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DESIGN OF NOVEL CELLS TO SIMULATE HIGH SPEED ELECTRODEPOSITION

by

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A thesis submitted in partial fulfilment of the regulations for the award of the degree of Doctor of Philosophy of Loughborough University of Technology

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Industrial Collaborator: Mr B. Sewell
Twickenham Plating Group

© A.F.S. Afshar, 1988
To my family:
especially to Barbara and my Father

*** *** ***
ACKNOWLEDGEMENTS

I wish to thank Dr D R Gabe, my supervisor, for suggesting the research topic and for his patient help and support throughout the work. I would also like to thank Mr Sewell, my external supervisor, and the Twickenham Plating Group for their help and guidance.

My sincere gratitude goes to Professor Menzies, Dr Ross, the technical staff of the University, to my colleagues for endless constructive discussions and for putting up with my radio, and finally Mrs Janet Smith for transforming this thesis with her typing prowess.
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<table>
<thead>
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<th>Symbol</th>
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<tr>
<td>$\overline{Nu}$</td>
<td>average Nusselt number $\frac{\overline{Ir}}{nFDAC}$</td>
</tr>
<tr>
<td>$\overline{Sc}$</td>
<td>Schmitt number $\frac{\nu}{D}$</td>
</tr>
<tr>
<td>$Re_0$</td>
<td>Reynolds number based upon the electrode radius $r_o$ (disc)</td>
</tr>
<tr>
<td>$\overline{I}$</td>
<td>average c.d. mA</td>
</tr>
<tr>
<td>$n$</td>
<td>number of electrons transferred per ion</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday's constant</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient of the active species cm$^2$/sec</td>
</tr>
<tr>
<td>$\Delta C$</td>
<td>concentration driving force for diffusion bulk concentration at electrode surface moles/litre</td>
</tr>
<tr>
<td>$\nu$</td>
<td>kinematic viscosity cm$^2$/sec</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angular velocity $\omega = 2\pi N$, $N = \text{rpm}$</td>
</tr>
<tr>
<td>$L$</td>
<td>characteristic dimension, cm</td>
</tr>
<tr>
<td>$q$</td>
<td>heat transfer rate per unit area cal/cm$^2$</td>
</tr>
<tr>
<td>$J$</td>
<td>flux, mass transfer rate per unit area mole/cm$^2$.sec</td>
</tr>
<tr>
<td>$k$</td>
<td>thermal conductivity of solution, cal/cm.sec.degree</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, degree</td>
</tr>
<tr>
<td>$C$</td>
<td>concentration of electroactive species moles/cm$^3$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of solution g/cm$^3$</td>
</tr>
<tr>
<td>$s$</td>
<td>specific heat of solution cal/g degree</td>
</tr>
</tbody>
</table>

The zero denotes the surface of the heat transfer probe or of the indicator electrode.

- $A$ effective area of electrode
- $\alpha$ half apex angle of cone
- $\nu$ velocity of flow passing the stationary electrode
- $U$ peripheral velocity
- $d$ diameter
- $f$ friction factor
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CHAPTER 1
INTRODUCTION

It is a well established fact that any kind of agitation in electrorefining and metal finishing processes increases the deposition rate and therefore reduces the plating time for the given coating thickness. There are several kinds of plants that are used in the electroplating industry which use a high degree of agitation. Methods such as stirring, air bubbling, pumping, cathode movement, vibration and rotation etc are now commonly used.

The types of processes specifically envisaged are:
- reel to reel plating for electronic applications
- wide strip plating, tinplate, electrogalvanised steel, wire plating with zinc
- jet plating, spot selective plating.

Today in the electroplating industry, especially in fast electroplating, many different kinds of plant can be used in parallel for the same purpose. However the most influential factor that differs from one plant to another is the degree of agitation. Therefore in order to acquire the same finish on different plants it is not sufficient to only control variables such as power temperature etc, but also the degree of agitation must be controlled. Since each plant has its own agitation characteristics a common ground measurement or parameter must be defined in order to make meaningful comparisons.

This thesis is concerned with agitation and its aim is to establish a scientific method to replace the old rule-of-thumb method which until the present has been used. The goal is to design and calibrate a cell which can be used as a reference point for different plants. Further a system by which the best plating condition can be easily and rapidly found and the results transferred to other plants with ease. For this purpose cells were designed which use the principles of a
rotating electrode whereupon different degrees of agitation can be obtained by adjusting the rotational speed of the cathode, in conjunction with the principles of the Hull cell which gives different throwing power along the cathode.
CHAPTER 2
PRINCIPLES OF ELECTRODEPOSITION

2.1 APPLICATION OF ELECTRODEPOSITION

Electrodeposition is an important method by which a substrate can improve in some of its properties such as corrosion oxidation resistance, electrical properties such as high surface conductivity, a low contact resistance, optical properties such as very high or low reflectance and mechanical properties such as resistance to wear. Electrodeposition is also routinely used in a range of other applications notably electroforming and electrowinning.

Theoretically there are many metals which can be electrodeposited on other metals, but in practice there are some serious limitations such as electrochemistry e.g. aluminium, and toxicity e.g. cadmium. The table below shows some of the commonly used metals for electrodeposition and their application.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Applications</th>
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<tbody>
<tr>
<td>Tin</td>
<td>Sacrificial or protective coating</td>
</tr>
<tr>
<td>Zinc</td>
<td>Non-sacrificial coating, decorative, and high electrical conductive for electronics</td>
</tr>
<tr>
<td>Nickel</td>
<td>Non-sacrificial coating, decorative, and high electrical conductive for electronics</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Non-sacrificial coating, decorative, and high electrical conductive for electronics</td>
</tr>
<tr>
<td>Copper</td>
<td>Non-sacrificial coating, decorative, and high electrical conductive for electronics</td>
</tr>
<tr>
<td>Silver</td>
<td>Non-sacrificial coating, decorative, and high electrical conductive for electronics</td>
</tr>
<tr>
<td>Gold</td>
<td>Non-sacrificial coating, decorative, and high electrical conductive for electronics</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>Non-sacrificial coating, decorative, and high electrical conductive for electronics</td>
</tr>
<tr>
<td>Rhodium</td>
<td>Non-sacrificial coating, decorative, and high electrical conductive for electronics</td>
</tr>
<tr>
<td>Lead</td>
<td>Soft metal bearing wear and corrosion, hard and decorative</td>
</tr>
<tr>
<td>Indium</td>
<td>Soft metal bearing wear and corrosion, hard and decorative</td>
</tr>
<tr>
<td>Chromium</td>
<td>Soft metal bearing wear and corrosion, hard and decorative</td>
</tr>
</tbody>
</table>
With respect to any given metal substrate, a coating may be:

a) base or sacrificial, such as zinc on steel
b) noble or non-sacrificial, such as nickel on steel

Selecting the best combination of coating and substrate requires particularly careful consideration of their relative behaviour in the particular environment. Problems such as polarity reversal and presence of ions like Cl\(^-\) which depassivate the protective coating must be borne in mind.

Electrodeposition can take place in several ways:

i) single metal, gold
ii) a sandwich of different layers of metals, duplex nickel
iii) metal alloy, copper-tin.

Table 2 below shows a selection of metal alloys and their solution type:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solution Type</th>
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<tr>
<td>Copper-tin</td>
<td>Cyanide-stannate</td>
</tr>
<tr>
<td>Copper-zinc</td>
<td>Cyanide-zincate</td>
</tr>
<tr>
<td>Tin-lead</td>
<td>Fluoborate</td>
</tr>
<tr>
<td>Tin-nickel</td>
<td>Chloride-fluoride</td>
</tr>
<tr>
<td>Tin-zinc</td>
<td>Alkaline-cyanide</td>
</tr>
<tr>
<td>Iron-nickel</td>
<td>Sulphate-complexant</td>
</tr>
<tr>
<td>Iron-zinc</td>
<td>Sulphate-complexant</td>
</tr>
<tr>
<td>Nickel-20% iron</td>
<td>a) Nickel-ferrous sulphate</td>
</tr>
<tr>
<td></td>
<td>citrate</td>
</tr>
<tr>
<td></td>
<td>b) Nickel-ferric sulphate</td>
</tr>
<tr>
<td>Cobalt-tin</td>
<td>a) Sulphate</td>
</tr>
<tr>
<td></td>
<td>b) Fluoride</td>
</tr>
<tr>
<td></td>
<td>c) Chloride-fluoborate</td>
</tr>
<tr>
<td>Palladium-nickel</td>
<td>Chloride-sulphate-amine</td>
</tr>
</tbody>
</table>
2.2 PRINCIPLES OF ELECTRODEPOSITION

The change in free energy $\Delta G^0$ which accompanies a chemical reaction measures the driving force of that reaction. The Vant Hoff Isochore equation relates this change in free energy to the equilibrium constant $K_p$ at constant pressure.

$$\Delta G^0 = -xRT \ln K_p$$

where $x$ is the number of moles reacting, $R$ is the gas constant and $T$ the temperature in degrees Kelvin. The equilibrium constant $K_p$ is defined as the ratio of the thermodynamic activities $a$ of the products to those of the reactants. For example

$$m^{n^+} + ne \rightarrow M^0$$

For the reaction to proceed forwards $K = \frac{a_n^{n^+}}{a_m}$ must be large and positive, which makes $\Delta G$ negative thereby thermodynamically spontaneous.

