

# The Effect of Impurities and Other Factors on the Current Density in Electro-Chemical Reactors

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**ABSTRACT:** The effect of impurities, smootheners and other factors on the current density in electrochemical reactions was studied using a parallel plate model in a circular glass reactor heated by a thermostat-controlled water bath. A reduction in current density of 50 mA/cm<sup>2</sup> and 40 mA/cm<sup>2</sup> was produced for an increase in volumes of thiourea and EDTA of 300 and 100 ml respectively. An increase in distance between electrodes of 3 cm reduced the current density from 34 to 12 mA/cm<sup>2</sup> at 60 °C. An increase of 41°C produced an increase in current density of 66 mA/cm<sup>2</sup> at 2 cm distance between electrodes while an increase in electrode-active area of 20 cm<sup>2</sup> produced a decrease in current density of 56 mA/cm<sup>2</sup> at 0.8 Amps. The presence of silver and bismuth removed the limiting current-density plateau more so at higher concentrations (>0.06%; >1.48%). A 30 g/L increase in concentration of electrolyte produced an increase in current density of 12 mA/cm<sup>2</sup> at 0.25 volts and 26 mA/cm<sup>2</sup> at 0.4 volts. The optimum operating current density was found to be dependent on different levels of factors. Therefore the factors that affect the current density need to be controlled if the electrochemical reactor is to be operated without problems of pitting, nodulation and passivation.

**Keywords:** Concentration; Optimum-current-density; Electrochemical-reactors; Impurities; Smootheners; Electrorefining; Electrowinning; Electrochemical-engineering.

## INTRODUCTION

The current density is the current per unit area of electrode<sup>1</sup>. It is created by the distribution of charges due to migration of electrons and ions in the anode-cathode-reactor electrolyte where the metal transfer takes place in electrodes of the first kind (Cu/CuSO<sub>4</sub>)<sup>2</sup>. The current distribution on the electrode is not uniform in most practical situations and so is the current density due to a number of factors. The factors that can affect the current density on the electrode include the temperature, concentration of electrolyte (Cu<sup>2+</sup>), distance between electrodes, electrode-active area, presence of impurities and the use of strong

depolarizing agents and smootheners. The evaluation of current density provides a means of assessing the optimum current densities that give optimum mass-transfer-process operating conditions<sup>3, 4, 5</sup>. Such evaluation can be achieved by investigating the effects of the stated factors on the current density.

In most electrorefining or electrowinning operations, problems of excessive nodulation, pitting and passivation are frequently encountered due to incorrect levels of the factors that affect the current density. Such problems can be solved by evaluating the levels of such factors and then determining optimum levels,

which set optimum current densities that can produce smooth deposits on the cathode. It is for this reason that this study was carried out using a parallel plate model in a circular casing forming an electrochemical reactor. The purpose of the study was to establish the effects of impurities, smootheners and other factors on the current density of a parallel-plate electrochemical system that uses the electrodes of the same material. The specific objectives were; (1) To determine the variations of temperature, distance between electrodes, electrode-active area, and concentration of electrolyte, impurities and smootheners with the level of current density and (2) To determine the optimum values of the factors that can produce optimum values of current density in order to prevent nodulation, passivity and pitting of the electrodes in electrochemical reactors.

### CURRENT DENSITY EVALUATION

In electrolytic reactors, the current density is limiting if it is independent of potential over a large range. Good metal deposit can be obtained through ionic mass transfer if the current densities are maintained at optimum limiting values in accordance with Faraday's Law<sup>6, 7, 8, 9</sup>. Any increase in voltage can affect the current density and therefore power consumption and capital costs can be decreased due to reduced electrode area<sup>10</sup>. This means that the electrode separation, electrode-active area and the temperature would have to vary in order to optimise the current density and efficiency. Since the contribution of free energy is small and can be assumed to reduce to unity, the current density ( $j_c$ , mA/cm<sup>2</sup>) at the cathode, is a function of concentration and voltage and inverse function with temperature ( $T$  °C) as given by equation (1) where  $z$  is the electrons transferred,  $F$  is the Faraday constant (96000 coulombs),  $k_c$  (s<sup>-1</sup>) is the reaction rate constant,  $R$  is the constant (kJ/kmolK),  $n$  is number of electrons and  $\eta$  is the potential (volts) across the reactor. At fixed concentration,  $j$  varies with temperature and at fixed  $T$ , it varies with concentration of electrolyte. The current density at the anode can be evaluated from equation (2) where  $k_a$  (s<sup>-1</sup>) and  $j_a$  (mA/cm<sup>2</sup>) represent the reaction rate constant and current density at the anode respectively.

$$\ln j_c = \ln(zFk_c) - \frac{\alpha n F \eta}{RT} \ln[Cu^{2+}] \dots \dots \dots (1)$$

$$\ln j_a = \ln(zFk_a) - \frac{(1-\alpha)n F \eta}{RT} \ln[Cu^{2+}] \dots \dots (2)$$

The rate of reaction is a function of temperature and concentration of limiting reactant according to Arrhenius Law<sup>11, 12, 13</sup>. The reaction rate is also dependent on the potential across the reactor. The variation of current density with the distance between electrodes, electrode active area and smootheners can be obtained by data exploration method in which the constants can be obtained from graphical illustration. The occurrence of passivity on the electrodes where electro-deposition ceases due to high levels of current and overvoltage is one problem. The other problem is that when the concentration of electrolyte drops, the current density may increase resulting in the development of passivity. These problems can be solved by maintaining the concentration of electrolyte at constant value<sup>14</sup>.

