	0.1495	1.01	0.3	0.8	0.2558	1.08
0.05	0.2	0.5	0.1483	1	0.3	0.8	0.2533	1.06
0.22	0.2	0.5	0.1419	0.96	0.3	0.8	0.2487	1.05
0.54	0.2	0.5	0.1341	0.91	0.3	0.8	0.2322	0.98
1.48	0.2	0.5	0.1314	0.89	0.3	0.8	0.2392	1.01
3.1	0.2	0.5	0.1357	0.92	0.3	0.8	0.2286	0.96

7D Potentials of some metals associated with copper ores

Metal Ion	*Potential (Volts)*	*Metal Ion*	*Potential (Volts)*
Silver Ag^{+}	+0.8	Bismuth Bi^{3+}	+0.32
Zinc Zn^{2+}	-0.76	Cobalt Co^{2+}	-0.28
Copper Cu^{2+}	0.34	Sodium Na^{+}	-2.71
Iron Fe^{2+}	-0.44	Potassium K^{+}	-2.92
Nickel Ni^{2+}	-0.25	Lead Pb^{2+}	-0.13
Gold Au^{3+}	+1.5	Gold Au^{+}	+1.83

Appendix 8: Equipment used during the study

Figure 1: The thermostat controlled water bath and electrodes

Figure 2: Electrochemical machine with 25 volts dc power

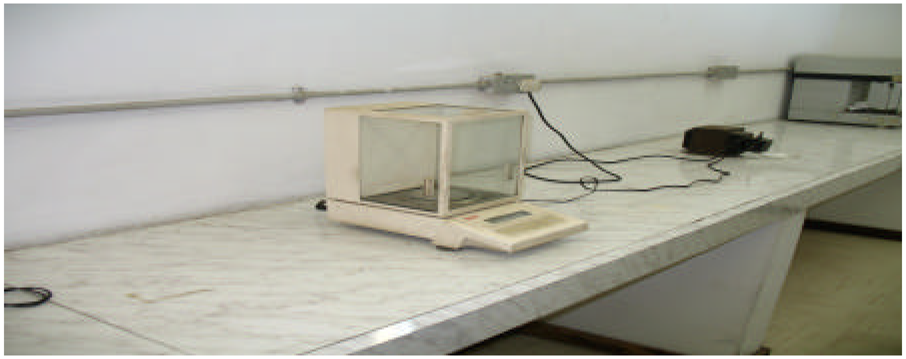

Figure 3: Weighing Scale

Figure 4: Cleaning solvents; dilute nitric acid and propan-2-ol

Figure 5: Batch reactor immersed in water bath

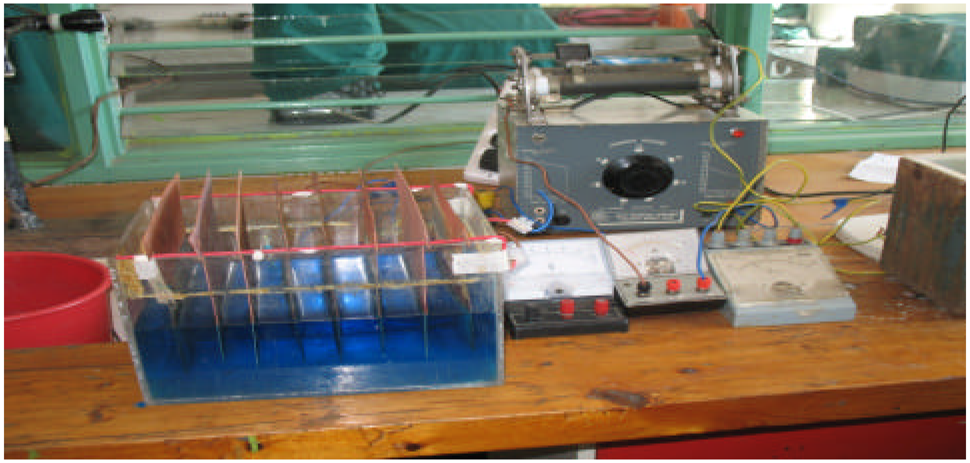

Figure 6: Multicell reactors constructed from Perspex material