The electrical potential which is necessary to drive such a reaction forwards is related to the free energy by

$$\Delta G = -nFE$$

where $n$ is the number of electrons involved per g-atom, $F$ the Faraday constant (96493 C/equiv).

When a metal is immersed in a solution containing its own ions a potential difference is established between the metal and the solution and is given by the Nernst equation.
\[ E = E^0 - \frac{RT}{nF} \ln \frac{a_m}{a_m^{n^+}} \]

where \( E^0 \) is the standard electrode potential referred to that of hydrogen which is taken to be zero. It can be noted that under standard thermodynamic state i.e. \( a_m = 1 \)

\[ E = E^0 + \frac{0.059}{n} \log a_m n^+ \]

Changing the concentration will affect the metal electrode potential, metals such as K, Na, Al forming very stable ions which in aqueous solution cannot be electrodeposited. This is due to a very large positive value of \( \Delta G \) which indicates non-spontaneity hence negative \( E^0 \). In contrast metals having a positive \( E^0 \) value and hence negative \( \Delta G \) values for ion reduction electrodeposit quite readily for example copper or gold.

During electrodeposition the following steps take place:

1. Migration of ion to the cathode and through the electrode double layer to the surface in which hydration molecules are lost.
2. Adsorption of the ion on the metal surface as an adion or incorporation in an intermediate surface film.
3. Adion diffusion across the surface to a discharge site of minimum surface energy.
4. Ionic discharge involving electron transfer.
2.3 TYPES OF SOLUTIONS

In aqueous solution ions can be present in several forms. They can be present as simple ions or more commonly the ions have other atoms, molecules, or ions associated with them. Hydrated ions have water molecules attached to them, this is due to water molecule structure where positive and negative charges of the molecule do not coincide. Therefore hydrogen ion for instance is present in an aqueous solution as $H_3O^+$. The anion and the cations are however capable of adding an atom or atoms to form higher order compounds. Such compounds are known as complexes.

Electroplating solutions are classified according to the nature of the main metal-containing ion. These can be classified as simple acid, complexed acid, alkaline hydroxide or complexed alkaline solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Metal Deposited</th>
<th>Source</th>
<th>Cation/Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple acid</td>
<td>Cu</td>
<td>$\text{CuSO}_4$</td>
<td>$\text{Cu}^{2+}$</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>$\text{Sn(BF}_4\text{)}_2$</td>
<td>$\text{Sn}^{2+}$</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>$\text{Ni(NH}_2\text{SO}_2\text{O)}_2$</td>
<td>$\text{Ni}^{2+}$</td>
</tr>
<tr>
<td>Complexed acid</td>
<td>Cr</td>
<td>$\text{H}_2\text{CrO}_4$</td>
<td>$\text{CrO}_4^{2-}$</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>$\text{K}_6\text{Cu(P}_2\text{O}_7\text{)}_2$</td>
<td>$\text{Cu}(\text{P}_2\text{O}_7)^{6-}$</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>$\text{NiCl}_2$</td>
<td>$(\text{NiCl}_4)^{2-}$</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>$\text{SnF}_4$</td>
<td>$(\text{SnF}_6)^{2-}$</td>
</tr>
<tr>
<td>Alkaline hydroxide</td>
<td>Sn</td>
<td>$\text{H}_2\text{SnO}_4$</td>
<td>$(\text{SnO}_3)^{2-}$</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>$\text{Zn(OH)}_2$</td>
<td>$[\text{Sn(OH)}_6]^2-$</td>
</tr>
<tr>
<td>Complexed</td>
<td>Cu</td>
<td>$\text{CuCN}$</td>
<td>$\text{Cu(CN)}_2^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[\text{Cu(CN)}_3]^2-$</td>
</tr>
</tbody>
</table>
In simple ion solution such as copper acid solution, deposition of copper takes place with very little activation polarisation. In the case of complex solutions such as copper cyanide, the activation polarisation is great. Due to a high degree of polarisation, or high excess energy available for electrocrystallisation, the deposits produced from complexed solutions are smoother, more amenable to brightening and offer better metal distribution or throwing power characteristics.

Alkaline baths are used for metals which form amphoteric oxides and hence anionic hydroxyl complexes in solution. Such an example is the alkaline stannate bath which incorporates sodium or potassium stannate, the stannate is stabilised by excess hydroxyl ion that formation of undesirable stannite is discouraged.

\[
K_2SnO_3 \cdot 3H_2O + K_2(Sn(OH)_6)
\]

\[
Sn(OH)_2^- \rightarrow SnO_2 + 2OH^- + 2H_2O
\]

The most common complexed bath is the cyanide bath. This is to avoid formation of hydrocyanic acid but there are two setbacks (a) they absorb carbon dioxide easily, and (b) they tend to passivate soluble anodes rather easily.

2.4 CONSTITUENTS OF ELECTROPLATING SOLUTIONS

The constitution of electroplating baths is governed by primarily the cathode reaction, cathode metal of an appropriate quality and the ease of control of the process.

The electroplating solutions consist of some or all of the following classes:
a) Metal salt
b) Complexant
c) Buffer reagent
d) Conductivity salt
e) Anode depassivator
f) Addition agents of various types

a) Metal Salt: the metal salt is primarily a source of metal ions and broadly controls the rate of deposition. It needs to be cheap, plentiful and have a high solubility. The metal can be supplied as solvated ion, such as $[\text{Cu(H}_2\text{O)}_4]^{2+}$ in simple acid solution but in some alkaline solutions the metal may be present as amphoteric salt, oxide or hydroxide, for example $\text{ZnO}_2^{2-}$ or $\text{Zn(OH)}_4^{2-}$. The activity of the metal ion depends on the concentration of ion in solution, the dissociation of the salt, the activity coefficient of the ion and the total concentration of other ions in solution.

b) Complexant: the metal may be added as the complex salt which dissolves as a complex anion in the presence of excess complexant, for example silver cyanide dissolves as $\text{Ag(CN)}_2^-$. It is also possible to add metal as one salt which in the present of excess complexant forms the complexed anion.

Complexant is added to the plating bath for several reasons: it increases the solubility of metal in solutions thereby increasing possible rate of deposition, it will lower the deposition potential to more base values thereby enabling deposition of an apparently more noble metal onto a base metal, it increases the cathodic polarisation which promotes the tendency to produce a levelled and brighter deposit.
c) **Buffer reagent**: the buffer reagent is added in order to stabilise the pH at optimum level such as $\text{H}_3\text{BO}_3$, $\text{Na}_2\text{HPO}_3$. The best known example is the "Watts" nickel solution where the best quality deposit is given at a pH range of 3-6. Boric acid is used to stabilise the pH within this range.

d) **Conductivity salt or complexant stabiliser** is added as supporting electrolyte. Here acid or alkali is used to maintain the pH at very high or very low values. The pH may change by relatively small amounts due to acid generation or alkali consumption by the anodic oxygen evolution reaction.

e) **Anode depassivator**, the primary consideration of the electrolyte constitution must be in terms of the cathode process or the cathode deposit quality and only when these are satisfied and can be maintained, may anode considerations be taken into account. Some metal salt or complexant used in the plating bath may passivate an active soluble anode or may activate an insoluble anode. Some anions such as halide ions are well known to depassivate soluble anodes. Passivation of the anode most commonly occurs at near neutral pH, for example, in the "Watts" nickel solution operating at a pH of 4-6 the anode may well passivate unless addition of chloride is made (> 5 g/l).

f) **Addition agents**. There are many addition agents and vary very much in their role in plating solutions. Oxidants and surfactants may be added to depolarise the hydrogen evolution reaction and thereby minimise cathode pitting. Organic adsorption agents are used to influence cathode growth thereby promoting brightening, levelling stress relief and grain refining.
2.5 ANODES

Although electrodeposition is a cathodic reaction and as such attracts the main attention during the process, there are many cases where the anodic reaction influences the process.

Anodes are generally divided into two groups: soluble and insoluble.

a) Soluble anodes: This group of anodes are preferable in a metal finishing operation and inherent in an electrefining process. The choice of the anode depends on the metal ion in the solution as soluble anodes enable cathodic solution depletion to be countered, thereby easing one problem of process control. However this may bring the need for a depassivating agent as discussed before. If impure anodes were to be used this would give rise to other problems such as sludge and slime formation during the process.

b) Insoluble anodes: Generally in metal finishing operations insoluble anodes are used where the use of soluble anodes is impracticable for any reason. The use of insoluble anodes is essential in electrowinning. Insoluble anodes may be made of carbon/graphite, platinum, titanium and lead.