### MATERIALS, EQUIPMENT AND METHODS

#### Materials

The materials used in the study were sodium chloride (NaCl), thiourea, Ethylene-diamine-tetra-acetic-acid (EDTA), Gum Arabic (G-Arabic) white crystals, copper sulphate (CuSO<sub>4</sub>) electrolyte, Krazy glue (K-glue), Bostick glue (B-glue), concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), copper cathodes, crocodile clips, insulation tape, distilled water and the metals bismuth and silver nitrates.

#### Equipment

The experimental set up was as shown in Figure 1. The Ammeter (A) was used to measure the current in series with the variable resistor (rheostat) and the electrochemical reactor but parallel to the voltmeter (V). The rheostat was used to adjust the current flow in the circuit. The voltmeter was used to measure the overpotential (E) across the reactor. The reactor was assembled using two electrodes; the cathode and anode, placed in a circular-glass casing which was heated by a thermostat-controlled water bath (Ntengwe, 2008)<sup>15</sup>. The overpotential was used to drive the current through the circuit and to distribute it on the surfaces of electrodes thereby creating the desired current density which was used to evaluate the effect of the factors; temperature, concentration of electrolyte, level of impurities in solution, electrode-active area, level of smootheners and distance between electrodes on the current density. Mercury in glass thermometer and metre rule was used to counter check the temperature controlled by the thermostat in the water bath and measure electrode dimensions.

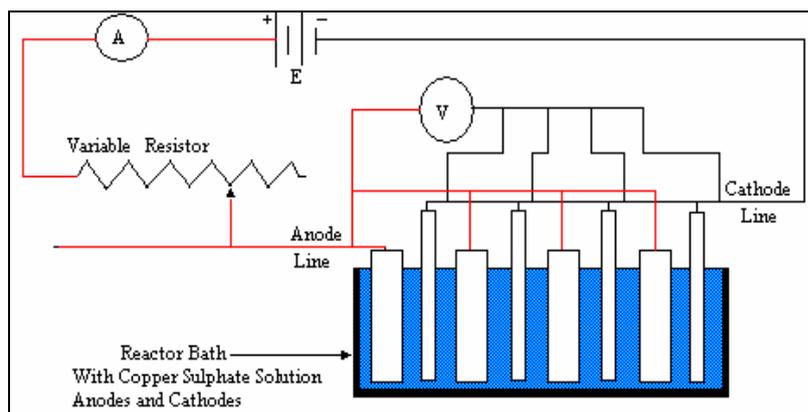


Figure 1: Experimental apparatus for the measurement of current density

## Methods

The effect of electrode-active area on the current density was studied using various electrode-active areas at fixed values of distance between electrodes and voltage in 250 ml samples of electrolyte. The current density was determined by dividing the level of current by the electrode-active area. A metre rule was used to measure the sides of the electrodes dipped in electrolyte in order to determine the electrode-active area. Any change in the current density meant that electrode-active area had an effect on the current density.

A known volume of each of the smootheners, NaCl, thiourea, EDTA, K-glue, B-glue, and G-Arabic was added to each of the 250 ml samples before the electrochemical reaction was conducted in order to establish the effect of smootheners on the current density at 2-cm distance between electrodes. Any change in the level of current density during electrochemical reaction would be the effect of smootheners on the current density. Similarly, a known amount of impurities of silver and bismuth was added to the electrolyte before passing the current. Any deviation from the characteristic curve meant that the impurities had an effect on the current density.

The temperature was measured using the mercury-in-glass thermometer. The values of current and current density were obtained at each temperature (24, 39 and 60 °C) in 250 ml samples. The results were compared in order to determine the effect on the current density at fixed values of electrolyte concentration (5 g/L), electrode-active area (12 cm<sup>2</sup>) and distance between electrodes (2 cm).

The electrolyte concentration was set at different values while the current was recorded at fixed values of voltage. The solution of electrolyte was prepared in varying concentrations from 1.5 g/L to 74 g/L. The individual concentrations were 1.5, 3, 6, 8, 9, 14.8, 29.6, 59.2 and 74 g/L. A voltamograph was taken for

each solution in order to determine the limiting currents and hence the current densities.

The distance between electrodes was set at 1, 2, 3, and 4 cm. The temperature, electrolyte concentration and electrode-active area were set at fixed values of 24 °C, 39 °C, 60 °C, 5 g/L and 12 cm<sup>2</sup> respectively. The voltage was varied in order to produce different levels of current and hence current density at set-distances between electrodes. The levels of current and current density for each distance between electrodes was compared to values at other distances.

## RESULTS

### Effect of temperature

The results in Figure 2 show values of limiting current density at different temperatures and distances between electrodes. It was observed that the current densities at 24 °C were lower than those at 39 °C which were lower than those at 60 °C which were lower than those at 65 °C. Increasing the temperature of the electrochemical reactor resulted in an increase in limiting current density. In a study by Hwang and Lai (2007)<sup>16</sup> at various conditions of temperature (T) the current density varied as a function of temperature using the least squares method of analysis. In a study by Shangguan *et al.*, (2008)<sup>17</sup>, the tribological behaviour of the chromium bronze/brass and surface temperature of the brass greatly depended on the current density. It can also be observed that the limiting current was higher for the 3-cm distance than those of 1 and 2 cm distance. This means that a longer distance between electrodes would produce higher limiting current density at the set temperatures. The optimum operating temperature range was 40-65 °C. Using temperatures above 65 °C resulted in quick evaporation of electrolyte water-H<sub>2</sub>SO<sub>4</sub> mixture and this would increase the cost to venting the reactors for countries lying in the cold hemisphere. Glue and G-Arabic would change their properties and therefore would not be effective in smoothening deposits on the cathodes.

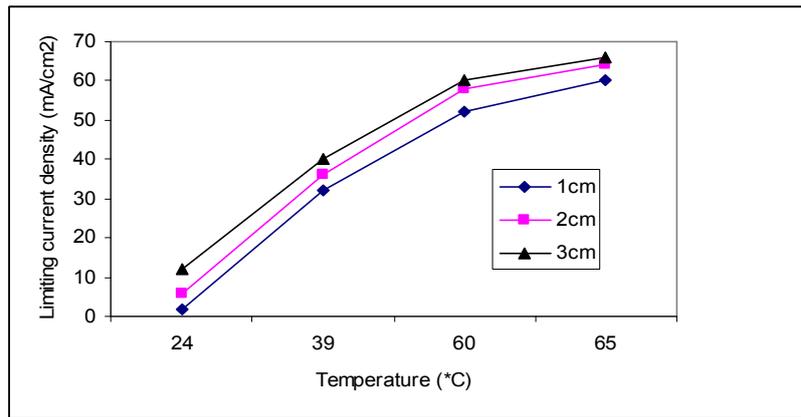


Figure 2: Effect of temperature on the limiting current density

**Effect of distance between electrodes**

The distance between electrodes had a significant effect on the current density. The current density was found to decrease with the increase in distance between electrodes at temperatures of 24, 39, and 60 °C (Figure 3). The highest values of current density (28 mA/cm<sup>2</sup>; 30 mA/cm<sup>2</sup>; 34 mA/cm<sup>2</sup>) were at 1 cm distance between electrodes whilst the lowest values (5 mA/cm<sup>2</sup>, 10 mA/cm<sup>2</sup>, 12 mA/cm<sup>2</sup>) were at 4 cm distance between electrodes at fixed value of potential. If one would like to use 4-cm distance between electrodes and maintain current densities attained at 1 cm, one would have to vary the potential in order to attain such levels at the chosen temperatures. Similarly, if one would like to use a 2-cm distance between electrodes, one would have to adjust the voltage in order to attain the current densities attained at 1 cm distance at the chosen temperatures. The optimum distance between electrodes was found to be 2 cm. At this distance there was no irregular deposition of metal on the cathode was observed; signifying that optimum current densities were attained at the fixed operating temperatures.

**Effect of concentration**

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 of electrolyte. The current density decreased with the decrease in concentration and the opposite was also true (Figure 4). The highest resistance was in 1 g/L at 25 and 20 Ω for the 0.25 volts (R0.25V) and 0.4 volts (R0.4V) respectively while the lowest was in 50 g/L concentration of electrolyte. The highest concentration in the study was 50 g/L while the lowest was 1 g/L of copper sulphate. This translates to 19.9 g/L and 0.398 g/L of copper respectively. The highest concentration of electrolyte produced the highest current densities of 40 mA/cm at 0.4 volts (j0.4V) and 20 mA/cm at 0.25 V (j0.2V) while the lowest concentration produced the lowest current densities of 2 mA/cm at 0.4 Volts and 1 mA/cm) at 0.25 Volts. The concentrations above 15 g/L produced good deposits on the surface meaning that optimum current densities were attained and these would be the recommended levels of concentrations to be used in electrorefining.

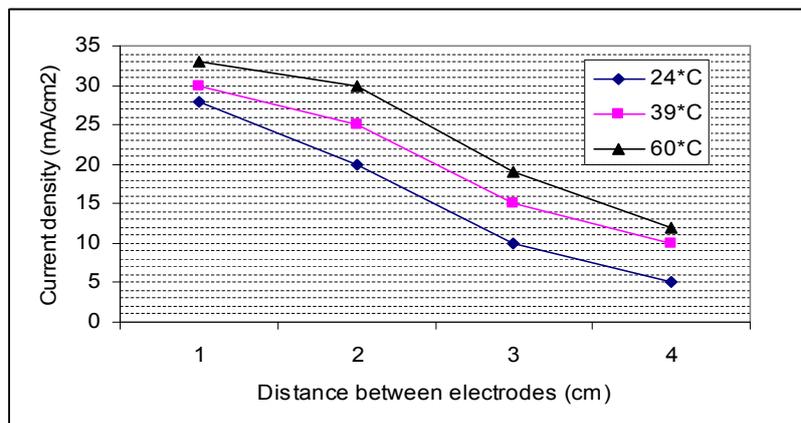
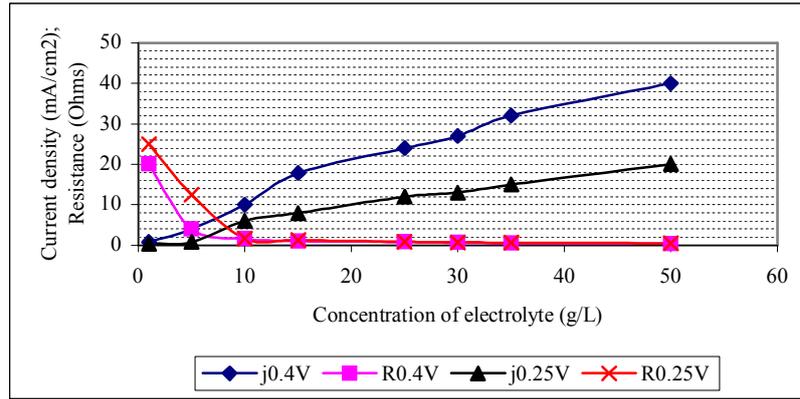