Anode current efficiencies for dissolution may often be greater than 98%, whereas cathode current efficiencies are up to 95%. This difference results in a slow build up of metal in solution.

Some of the important factors which must be taken into account, apart from soluble/insoluble considerations, are as follow:

a) Corrosion, including dissolution or passivation; this should take place smoothly and without preferential etching at all current densities.
b) Polarisation should be minimal, thereby ensuring high current densities at low overpotentials.

c) Corrosion in the absence of an electric current should be minimal thereby avoiding the need for removing the anodes from solution on all but the longest stoppages.

d) A minimum amount of sludge should be produced by spalling.

e) The contact resistance should be low and some easy connection system be available.

f) The anode should have a high intrinsic limiting current density with even current distribution.

The anodic reaction during electrodeposition depends on the nature of the anode and the electrolyte used. Nevertheless the anodic reaction can be divided into three categories:

1. Metal dissolution is the main reaction of the soluble anodes

\[ M \rightarrow M^{n+} + ne \]

The ions are hydrated in aqueous solution, for example, cupric ions exist as \( \text{Cu(H}_2\text{O)}_{4}^{2+} \), not as \( \text{Cu}^{2+} \).

2. Oxygen evolution is the main source of anode inefficiency which depends on pH

\[ \text{pH} < 7 \quad \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 \]

\[ \text{pH} > 7 \quad 2\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \]

In both cases the pH is lowered, either by creation of hydrogen ions or by consumption of hydroxyl ions.

3. Oxidation of the anode, which may inhibit dissolution of the anode, or of ions in solution

\[ M + \frac{1}{2} \text{O}_2 \rightarrow \text{MO} \]

\[ M^+ \rightarrow M^{2+} + e \]
2.6 PLATING PARAMETERS

During electrodeposition the deposit or coating is very sensitive to small changes in the bath. This enables us to control the process of electrodeposition by controlling the bath's composition and condition such as pH, temperature, current density, agitation addition agents and metal ion concentration.

In electroplating a fine grained, strongly adherent, bright or easily polishable layer of crystals is necessary. The mechanism of crystal growth is as follows: first nuclei or minute new crystals form followed by the growth of existing crystals. Any factor that increases the rate of formation of nuclei tends to increase the number of crystals and opposing conditions inhibit the increase.

Temperature: Generally an increase in temperature of the bath increases metal solubility, the diffusion rates, dissolution of anodes and conductivity of the electrolyte, thereby decreasing the polarisation and lowering the cell voltage. With a decrease in solution resistivity, development of irregularities on the cathode by uneven current distribution is lessened. Increase in the temperature stimulates crystal growth rather than encouraging the formation of new nuclei. Hydrogen evolution is also lessened through reduction of the polarisation. However more base metals such as zinc, which have high hydrogen overvoltage, behave differently. Temperature increase promotes hydrogen evolution.

Conductivity: In most baths the addition of acids, bases or salts increases the conductivity thereby reducing the potential drop across the cell for the same current density. Resistive solutions consume excess electrical power which manifests itself as heat.

pH: pH is an indication of acidity of a solution. It is described as $\text{pH} = -\log a_H$ where $a_H$ is the activity of $H^+$ ion. The maximum concentration of $H^+$ and $OH^-$ in aqueous solution can be assumed to be 1 g/l. In pure water the concentration of these ions is equal
(pH = 7). However the concentration of $H^+$ can vary from $10^0$ (pH = 1) to $10^{-14}$ (pH = 14). The pH can be very crucial in electrodeposition solutions such as Ni plating solution where the pH is buffered at a constant value of 4-6 otherwise nickel hydroxide may precipitate. Also in cyanide baths the pH must be controlled in order to avoid formation of HCN which occurs at pH below 8. Moreover, changes of pH can also cause corrosion of the electrodes or reduce adhesion of the coating on the cathode.

Current density: By increasing the current, hence the current density, the plating condition can be changed dramatically. Too high a current density may cause powdery coatings as a result of crystal and dendritic growth, or even burnt deposits on the one hand, and on the other decreasing the efficiency of the process by exceeding the limiting current thereby evolving hydrogen at the cathode. In most electroplating operations, the range of current density is limited by the physical character of the deposit. However the employment of higher current density ranges is constrained by the capital cost of power units and the cost of power used.

Throwing power: Throwing power is defined as the ability of an electrolyte to plate in recesses. Throwing power is a very important factor in electroplating as the quality of the coating depends greatly on distribution of the metal on the substrate metal needing to be protected. Here not only the mean coating thickness is important but the minimum at the critical points such as inside grooves is decisive. Throwing power is dependent on the rate of change of cathode potential with current density, resistivity of the electrolyte and the cathode efficiency at various current densities.
CHAPTER 3
ROTATING ELECTRODES

3.1 INTRODUCTION

Since late last century the flow around solid rotating bodies has been widely investigated. Many experiments have been performed to determine the power expended by the rotation of steam turbine plates. Also in connection with gas turbines the heat transfer from different parts of the turbines has been investigated. Many mechanical parts of the machinery can be considered/approximated to rotating disks, cylinders, cones, spheres etc.

Apart from the interest shown by scientists for the above reasons many electroplaters have also been interested in these solid rotating bodies. Their interest is mass transfer phenomena as well as hydrodynamics.

The use of rotating cathodes (anodes to a lesser extent) has been known for many decades, but its use has not yet found wide application in commercial electroplating due to irregularly shaped articles that are required to be handled for plating.

The advantages of rotating cathodes during electroplating are as follow:

1. For a given plating condition, more dilute solutions may be used;
2. A greater current density may be used and hence quicker deposition;
3. A better levelling action, therefore a smoother deposit is possible;
4. Harder deposit is obtained, this is due to fine grain size which depend on rotational speed;
5. Tensile strength of deposits also increased with increase in rotation speed;
6. Deposition of metals present at low concentration is possible such as silver recovery from photographic solution;

7. Impurities can be removed from plating solutions i.e. plating one metal in preference to another e.g. copper can be plated out from a nickel plating bath;

8. Due to stirring action, the pH, temperature and concentration of ions can be kept uniform throughout the bath.

3.2 BRIEF REVIEW OF HYDRODYNAMICS

Whenever mass transport phenomena is important, the effects of hydrodynamics too must be included. This relationship can be seen in a forced convection electrolysis. For example, in order to determine the limiting current in the solution one needs to consider the flow velocity, viscosity, cell geometry, etc. The flow may be laminar, that is fluid elements move along parallel streamlines without mixing, in this case the fluid flow pattern is well established and well defined, therefore the limiting current equation for instance can be obtained with certainty. In turbulent flow, there is no fixed flow pattern, here the effective viscosity (from a macroscopic viewpoint) is larger than the molecular viscosity, because neighbouring layers of different mean velocity not only transmit momentum to each other by molecule interaction, but also by eddies.

Furthermore the flow around a solid has different characteristics. On the surface the fluid flow velocity is zero, a very small distance away from the surface there exist the hydrodynamic boundary layers where the fluid flow velocity changes from zero to the actual fluid velocity at the outer layer. This boundary layer is very thin yet important as the diffusion boundary layer is proportional to its reciprocal.

Relations between some parameters which were discussed earlier, are often expressed by means of dimensionless combinations of physical variables. This allows an easier control of constants and variables which, by reducing the number of variables, simplifies the planning
of experiments. Furthermore, dimensionless numbers form the basis for experimental work with models and model fluids. Some of the more important dimensionless groups are as follows:

Reynolds Number: it may be defined as the ratio of the momentum transport by convection \( (\rho v^2) \) and the momentum transport by diffusion \( (\frac{qv}{v}) \). In turbulent flow the transport by convection i.e. by eddies, prevails. It can vary from unity to \( 10^5 \) or more, \( Re = \frac{UL}{v} \).

Sherwood Number: is defined as the mass transfer rate or flux to concentration and diffusion coefficient. \( Sh = \frac{fL}{D(C_b - C_o)} \).

Schmidt Number: is the ratio of the kinematic viscosity to the diffusion coefficient (kinematic viscosity in turn is defined as the ratio of viscosity to density). \( Sc = \frac{v}{D} \).