Figure 3: Effect of distance between electrodes on the current at 0.2 volts



**Figure 4: Effect of concentration on resistance and the current density**

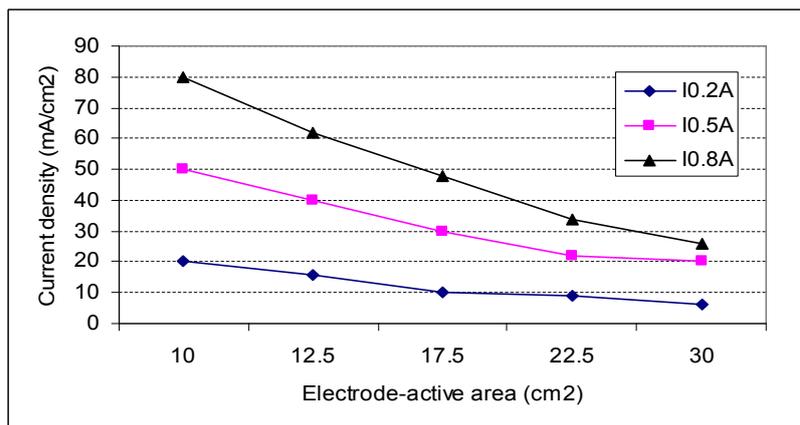
**Effect of electrode-active area**

The current density was found to vary with the electrode-active area. As the electrode-active area increased the current density decreased (Figure 5). The highest values of current density were at the lowest value of electrode-active area while the lowest values were at the highest electrode-active area. The optimum current densities were attained for electrode active areas of 12.5-17.5 cm<sup>2</sup>. This is the range that produced smooth deposits without irregular depositions.

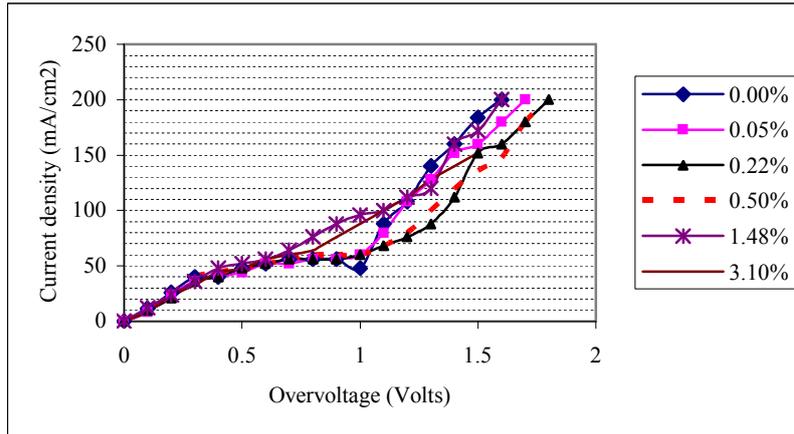
**Effect of impurities on current density**

Two impurities were used in the study; silver and bismuth nitrates. A voltamograph was used to establish the effect of the impurity on the current density. In the case of bismuth nitrate, a check on the

current density for an active area of 25 cm<sup>2</sup> revealed deviations from that of the control sample (0.00%). The current density was unstable and removed the limiting current plateau for voltage values greater than 1.1 V. This was exhibited in all the samples more so in samples with 0.22 and 0.5 % concentration of bismuth nitrate (Figure 6). The optimum current density that can give best results is that below the limiting current density of 50 mA/cm<sup>2</sup> and above 20 mA/cm<sup>2</sup> produced at concentration of bismuth of 0.22 % and below. The advantage with bismuth is that it precipitates into white crystals when the electrochemical deposition of copper proceeds. It also precipitates readily in the presence of chlorides to bismuth-chloride white crystals. This characteristic can be used to reduce its concentration in solutions undergoing electrochemical reactions.



**Figure 5: Effect of electrode-active area on the current density**



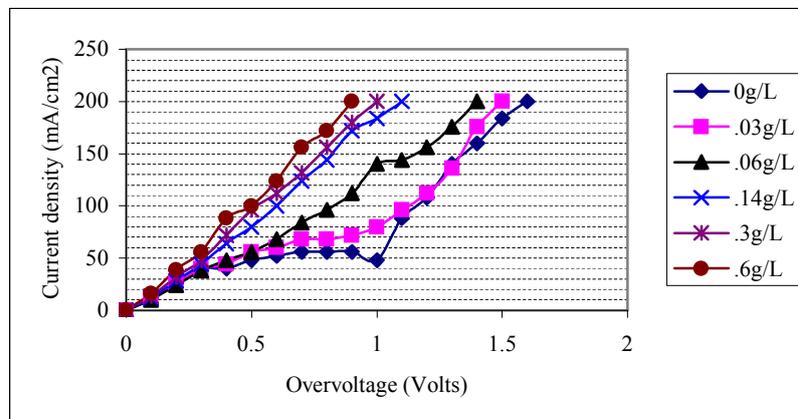
**Figure 6: Effect of bismuth nitrate on the current density**

The silver nitrate affected the current density at different concentrations (Figure 7). The control sample (0 g/L) produced the limiting current density of 50 mA/cm<sup>2</sup> while that produced by 0.3 g/L of silver nitrate was 70 mA/cm<sup>2</sup>. The concentrations above 0.03 g/L of silver nitrate interfered with the limiting current density plateau and the voltamographs became linear. 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 density for samples that contain high levels of impurities, as the voltamographs would be linear in such cases. The optimum current densities would be those below the limiting current density and impurity concentration of 0.03 g/L and below.

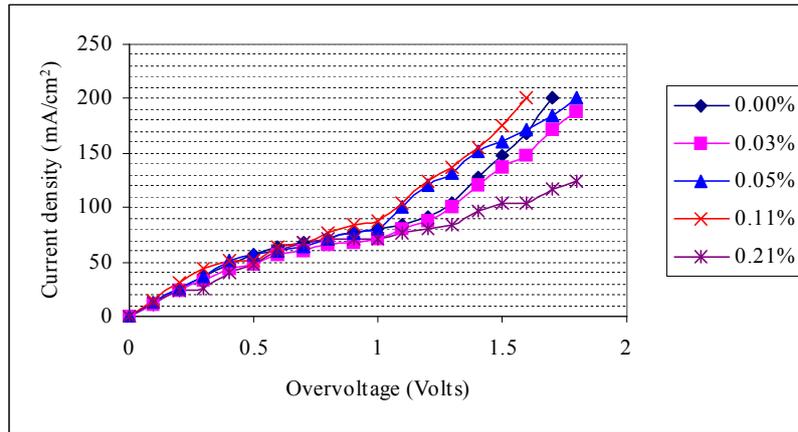
**Effect of smootheners on current density**

*Effect of sodium chloride*

The results in Figure 8 show that the current density increased with the increase in voltage up to the current density of 50 mA/cm<sup>2</sup> and voltage of 0.4 Volts in the presence of different concentrations of sodium chloride (NaCl) in 50 g/L copper-sulphate electrolyte. The operation of the system above the limiting current density (80 mA/cm<sup>2</sup>) revealed abnormal nucleation of copper and gas bubbles appeared on the surface of the cathode simultaneously. The 0.03 and 0.05 % NaCl-impurities affected the current density above the limiting value and not below. This means that the concentrations of NaCl above 0.05 % increase the current density and those below did not produce any effect. Therefore NaCl as an additive did not affect the limiting current density but increased the current density after the limiting value. Therefore the optimum level of NaCl was from 0.03% and below while that of the current density was found to be below the limiting value but above 20 mA/cm<sup>2</sup>.



**Figure 7: Effect of silver nitrate on the current density**

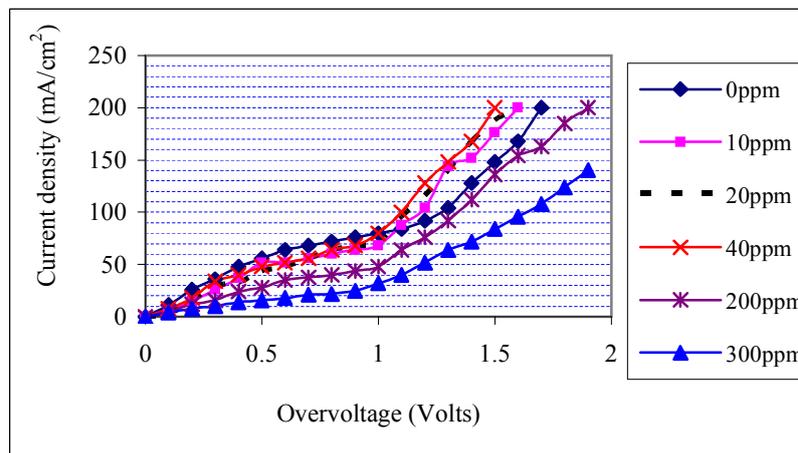


**Figure 8: Effect of NaCl on the current density**

**Effect of thiourea**

The results in Figure 9 show reduced values of limiting-current density when the concentrations of thiourea increase from 0 to 300 ppm. The thiourea lowered the limiting current density from 80 to 40 mA/cm<sup>2</sup> at 200 ppm and 80 to 20 mA/cm<sup>2</sup> at 300 ppm indicating a strong inhibition of the flow of current of ions in the system. On the other hand, the levels of thiourea from 40 ppm and below lowered the limiting current density by 10 mA/cm<sup>2</sup> at 0.5 volts, i.e., from 60 to 50 mA/cm<sup>2</sup>. The results revealed also that the potential required to overcome resistance in the system was 0.5 volts for all the cases of the concentrations of

thiourea, which represents a range of 0.5 to 1 volts potential. The 1-volt potential is also the point where concentrations of thiourea below 40 ppm failed to inhibit the current density above the limiting value. Therefore, at concentration levels below 40 ppm, thiourea was able to inhibit the limiting current density at potentials below 1 volt. The increased overvoltage did not have any effect on the inhibition process of thiourea at concentrations above 40 ppm. Therefore, the optimum values of thiourea were those above 40 ppm at overvoltages below 1 volt and current densities below the limiting value of 80 mA/cm<sup>2</sup> and those above 20 mA/cm<sup>2</sup>.