3.3 AGITATION FACTOR

As described before, the limiting current density is inversely proportional to the diffusion layer thickness. Therefore one of the most effective ways of increasing the limiting current density is by reducing the diffusion layer. This is achieved by agitating the electrolyte. The type of agitation might include stirring, cathode rotation, cathode oscillation, gas bubbling and ultrasonics. The table below shows the effect of agitation on the diffusion layer:

<table>
<thead>
<tr>
<th>Method of Agitation</th>
<th>mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural convection with vertical electrode</td>
<td>0.2</td>
</tr>
<tr>
<td>Natural convection with horizontal electrode</td>
<td>0.08</td>
</tr>
<tr>
<td>Plain electrode with longitudinal flow (V = 25 cm/s)</td>
<td>0.1</td>
</tr>
<tr>
<td>Rotating cylinder (180 rpm)</td>
<td>0.036</td>
</tr>
<tr>
<td>Gas producing electrode (1.3 cm³ gas cm⁻² min⁻¹)</td>
<td>0.004</td>
</tr>
<tr>
<td>Gas led in through frit (6.5 m pore size, gas flow 0.11/min)</td>
<td>0.1</td>
</tr>
<tr>
<td>Periodic disturbances of diffusion layer by net moved along electrode</td>
<td>0.013</td>
</tr>
<tr>
<td>Ultrasonic (7W/cm²)</td>
<td>0.006</td>
</tr>
</tbody>
</table>

(Data derived from L.E. Vaaler, Ibl, Gabe et al.)
3.4 ROTATING DISC ELECTRODES (RDE)

The RDE is the most used, best studied and best known electrode in electrochemical studies.

The RDE consists of a metal disc embodied at the top of a cylindrical shaft which is connected to a motor either directly or via a belt. The shaft is chemical resistant and isolated, it can be rotated at various speeds with very good control (typically 0-5000 rpm). The disc itself is typically made of platinum with a diameter of 2-5 mm. It can be removed for evaluation of the deposit.

The disc is rotated with a constant angular velocity about an axis perpendicular to the plane.

The rotation of the disc results in a pumping action. According to Adams\(^4\) as the disc rotates, liquid in an adjacent thin layer acquires the rotational motion of the disc. Liquid thus entrained has a tangential velocity and from the centrifugal force, also develops a radial velocity away from the centre of the disc. This flow pattern, which moves liquid horizontally out and away from the centre of the disc, requires an upward axial flow to replenish liquid at the disc surface.

Some of the reasons for the success of the RDE are as follows:

a) The RDE is normally used in an essentially laminar flow regime giving flow stability over a wide range of rotation speeds, thus making it preferable for electrode kinetics studies.

b) An exact and vigorous solution of the mass transfer equations for the electrode exists, based on theoretical and experimental studies.

c) Construction and operation of the RDE is somewhat easier than various other geometries.
d) The relatively low rate of mass transport to a RDE restricts current requirements to a low level, allowing the use of modest power supplies.

e) The thickness of the diffusion boundary layer has a constant value over the entire disc surface. This means regardless of the distance from the axis of rotation, the conditions for transport of material to any point on the surface of the disk are absolutely identical.

There are several styles of RDE that can be used (Figure 1). Type A consists of a piece of platinum, gold, or other metal wire, sealed into thick walled glass tubing. The end is then ground flat to form a centre disc with protecting rim.

Type B is a cone shaped electrode, where the disc occupies the entire end surface of the cone. The advantage of this design is that the edge effect is minimised, however due to the large surface area of the electrode, high current is needed.

Design C is a combination of A and B designs.

3.4.1 Flow Pattern
The flow regime varies from laminar flow near the centre to fully developed turbulent flow near the periphery. However it is possible to obtain fully developed turbulent flow across the disc at very high rotational speeds (10 000-20 000 rpm). The flow transition occurs at Reynolds numbers from $2 \times 10^5$ to $3 \times 10^5$ (6).

3.4.2 Mass Transfer
The fundamentals of fluid flow and mass transfer are well characterised in laminar flow, the contributions of V.G. Levich being outstanding.
The hydrodynamic boundary layer $\delta_o$, can be given approximately as

$$\delta_o \approx 3 \left( \frac{V}{\omega} \right)^{1/3}$$

where $\omega$ is the angular velocity of the disc.

Within the thickness $\delta_o$, the radial and tangential fluid velocities decrease as a function $Z$ measured vertically downward from the disc surface at $y = \delta_o$. The tangential velocity has decreased to 1/20 of its value at the disc surface, according to Levich. At $y > \delta_o$ only axial motion exists.

The boundary layers, both laminar and turbulent, have been studied in detail both theoretically and experimentally. The Reynolds number for a well polished and centred disc is found to be

$$Re_o = \frac{r_o^2 \omega}{\nu}$$

where $r_o$ is the radius of the disc and $\omega$ the angular velocity of the disc. $\omega = 2\pi N$ and $N = \text{rpm}$ and $\nu$ the kinetic viscosity, $\text{cm}^2/\text{sec}$ of the fluid.

The mass transfer rate for laminar flow described by Levich is given as

$$Sh_L = 0.6205 \left( \frac{Re_o}{Sc} \right)^{1/2}$$

where the Sherwood number $Sh = i r_o / n F \Delta C$, the Schmidt number $Sc = \nu / D$.

Also $i$ is the current density, $n$ the number of electrons transferred per ion reacting, $F$ = Faraday's constant and $\Delta C$ is the concentration driving force for diffusion that is bulk concentration minus concentration of the electrode surface.
The transfer rate for well developed turbulent flow is less precise and has been shown in several forms. Ellison and Cornet\textsuperscript{7} described the mass transfer rate as $\overline{Sht} = 0.0117 \text{Re}_c^{0.896} \text{Sc}^{0.249}$ whilst Daguenet's\textsuperscript{8} version is $Mt = (0.0078 \text{Re}_c^{0.9} - 1.38 \times 10^5 \text{Re}_c^{-1/2}) \text{Sc}^{1/3}$ and for large $\text{Re}_c$, $\overline{Sht} = 0.0078 \text{Re}_c^{0.9} \text{Sc}^{1/3}$.

The difference in $\text{Re}$ and $\text{Sc}$ numbers is due to scatter in the data; this also makes distinguishing between a 1/3 and 1/4 power Schmidt number more difficult.

Mohr and Newman\textsuperscript{6} presented a graph (Figure 2) showing experimental results they obtained for overall mass transfer rate $\text{Nu Sc}^{-1/3}$ vs Reynolds number for laminar, transition and turbulent regimes.

In terms of limiting current for a reaction controlled only by mass transfer, $i_L$ describes the limiting current as

$$i_L = 0.62 \, \text{nFA} \, C_b \, D^{2/3} \, v^{-1/6} \, \omega^{1/2}$$

where $C_b$ is the bulk concentration.

3.4.3 Application

The RDE is useful for studies where flow control, flow stability and reproducibility are important factors. It is possible to obtain laminar, transition and turbulent flow across the disc at the same time. The RDE is widely used in investigations of the rates and mechanisms of electrode processes such as studies of corrosion, when the effect of a varying local rate of oxygen transport to the surface of the corroding metal is of interest. It may also be used very effectively in analytical chemistry and as a means of measuring values of the diffusion coefficient $D$ or the ion concentration $C$. 
3.5 ROTATING CYLINDER ELECTRODE (RCE)

In recent years considerable attention has been given to the RCE. The fundamental concepts and theory are still valid, but extended. The RCE is also being exploited by the industry more than ever.

The RCE is manufactured mainly from stainless steel and takes many sizes from several millimetre in length to several decimetres. The principle by which the cylinder is rotated is similar to that of the RDE. It is rotated along its axis by means of a motor either directly through an insulating shaft or indirectly by means of belts or gears. The cylinder is rotated at both low and high speeds (10 rpm-20000 rpm) ideally continuously variable over the whole range. The speed must be accurately measured and maintained. Design of the bearings is probably the most important part of the apparatus as correct design enables a smooth rotation and eliminates any eccentricity. The electrical supply and connections must be capable of handling large currents and ensuring minimum resistance. The main characteristics of the RCE geometry, given by Gabe\textsuperscript{9}, are as follows:

1. An equipotential surface capable of allowing complete potential-static control;
2. A uniform current density when employing a concentric or symmetrical anode format;
3. Onset of turbulence at low rotation rates;
4. Uniform mass transfer over the cylinder surface, its quantitative relationships being well established;
5. Rough surfaces enhance mass transfer;
6. Superimposed axial flow can promote mass transfer without being rate controlling.

With superimposed axial flow a wide variety of flow conditions is possible, however the most convenient geometry for practical purposes is an inner rotating cylinder, a stationary outer concentric cylinder acting as counter electrode and a low axial flow.
3.5.1 Flow Pattern
Although the rotating cylinder possesses a simple geometry, the induced flow pattern is of a complex nature. At very low rotational speed, flow is tangential and laminar but as the rotational speed is increased this simple flow pattern becomes unstable and a cellular motion is imposed upon the flow producing toroidal Taylor vortices. These contain a radial component of velocity yet the bulk flow is still essentially laminar. Further increase in rotational speed results in development of eddies which break up the regular flow, pattern under this condition the flow pattern is fully turbulent. The flow transition occurs at Re = 100-200 and the transition is also defined as

\[ \text{Re}_{\text{crit}} = (11.8 \frac{r}{e})^{1.18} \]

where \( r \) is the radius of the cylinder and \( e \) is its saturated roughness.