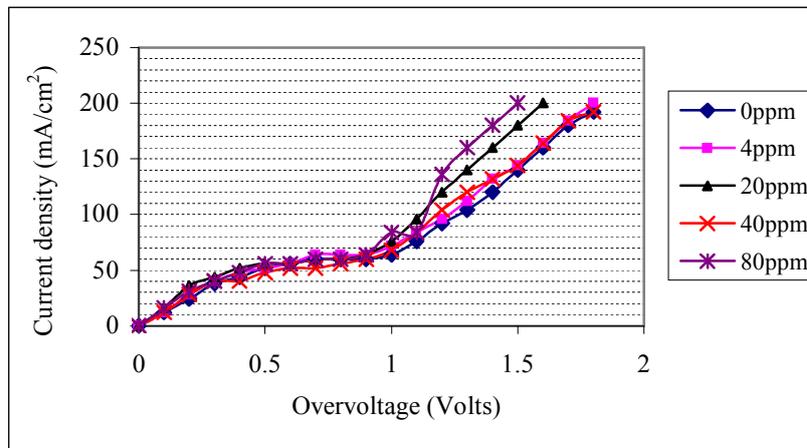
**Figure 9: Effect of thiourea on the current density**

**Effect of K-glue, thiourea and NaCl**

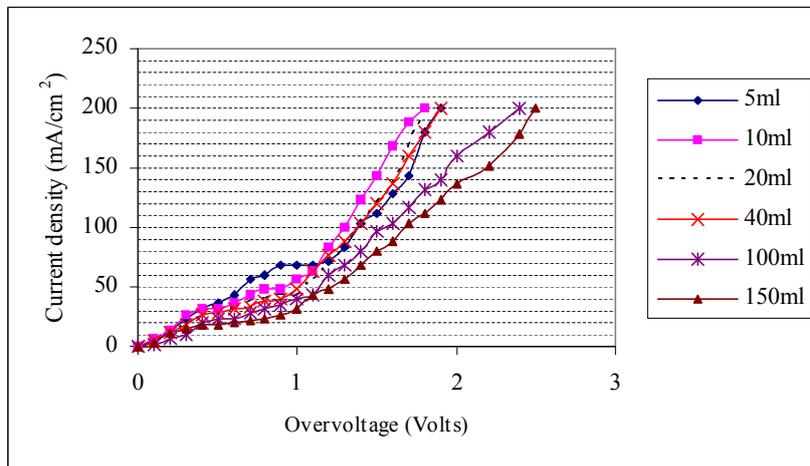
The results in Figure 10 indicate that glue did not have any effect on the limiting current density in the potential range 0-1 volts. However, it increased the current densities at potentials above 1 volt for all the concentrations of glue except that of the control sample.

The results in Figure 11 show the effect of K-glue, thiourea and NaCl on the current density. Since K-glue and NaCl did not produce any significant changes in the limiting current densities, the changes were

therefore due to inhibition by thiourea. The inhibition produced a lowering of limiting current density from 60 to 50, 40, 30, 25 and 20 mA/cm<sup>2</sup> for the 10, 20, 40, 100, and 150 ml representing concentrations of 0.071, 0.129, 0.216, 0.364, and 0.429 g/L respectively. The 5 ml volume of thiourea, representing a concentration of 0.04 g/L did not produce any effect on the limiting current density. Therefore the optimum operating conditions when a combination of this type of impurity is used are a current density below the limiting value (70 mA/cm<sup>2</sup>) but above 20 mA/cm<sup>2</sup>, a potential below 1 volt and thiourea concentration of 0.129-0.429 g/L.



**Figure 10: Effect of K-glue on the current density**



**Figure 11: Effect of K-glue, thiourea and NaCl on the current density**

**Effect of G-Arabic, thiourea and NaCl**

The results in Figure 12 indicate that the decrease in the limiting current density can be attributed to thiourea and not G-Arabic and NaCl as these substances did not affect the current density significantly. The decrease in current density was, therefore, due to thiourea. A decrease of limiting current density was produced from 65 mA/cm<sup>2</sup> for the 1 and 5 ml volumes of thiourea representing concentrations of 0.008 and 0.038 g/L respectively to 40 mA/cm<sup>2</sup> for the 10 and 20 mL representing concentrations of 0.071 and 0.129 g/L, to 25, 20, and 15 mA/cm<sup>2</sup> for the 40, 100, and 150 mL representing concentrations of 0.216, 0.364 and 0.429 g/L respectively.

Thiourea was found to be a strong inhibitor at concentrations above 0.216 g/l than at concentrations below 0.129 g/L, i.e., by maintaining low current densities above the limiting values when compared to those at concentrations below 0.129 g/L. Thiourea was found to produce increased resistance to the flow of electrons and hence the flow of ions in solution resulting in reduced deposition on the cathode. The optimum values of current density ranged between 20-

70 mA/cm<sup>2</sup> at potentials below 1 volt and thiourea concentrations represented by the range 20-150 ml.