3.5.2 Mass Transfer
Only a few investigators have attempted to correlate rotational speed of the cylinder to the limiting current density and in many cases the cell geometry was sufficiently peculiar to make the results unique. Generally the relationship

\[ i_L = kU^n \]

has been accepted by several investigators, however Brunner\textsuperscript{10}, Nernst and Merrian etc have given a value of 0.67-0.7 to the index \( n \), but Van Name and Edgar\textsuperscript{11} suggested a value as high as 0.9. This discrepancy is now known to be due to developing roughness in a turbulent regime.

Eisenberg et al\textsuperscript{12} obtained the following relationship for the ferri-ferrocyanide redox reaction
\[ i_L = 0.0791 nF U^{0.7} d^{-0.3} v^{-0.344} D^{0.641} \]
or
\[ Sh = 0.079 \ Re^{0.7} Sc^{0.356} \]
or
\[ St = 0.079 \ Re^{-0.3} Sc^{-0.644} \]

This relationship was confirmed by Robinson and Gabe\textsuperscript{13-15} who obtained, for the cathodic electrodeposition of copper from CuSO\(_4\)-H\(_2\)SO\(_4\) solutions

\[ St = 0.0791 \ Re^{-0.31} Sc^{-0.59} \]

The surface roughness of the cylinder is an important factor which must be taken into account. For turbulent flow and for a surface of saturated roughness the drag on a RCE is independent of Re but a function of relative roughness (e/d) as described by the Theordorsen-Regier equation

\[ \frac{1}{f^{1/4}} = 1.25 + 5.76 \log \left( \frac{d}{e} \right) \]

where e is the average height of roughness.

The mass transfer may then be described by

\[ St = [1.25 + 5.76 \log \left( \frac{d}{e} \right)]^{-2} Sc^{-0.644} \]

and reasonable agreement has been reported. Recent research in this field has been reported by Walsh and Makanjuola.

The surface roughness on the cylinder enhances the mass transfer in two different ways:

a) by increasing the active surface area of the electrode;

b) by improving the hydrodynamic shear at the electrode.
3.5.3 Applications

The RCE has found a wide range of applications, primarily in the electrochemical field. Nevertheless the RCE has been used for viscosity measurements, heat transfer studies, rotating cylinder extraction columns, cyclone chamber behaviour and journal bearing simulation.

The electrochemical applications are in several fields as follows:

Electrodeposition: essentially qualitative making use of the motion to increase rates of electrowinning and improve surface finish of protective plated coatings. Another important application of the RCE is the electrowinning of metals from waste effluent and dilute leach or pickle liquors.

Cementation: agitation improve a cementation type of reaction when it is controlled by ion diffusion through solution, RCE and RDE have been used in this field.

Corrosion and dissolution: As the behaviour of the RCE is well known (current distribution and flow pattern) therefore corrosion or dissolution can be accelerated and monitored without any difficulty. Recent work involves the effects of dissolved oxygen and chlorides on the rates of corrosion efficiency of inhibitors in controlling corrosion and cathodic protection in flowing conditions. More recently the RCE has been used to examine transport behaviour in liquid metals and fused salts.

3.6 CONICAL ELECTRODES

In recent years the conical electrode has gained considerable interest among scientists. This is partly due to a simple ideal model for theoretical and experimental investigations of three dimensional boundary layer characteristics. Most of the theoretical and experimental investigations have been carried out with heat transfer in mind. However in the field of electrochemistry some of
the investigators such as Jordan\textsuperscript{16} have converted the heat transfer data to mass transfer data. On the other hand Subramanyan\textsuperscript{17} et al have related the equations of RDE to conical electrodes. One interesting feature of conical electrodes is that it comes in many different shapes yet all comparable. It can be truncated, have an apex angle of $0^\circ$ (cylinder) right through to $180^\circ$ (disc). The conical electrode has been investigated in two different ways: either the electrode is kept stationary and the flow passed around it (Jordan et al) or the electrode is rotated at various angular velocity along its axis. The apparatus of this kind of work is exactly the same as that of the RDE and RCE.

3.6.1 Flow Pattern
The flow pattern of a rotating cone can be quite complex. At low rotational speed the flow is laminar all over the surface. At higher speeds laminar and turbulent flow can exist simultaneously. The laminar flow exists at the region where the radius of the electrode is small and the turbulent flow at the region where the radius is greater. However due to changes in radius of the cone the flow can become very complex since the centrifugal force imparted to the adjacent liquid element depends on the distance from the apex of the cone i.e. radius. Therefore the liquid at a distance away from the apex will experience a greater centrifugal force, hence impelled from the surface of the cone with a greater force than the liquid near the apex. This induces a flow along the surface away from the apex (Figure 3). This tangential flow will affect the turbulence flow by reducing it for a given rotational speed.

3.6.2 Mass Transfer
Jordan et al\textsuperscript{16} investigated the mass transfer of a conical micro electrode, which was kept stationary and the flow passed round it. Generally both heat and mass transfer can be described in the form

$$Nu = \phi(Re, Pr) \text{ for heat transfer}$$

and

$$Sh = \phi(Re, Sc) \text{ for mass transfer}$$
In comparable geometric and hydrodynamic situations a heat transfer relationship of the type of equations above can be adapted to mass transfer by substituting the appropriate parameters

<table>
<thead>
<tr>
<th>Heat transfer</th>
<th>Mass transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \frac{q}{k(T-T_0)} ]</td>
<td>[ \frac{J_i}{D(C-C_0)} ]</td>
</tr>
<tr>
<td>[ Pr = \frac{\nu S_0}{k} ]</td>
<td>[ Sc = \frac{\nu}{D} ]</td>
</tr>
<tr>
<td>[ Re = \frac{\nu l}{\nu} ]</td>
<td>[ Re = \frac{\nu l}{\nu} ]</td>
</tr>
</tbody>
</table>

For laminar flow the mass transfer relationship is as follows:

For heat transfer \[ Nu = \frac{4}{3} Re^{1/2} Pr^{1/3} \]

and for mass transfer \[ Sh = \frac{4}{3} Re^{1/2} Sc^{1/3} \]

In a comprehensive study of voltammetry at solids, Jordan et al.\(^{16}\) constructed a conical platinum electrode with a slant height of 0.04 cm and surface area of 0.003 cm\(^2\). Under 100% current efficiency the mass transfer flux at the electrode surface is correlated with limiting current:

\[ i_L = n F A f_0 = n F A S h D R C \]

Under extreme polarisation \( \Delta C + C_b \)

hence \[ i_L = 0.77 n F A C_b \nu^{3/2} D^{2/3} l^{-1/2} \nu^{-1/4} \]

where \( l \) denotes the slant height of the cone.

Tien\(^{18}\) obtained a theoretical relationship for heat transfer in laminar flow at Prandtl number of 0.72
\[ Nu = 0.329 \left( \frac{\ell^2 \omega \sin \alpha}{v} \right)^{0.5} \]

where \( \alpha \) is the half apex angle of the cone.

Therefore for Schmidt number of 0.72

\[ Sh = 0.329 \left( \frac{\ell^2 \omega \sin \alpha}{v} \right)^{0.5} \]

incorporating \( Sc^{0.4} \) it resulted in

\[ \left( \frac{Sh}{Sc^{0.4}} \right) = 0.375 \left( \frac{\ell^2 \omega \sin \alpha}{v} \right)^{0.5} \]

The agreement between this theoretical formula with the data obtained for different cones by Subramanyan et al. showed it to be fairly good. Subramanyan et al. plotted \( \frac{Sh}{Sc^{0.4}} \) versus \( \frac{\ell^2 \omega \sin \alpha}{v} \) and included the equation for the cones with apex angle greater than 40° will be \( \frac{Sh}{Sc^{0.4}} = 0.345 \left( \frac{\ell^2 \omega \sin \alpha}{v} \right)^{0.5} \). According to Kirowa-Eisher and Gileadi, the equation for a rotating cone electrode has been derived by Newman and Mohr. The result for the local mass transfer rate at the limiting current is

\[ J = 0.62 \ C_b \ (v \omega \sin \alpha)^{0.5} \ Sc^{-2/3} \]

and the overall mass transfer rate for a conical electrode of base radius \( r \) is

\[ J_{\text{total}} = 0.62 \ C_b \ r^2 \left( \frac{v \omega}{\sin \alpha} \right)^{0.5} \ Sc^{-2/3} \]

The above investigators treated the rotating cone as a modified rotating disc, hence the limiting current of the rotating cone is related to that of the rotating disc by
It must be noted that so far all the investigations were under laminar flow and very little work has been carried out under turbulent boundary layer conditions. Kappesser et al.\textsuperscript{20} transformed the mass transfer equation in laminar flow for a disc given by Newman

\[ \frac{S_{d}}{L} = \frac{0.62048 \left( \frac{R_{d}}{2} \right)^{1/2} \left( \frac{S_{d}}{c} \right)^{-2/3}}{1 + 0.2980 \left( \frac{S_{d}}{c} \right)^{1/3} + 0.1451 \left( \frac{S_{d}}{c} \right)^{-2/3}} \]

to that of rotating cones by substituting the appropriate parameters and obtained the following expression

\[ \frac{S_{c}}{L} = \frac{0.62046 \left( \frac{R_{c}}{2} \right)^{1/2} \left( \frac{S_{c}}{c} \right)^{-2/3}}{1 + 0.2980 \left( \frac{S_{c}}{c} \right)^{1/3} + 0.1451 \left( \frac{S_{c}}{c} \right)^{-2/3}} \]

where \( S_{d} = \frac{J_{L}}{D_{MC}} \) and \( R_{c} = \frac{\omega R_{d}}{v} = \frac{\omega d^2 \sin \alpha}{v} \) and when \( d \) denotes disc and \( c \) denotes cone.

The above equation was valid for experimental results in the range

\[ 0.7 < (S_{c}, Pr) < 2.4 \]

For turbulent flow, Kreith\textsuperscript{21} used the Reynolds analogy to obtain an expression for the heat transfer for a rotating cone at Pr number of unity, according to Kappesser. The results are in good agreement with the experimental data for \( 0.7 < (Pr, Sc) < 2.4 \). However, Kreith extended his work in order to determine the heat and mass transfer for Prandtl or Schmidt numbers differing from unity. The final result is

\[ Sh_h = 0.0212 \left( \frac{2.6}{Sc} \right)^{0.2} \frac{Re^{0.8}}{\left[ 1 + \left( \frac{x}{f} \right)^{1} \right]} \frac{Sc}{5Sc + 5 \ln(5Sc+1) - 14} \]
where \( x \) denotes local condition and \( f_x/2 = \text{local friction factor} = \frac{\tau}{\rho \omega x^2 \sin^2} \) and \( \tau \) wall shear stress \( \text{dynes/cm}^2 \).

Alternatively Kappesser\(^{20}\) obtained a simplified expression

\[
Sh_x = 0.0182 \, Re_x^{0.9} \, Sc^{0.25}
\]

To account for the effect of laminar flow over the surface of the cone near the vertex, the following expression was given by the investigator

\[
\overline{Sh} = \frac{Sh_L - Sh_T}{x_c} \, \frac{x_c}{l} + Sh_T
\]

where \( x_c \) is the length where the transition is made from laminar to turbulent flow, which can be obtained from the results of Kreith et al\(^{21}\)

\( l \) is the slant length

\( \overline{Sh}_L = \text{laminar Sherwood number} \)

\( \overline{Sh}_T = \text{turbulent Sh number} \).

Figures 4 and 5 show the results obtained by Kappesser et al which indicate a good agreement between theory and experimental results.

3.6.3 Application

The conical electrode has attracted investigators' attention for several reasons

1. Its geometry approaches that found in engineering systems and scientific apparatus;
2. Many analytical solutions are available to permit comparison between theory and experiment.
According to Jordan the hydrodynamic voltammetry can be used as a tool for accurate determination of the rates of electron transfer processes involving interactions between soluble electroactive species and the electrode.

3.7 OTHER ROTATING ELECTRODE GEOMETRIES

3.7.1 Rotating Ring Electrode$^{22,23}$

The problem with rotating disc electrodes is that at higher current densities, where gas may evolve, the gas tends to block the centre of the disc, hence reducing the surface area of the disc, etc. To avoid this problem a rotating ring electrode RRE may be used. The RRE is often used in conjunction with an RDE, and is hence called a Rotating Ring Disc Electrode. This is basically a RDE with a second ring electrode mounted concentrically at a very small distance around the disc. The disc and ring are connected separately.

The reaction product which is formed at the disc is transported by the fluid flow to the ring. If these components are electrochemically active they can be detected at the ring. Icor V. Kadija et al$^{23}$ gives the following equation for the limiting current for a rotating ring disc electrode

$$i_L = 0.62CD^{2/3} v^{-1/6} \omega^{1/2} 3^{2/3} \pi r_o^{2/3} (\Delta r)^{2/3} ZF$$

where $r_o$ is the radius of the electrode and $\Delta r$ is the thickness of the ring.

3.7.2 Rotating Spherical Electrode (RSE)

Another problem with RDEs and RRDEs is that they have to be manufactured with a perfect flat surface and maintain this throughout the experiments. Therefore the disc is mounted concentrically on the surface of an electrically inert rotating disc and polished carefully until the central disc and the inert
surrounding reaches exact levels. This need for flatness arises from hydrodynamics consideration by Levich's theory. However, if the disc is used where the metal dissolves, it will not be possible to maintain a perfectly flat surface and inevitably irregularities appear on the electrode surface which in turn interferes with the hydrodynamic boundary layers. Finally Levich's theory is no longer valid.

One way to overcome this is by substituting the disc electrode with a sphere electrode. This combination is less subject to change in surface geometry due to dissolution.

Kobashi\textsuperscript{24}, Kreith et al\textsuperscript{24} and Bowden et al\textsuperscript{25} have investigated the RSE. They suggest that the boundary layer originates at the polar and develops with increasing thickness towards the equator. The fluid is drawn in towards the sphere along the axis of rotation and over the surface towards the equator where a radial outflow jet is formed.

The dimensionless mass transfer given by Der-Tan Chin\textsuperscript{26} is as follows:

\[
Sh = \frac{Re^{1/2} Sc^{1/3} \left[0.62045 - 0.12833 \left\{ \frac{2(\cos^\theta - 1) + 2\theta \sin \theta - \theta^2 \cos \theta}{1 - \cos \theta} \right\} \right]}{1 - \cos \theta}
\]

where $\theta$ defines the active surface area, therefore for a hemispherical electrode $\theta = \pi/2$ hence

\[
Sh = 0.474 Re^{1/2} Sc^{1/3}
\]

The average limiting current density is given by

\[
i_L = nFACD^{2/3} \omega^{1/2} \left[0.62045 - 0.12833 \frac{2(\cos^\theta - 1) + 2\theta \sin \theta - \theta^2 \cos \theta}{1 - \cos \theta} \right]
\]
and for hemispherical electrodes

\[ I_L = 0.474 \, nFACD^{2/3} \sqrt{\nu^{-1/6} \omega^{1/2}} \]

The correlations apply at large Schmidt numbers, also the theory fails near the equator, this is due to shortcomings of the boundary layer at the equator.
CHAPTER 4

CELL REQUIREMENTS

4.1 INTRODUCTION

An electrochemical cell can be defined as a tank or a vessel where chemical reactions take place directly due to the input of electrical energy through electrode connections. In simple terms a cell may consist of a tank or a beaker of "off the shelf" dimensions or in specific terms it will be designed specially for a process, reaction or product and in these circumstances may be termed a process reactor. Reactor design has been developed by chemical engineers to a relatively advanced state in recent years and many of the principles are now derived from that field.

An electrochemical cell must necessarily consist of two electrodes immersed in a bath of electrically conductive solution called the electrolyte. A power supply is connected to the electrodes. Here when an electromotive force (emf) of a sufficient magnitude is applied electrochemical reaction will take place in the cell. Other necessary parts for a cell are the container and lining, membrane, control probes such as thermometer and heating elements and means of agitation. During electrochemical reactions other sources of power consumption are pumps, rotating motors heating etc with losses by heat transfer. Optimization can be related to Faradaic factors (electrochemical reactions, overvoltage, IR drop etc), to peripheral factors (energy to stir, heat, etc) or to production rates and efficiency.

4.2 CELL REQUIREMENT

In chemical engineering terminology there are several types of reactors (Figure 6):
1. Batch reactor: here the reactor is fed with the reactants and well mixed. The system is left to stand for a predetermined time for reactions to proceed, after which the resulting solution is then discharged.

2. Plug flow reactor: this system is a continuous one where reactant is fed from one end, as the solution passes through the reactor appropriate reactions take place and the product comes out from the other end of the reactor.

3. Backmix reactor: this system is a mixture of the other two systems.

The reactant is fed continuously, the well stirred tank keeps the composition uniform throughout the reactor and a product stream is removed continuously at the same rate.