**Effect of EDTA, B-glue and NaCl**

The effect of EDTA as an inhibitor to electrochemical reaction was studied in the presence of NaCl (2000 ppm or 2 g/L) and B-glue with a concentration of 18800 ppm. The concentrations of EDTA in the samples were 0.377, 0.714, 1.29, 2.16, 3.64, and 4.29 g/L for volumes of 5, 10, 20, 40, 100, and 150 ml respectively. The results in Figure 13 show that the increase in concentration of EDTA produced a decrease in current in the reactor. The decrease in current was due to the increase in resistance created in solution by the ions from EDTA. The results also show that the lowest value of current I1 (0.15 A) was observed at the highest EDTA concentration (4.29 g/L) while the highest value of current (0.3 A) was observed at the lowest EDTA concentration (0.377 g/L). Similarly, the highest levels of currents for I2 (0.65 A), I3 (0.76 A), I4 (1 A), I5 (1.2 A) and I6 (1.4 A) were observed at EDTA concentration of 0.377 g/L while the lowest values were at I2 (0.8 A), I3 (0.3 A), I4 (0.4 A), I5 (0.45 A), and I6 (0.41 A) at EDTA concentration of 4.29 g/L.

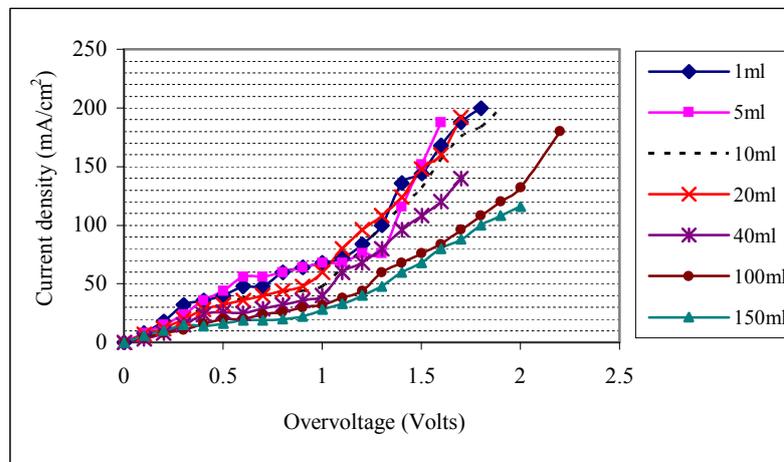


Figure 12: Effect of G-Arabic, thiourea and NaCl on the current density

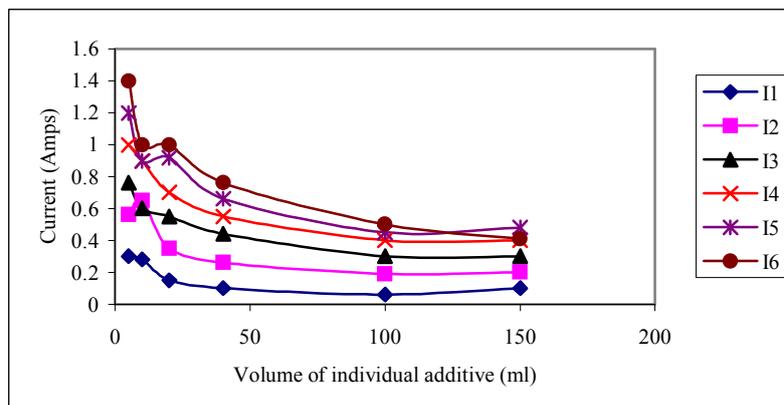
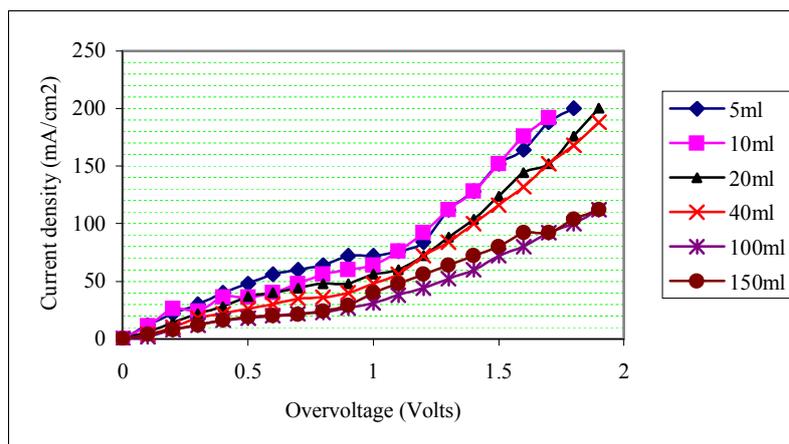


Figure 13: Effect of EDTA, NaCl and B-glue on the current



**Figure 14: Effect of EDTA, NaCl and B-glue on the current density**

The inhibitors lower the current density particularly, the limiting current density. The EDTA was found to be a strong inhibitor when compared to B-glue, and NaCl as smootheners. B-glue was found to have similar characteristics to K-glue and therefore would exhibit the same inhibition strength. The limiting current densities decreased from 70 mA/cm<sup>2</sup> for the 5 ml (0.377 g/L) to 20 mA/cm<sup>2</sup> for the 100 and 150 ml (3.64 and 4.29 g/L) volumes of EDTA indicating a strong inhibition of current flow and hence a decrease in current density was produced (Figure 14). The results indicate therefore that the optimum operating conditions for this system would a current density below the limiting value, a voltage below 1 volt and a concentration of EDTA above 0.714 g/L and below 4.29 g/L.