Basically cell design is dominated by the product requirement in electroplating. For instance, the quality of the product is of key importance and energy efficiency is not a prime consideration, because the charge used in plating is relatively small. On the contrary in an aluminium production unit, energy yield and space time yield are the important factors. However, despite this diversity there are some general requirements which need to be satisfied in any cell design. These are as follow:

  i) Low cost both in design consideration and in operation;
  ii) Maximising the mass transfer rate to the cathode;
  iii) Automation, thereby reducing labour cost;
  iv) All materials of construction must be compatible with the electrolyte and the electrolysis products;
  v) Easy access to all parts of the cell for inspection and maintenance;
  vi) Uniform current distribution over the electrode surface;
  vii) Compactness;
  viii) Cell must be easily flushed in case of any contamination.
As the electrochemical reactor forms only one item in a complete system, therefore the operational mode of the reactor is influenced by the remaining items of plant. For example the reactor feed preparation and the production separation stages could influence the flow rate of electrolyte into and out of the reactor.

One of the most important parameters is the total power requirement assuming 100 per cent efficiency. This can be obtained by overall material balance over a given time. The material balance is made using a projected feed composition, percentage conversion of reactants and operational mode\textsuperscript{26}. At this stage the operational temperature and its control plus the total electrode area must be considered before going into detailed analysis.

4.3 ELECTROCHEMICAL DESIGN PARAMETERS\textsuperscript{29}

Some of the design parameters which need careful consideration before proceeding in the construction of a new cell are as follows: voltage/current distribution, throwing power, anode, cathode, conductivity, power source, reference electrode.

4.3.1 Voltage/Current Distribution
As mentioned before the current distribution over the electrode can have a marked effect not only on the quality of products, but also on the yield of products and the energy consumption.

Unwanted products may be generated as a result of uneven distribution of potential and current on the working electrode. Simple design of electrodes i.e. avoiding complex shapes, will ensure better voltage/current distribution. However, consideration must be given to polarisation. Polarisations such as activation and concentration do affect the primary current distribution.
4.3.2 Throwing Power

Throwing power is a relative term used to denote the degree of uniformity of metal distribution that can be obtained on an irregular working electrode. Throwing power is influenced by many factors such as: electrolyte composition, current density, cathode efficiency, pH, conductivity of the solution, agitation, temperature and relative position of cathode to the tank wall and its shape.

4.3.3 Current Distribution

The metal distribution over a surface during electroplating is due to current distribution providing the cathode current efficiency is constant. Current distribution is affected by IR-drop effects in the electrolyte between the electrodes and polarisation at the cathode-electrolyte interface. There are three aspects of current distribution:

1. **Primary distribution:** this depends only on the shape and arrangement of the electrodes and the cell i.e. purely due to IR effects in the solution and independent of the properties of the electrolyte

2. **Secondary current distribution:** this is the primary distribution as altered by the chemical and electrochemical properties of the electrolyte such as polarisation, conductivity and a dimensional factor specific to the cell

3. **Effective distribution:** this results from the secondary distribution. This is because only part of the secondary current is used to deposit metal and the rest is used to discharge hydrogen or to produce other phenomena.

4.3.4 Electrode Considerations

As described in the previous chapter, the anode must satisfy several conditions such as solubility, film formation, impurities etc. The electrodes should be of the simplest shapes possible. They should be as close as possible in order to reduce the ohmic drop in solution
yet the electrodes must not block the electrolyte flow. Easy access is also important as the anode may need to be replaced often and the cathode either replaced in the case of metal finishing, or cleaned in the case of metal removal. The electrodes must be easily manufactured and should be of low cost.

4.3.5 Power Source

The DC power source that is employed in electrochemical work needs to have high enough voltage to overcome voltage drops in the circuit and the cell such as contact resistance etc. Power sources nowadays have both voltage and current control and limiters which give greater control. By using precision potentiostats which employ three electrode systems; anode, cathode and reference electrode, the voltage and the current can be adjusted so that the potential between the working electrode and reference electrode can be kept at a precise value at all times. If operating at high current densities, the electrical circuit must be designed accordingly, thereby avoiding overheating of wires and sparks at contacts.

A general equation describing potential drop through an individual cell is given

\[ V_{\text{cell}} = (\text{anodic} + \text{cathodic polarisation}) + \rho_o S \]

where \( \rho_o \) is the electrolyte resistivity and \( S \) the inter-electrode gap. This general equation has several limitations. Firstly it assumes potential drop through the contacts is negligible and secondly it ignores the effect of gas evolution. However in the presence of gas evolution the electrolyte resistivity is modified by a gas fraction, \( G \), term

\[ V_{\text{cell}} = (\text{anodic} + \text{cathodic polarisation}) + \rho_o (1-G)^{-1.5} \]
4.3.6 Power Dissipation
In any electrochemical reactor power is dissipated in several ways:

a) Conductors/wiring;
b) Contacts and connectors;
c) Instrumentation;
d) Leakage;
e) Thermodynamic reaction energy, Faradaic inefficiency;
f) Overpotentials;
g) Ohmic loss in cell manifested as heat.

(a-d) can be minimised by good engineering design and 'housekeeping'; (e) and (f) are necessary to the process and may sometimes be regarded as fixed; (g) may be an unnecessary loss although process heating is sometimes necessary.

4.4 CELL DESIGN CRITERIA

In order to assess a cell, there are several criteria which may be used such as current efficiency, material yield, space-time yield, area/volume ratio etc. However it may be difficult to compare two cells by considering only the figures of merit as they vary substantially. Moreover it is not possible to optimise all figures of merit, improving one criterion may be detrimental to another. However let us consider each criterion in turn.

4.4.1 Current Efficiency
The current efficiency CE is the yield based on the charge passed during the electrolysis and is defined as

\[
\text{C.E.} = \frac{\text{charge used in forming product}}{\text{total charge consumed}} \times 100
\]

where the charge used in forming the product is calculated using Faraday's law.
4.4.2 Material Yield

The material yield is defined as

\[
\text{Material yield} = \frac{\text{moles of starting material converted to product}}{\text{moles of starting material consumed}} \times 100
\]

Material yield is usually used to determine the annual consumption of raw material. Usually material yield is less than 100%, this represents the amount of impurity in the raw material. Therefore, to maximise the material yield pure raw material is required which often cannot be justified.

4.4.3 Space Time Yield

The space time yield is defined as the rate of production per unit volume of reactor and is normally quoted in units such as mol dm\(^{-3}\) h\(^{-1}\). The space time yield is proportional to the effective current through the cell per unit volume of reactor and hence on the current density, current efficiency and the active surface area of electrode per unit volume. A drawback to space-time yield is that it is dependent on the reaction used to define them, and the concentrations used.

4.4.4 Area/Volume Ratio

This is the ratio of electrode surface area to the volume of the cell: this ratio is maximised to produce a compact design. It results in a reduction of the inter-electrode gap which in turn reduces the joule heating and IR drop. This ratio can be useful in planar electrodes but not so much in true three dimensional electrodes such as packed beds where increasing bed thicknesses bring diminished returns.

4.4.5 Energy Consumption

Energy consumption or energy yield is defined as the electric power required to make unit weight of the product.
Energy consumption = \( \frac{nFV}{3.68 \times 10^4 \times \text{current efficiency} \times m} \) kW h kg\(^{-1}\)

where \( m \) is the molecular weight in kilograms. Energy consumption is a function dependent both on the electrolysis conditions and the cell design. As it can be seen it is proportional to cell voltage and current efficiency. Therefore in order to minimise the energy yield the cell voltage must be reduced as much as possible and selecting the electrolysis conditions so that the current is used solely for the reaction of interest.

4.4.6 Membrane Dividers

Often a cell is divided into two compartments by means of membranes. These membranes allow ion transfer to take place yet the solution in either compartments is not mixed. There are several reasons for dividing the reactor into separate anolyte and catholyte compartments. Some are as follow:

1. The anode may be protected from aggressive process solutions.
2. In the case of soluble anodes, the membrane prevents the anode slime from spoiling the cathode deposit.
3. A reactor may be utilised for a variety of metal containing catholytes while retaining the same anode.
4. In the case of secondary reactions, such as OER and HER etc, the membrane serves to separate a potentially hazardous combination of gases. This also applies if chlorine is being generated at the anode as a main product and must be separated from cathodic hydrogen.

4.4.7 Agitation

As stated before, it is necessary to agitate solutions in order to prevent local variations in concentration, i.e. around the cathode. Thereby an increase in mass transfer and ultimately higher efficiency in electroplating processes may result. Solution agitation is achieved in several ways such as:
4.4.7.1 Air agitation
This is the most popular method used in industry. By means of a low pressure pump, compressed air is driven into pipes which run on the bath floor, where the air escapes from the pipes through many small holes. Air agitation coils are made from mild steel, stainless steel, titanium and PVC extruded pipe.

4.4.7.2 Cathode movement
This method of agitation is employed when air agitation is not a satisfactory means, for instance, the solution contains easily oxidisable constituents, e.g. stannous sulphate solution. The cathode movements are also used where the solution contains a wetting agent. The mechanical movement is usually horizontal, where the workpiece is moved along the bath. However vertical movement of the cathode is also used where there is not enough room around the workpiece.