## DISCUSSIONS

The presence of impurities; silver and bismuth in electrolyte was found to inhibit the deposition of copper on the cathode. This was vindicated by the characteristic curves which turned into linear lines without the limiting current density plateaus. Some metals likely to produce a similar effect in electrowinning and electrorefining of copper include lead (Pb), iron (Fe), cobalt (Co) and zinc (Zn)<sup>14</sup>. A study by Lonzo-Morales and Podlaha (2004)<sup>18</sup> showed that low particles of aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) concentration (12.5 g/L) resulted in inhibited deposition rate of copper while high particle concentration (60 g/L) inhibited the deposition rate at low over-potentials and accelerated it at high overpotentials. In another study, the conductive particulates of copper and graphite produced dense nodulation at 50 °C while antimony and silver powders caused pitting as well as nodulation<sup>15</sup> since these impurities are conducting and therefore interfere with the current density. The non-conducting powders such

as Pb-sulphate, Pb-dioxide and gypsum produced no nodulation<sup>19</sup>. Therefore impurities that are conducting like silver and bismuth would have an effect on the current density and hence the rate of deposition of copper on the cathode. It is important therefore that the metals Fe, Co, Zn should be reduced or removed altogether or provision must be made so that such metals can be precipitated into their salts during electro-refining or electro-winning of copper in order to prevent the formation of unstable current density at the electrodes.

The distance between electrodes affects polarisation<sup>20</sup>. The increase in distance between electrodes was found to reduce the current density which is in agreement with the polarisation on current density. In a study elsewhere, the current density and efficiency were different for different distances between electrode beds<sup>21</sup>. It means, therefore, that the electrode distance is important in electrochemical processes. The current density has to be set for each distance in order to have effective deposition, i.e., deposition without nodulation on the cathode.

The concentration of electrolyte has been observed to contribute to the increase in current density<sup>22</sup>. The result obtained in this study is in agreement with this observation. The current density increased with the increase in concentration of electrolyte. In order to produce a good level of current density, it is suggested that the reactor electrolyte should be above 10.8 g/L as the resistance is increased at values below this level due to the reduction in pH and increased level of water molecules. Similarly, the increase in temperature produced an increase in the current density. In another study, the temperature was found to increase the electro-deposition of cuprous oxide<sup>23</sup> which is synonymous with the increase in current density. High current densities have been reported to produce

problems of nodulation or passivity<sup>24</sup>. One way of resolving this problem is to lower the current density by increasing the electrode-active area or applied voltage as demonstrated by this study. A large electrode-active area lowers the current density in the system<sup>25</sup>. A small electrode-active area is unproductive unless lower values of current densities are used.

Additives such as animal glue have been reported to enhance smoothness of the resulting cadmium cathode during electrolysis<sup>26</sup> but do not have a reducing effect on the current density. Although K-glue and B-glue reduced polarisation created by thiourea and EDTA, it did not restore the limiting current density to a normal level, i.e., level attained when there is no inhibitor. However, they improved the smoothness of the deposited copper and the current efficiency<sup>15</sup>. The advantage of using K-glue and B-glue is that they are effective in producing smoother deposits even at high densities<sup>27</sup>. The use of high current densities resulted in the evolution of gas bubbles which disturb the normal granulation process of the metal at the cathode. Depolarisers can be used to control the evolution of gas and irregular deposition of copper<sup>28, 29</sup>. Thiourea has been extensively used as grain refiner<sup>30</sup> but the effect of K-glue, B-glue on granulation and smoothing has not been reported in literature. While thiourea and EDTA were good current inhibitors, K-glue and B-glue were good smootheners and increased the smoothening over a wide thiourea-concentration range.

Although the cost per tonne of K-glue (\$7,500/tonne), B-glue (\$21,000/tonne), G-Arabic (\$5,000/tonne) are

high compared to that of thiourea (\$1,100/tonne) and EDTA (\$2,000/tonne), the smoothness of deposit on the cathode appeared to be much better than when thiourea and EDTA were used without adding such glues. Apart from increasing the current efficiency, K-glue and B-glue provided smooth deposition environment in electrolyte. On the other hand, it would be advantageous to operate the reactors at high current densities by using the limiting current-density reducers such as thiourea and EDTA.

## CONCLUSIONS

The increase in electrode-active area and distance between electrodes at fixed values of potential reduced the current and current density in the reactor. However, the increase in temperature at fixed values of concentration and potential increased the current density. The impurities silver nitrate and bismuth nitrate cancelled the limiting current plateaus thereby reducing the characteristic curves into linear lines indicating that the flow of copper ions was hindered and what was indicating was the flow of impurities in the system. The smootheners; thiourea and EDTA reduced the current density and increased the polarisation potential in the reactor. The resistance of electrolyte increased as the concentrations of smootheners increased. The presence of K-glue, B-glue and G-Arabic resulted in the depolarisation of the electrodes and thus reduced the polarisation effect of thiourea and EDTA without changing the level of current density attained due to polarisation. This effect allowed the flow of copper ions from anode electrolyte and from electrolyte to cathode.

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