4.4.7.3 Pumping
This is another method of agitation where the solution is pumped into and out of the plating bath and possibly as part of a filtration circuit. Although the pumping method is a more expensive way of agitation compared to other methods, it enables us to have a continuous plating bath. That is the solution can be changed or renewed while plating. Therefore this method can be a favourable way in a fast electroplating plant where many items are electroplated.

4.4.7.4 Particle fluidization
This method provides another system of agitation. A fluidization bed is the reactor which uses this method. Here the electrolyte is passed through the cell and electrochemical reaction takes place between the electrode attached to the bed and many small particles.

The existence of a fluidised phase provides several essential advantages:
1. A large electrode surface area throughout the cell
2. Good mass transfer
3. Continuous growth and extraction of product.

One important question one must ask is "How can agitation be measured?" One way of quantifying the agitation is by considering its physical effect during electroplating.

The most important effect of agitation is the reduction of diffusion layer thickness $\delta$. Therefore by measuring the diffusion layer thickness, the agitation rate is measured. However it is difficult to measure this layer directly on a routine repetitive basis and therefore has limited use for direct process control but can be used as a measure of the effectiveness of agitation in differing cell geometries.

An easy way of measuring $\delta$ is by measuring the limiting current $i_L$. The relationship between $\delta$ and $i_L$ is given by the Nernst-Fick equation

$$ i_L = \frac{nFCD}{\delta(1-t)} $$

Therefore by fixing all other parameters i.e. $n$, $F$, $C$, $D$, $t$ a simple relationship between $i_L$ and $\delta$ results. By means of the limiting current technique i.e. polarisation curves, a specific value of limiting current at a specific agitation rate is obtained. Another way of representing the agitation effect is by using Sherwood or Stanton numbers. These dimensionless groups include the limiting current term, hence their usefulness in this respect.
5.1 REVIEW OF THE HULL CELL

In plating it is important to find the optimum plating range. However this cannot be found by chemical analysis or polarization alone, therefore Hull cell and bent cathode tests are widely used to determine the throwing power, brightness range, presence of impurities and the effects of additions or specific treatment in the bath.

In 1935 R.O. Hull proposed a standard design of a cell, as shown in Figure 7. The Hull cell may also be used to investigate properties such as hardness, ductility and metal distribution and the effects of current density variation on such properties can then be ascertained.

According to R.C. Armet, "the Hull cell may be employed usefully for the control of most types of plating solutions. One of its great advantages is the fact that it is possible for the skilled worker to assess the deposit characteristics of varying current densities all on one test panel. It is furthermore possible to carry out tests at various temperatures and current densities and so get a good idea of the batch characteristics and of the changes due to the variables introduced."

5.1.1 Hull Cell Characteristics
The shape and actual dimensions of the cell are most important in determining the cell current distribution. The cathode angle of inclination was specifically chosen after careful investigation and experiment, and if the angle is changed current distribution will no longer remain independent of the nature of the electrolyte.
Four basic conditions are defined by Kasper\textsuperscript{37} for which a cell can be designed:

1. the electrolyte obeys Ohm's law;
2. the electrolyte is homogeneous, that is, electrically isotropic;
3. voltage changes along an electrode are negligible so that it may be considered as an equipotential surface;
4. a discontinuity in potential between the electrode and the solution may exist (polarization) but it must be uniform over the electrode surface.

Condition 2 may generally be satisfied by vigorous stirring and avoiding extremely high current densities.

The 267 ml cell was developed which permits rapid calculation of required additions to the plating bath since 2.0g of any addition per 267 ml are equivalent to 1.0 oz per US gallon. Similarly the 320 ml cell was developed for British usage (i.e. 20g added is equivalent to 1 oz per Imperial gallon). A typical test is run for 5 min at 25 to 30°C with total cathode current of 1 to 3 amps.

The cell is constructed from non-conductive materials such as perspex. The choice of anode material is governed by the solution under test e.g. cadmium, copper, lead, nickel, tin and zinc. The cathode material and its surface condition should ideally be the same as that of the work which is plated in practice e.g. steel. The primary current distribution in a Hull cell follows a logarithmic curve and can be represented as:

\[
\text{C.D. at any point} = I \left( C_1 - C_2 \log L \right)
\]

where \(L\) = distance along the cathode

\(I\) = total cell current

\(C_1\) and \(C_2\) are constants which depend on the nature of the electrolyte.
Hull found that these constants vary little from one electrolyte to another, hence by rearranging them the following was found:

- For 100 ml cell  \[ \text{C.D. at any point} = I \ (18.8 - 28.3 \ \log L) \]
- For 267 ml cell  \[ \text{C.D. at any point} = I \ (27.7 - 48.7 \ \log L) \]

where the C.D. is in amp/sq ft, I is in amperes and L is in inches.

5.1.2 Hull Cell Disadvantages

However the Hull cell has some drawbacks which need to be borne in mind, some of which are listed below:

- stirring the solution during the test is not recommended and not normally convenient
- an error of 10 ml in the cell will invalidate the equations and diagrams for current distribution
- temperature control may cause problems
- small Hull cells have been criticised for being too small in the context of solution composition which may change rapidly.

5.2 Modified Hull Cell

This cell consists of a standard Hull cell in which 1/2 inch diameter holes have been introduced into the two parallel sides of the cell, Figure 8. The modified cell is used inside another vessel and slow stirring may be introduced. (These holes allow the solution movement in the vessel to agitate the solution in the Hull cell thereby giving a more realistic plating condition as it occurs on the shopfloor). It is used for high C.D. solutions such as chromic acid for chromium plating.

5.3 Hanging Hull Cell

This cell operates directly in the plating solution; therefore a much closer picture of the actual plating range present in the bath is obtained on the test panels than in the laboratory Hull cells.
This cell is extensively used when a source of trouble in the plating bath needs to be found. This cell is also used for making a current survey of a plating tank, Figure 9.

5.4 GILMONT AND WALTON CELL

This cell is designed with two straight sides of equal length at an angle of 45° with the other two sides as rectangular hyperbolas orthogonal to each other and to the other two straight sides. The cathode is placed on one of the straight sides and the anode is placed on the opposite curved side, Figure 10.

The purpose of this cell is to obtain a linear relationship between current density and distance along the cathode. The Hull cell has simple geometry but the theoretical analysis of the variation of current density along its cathode is extremely complicated.

The current density along the cathode \( i \) in the Gilmont and Walton cell is given by:

\[
\frac{\text{current density}}{\text{distance}} = \frac{-2I}{LA} x
\]

where
- \( I \) = total current
- \( L \) = total length of the cathode
- \( A \) = area of cathode
- \( x \) = distance along cathode

and the minus sign indicates that the flow of current is in the direction of decreasing potential.

5.5 TENA CELL (ALTERNATIVE TO THE HULL CELL)

The Tena Cell is constructed from two concentric cylinders with any radii where the anode and cathode are inserted along the radii at any position between the two cylinders, Figure 11. There is also the possibility of using two cathodes, either side of the anode, i.e. similar to the Haring cell.
The current density on each cathode is:

\[ i_A = \frac{\beta}{(a + \beta)t \log \left( \frac{\beta}{a} \right)} \cdot \frac{1}{r} \]

\[ i_B = \frac{\alpha}{(a + \beta)t \log \left( \frac{\beta}{a} \right)} \cdot \frac{1}{r} \]

5.6 THROWING POWER CELLS

In the electroplating industry, it is generally desirable to maintain uniform deposit thickness over the plating surface. The "throwing power" refers to the properties of the solution whereby the actual distribution of metal thickness is greater or less than the primary distribution. This may be defined in several ways (see Section 5.10). It is necessary to test the plating solution in a laboratory scale prior to full scale plating on the shopfloor. For this purpose several cells have been designed to carry out such tasks.

5.6.1 The Bent Cathode
This cell is used for qualitative tests. The bent cathode cell produces a wide range of current densities due to the bent panel which presents edges and corners which in turn influence the current, see Figure 12.

5.6.2 The Haring Cell
This cell is divided into three uniform current compartments and the voltage drop across each compartment is measured with a potentiometer, Figure 13. The two central gauze electrodes are not connected to a source of current. The voltage drop in the cell is due to electrolyte resistance. Hence the anode polarization may be obtained by subtracting the voltage drop from the voltage of the anode compartment.
5.7 THE HARING AND BLUM CELL

This cell is used for throwing power measurements. The throwing power is expressed as the percentage improvement of the metal ratio on the two cathodes as compared to the non-polarized current ratio of 5, Figure 14.

However it is important to note that the data will be significant only if the test is made in a box of the same dimensions as the data to which the results are compared.

5.8 SLOT CELL

A wide range of C.D. may be obtained which vary exponentially by the end position of the slot in the box, Figure 15. A linear variation of C.D. has been produced by the use of multiple slots.

5.9 THROWING POWER FORMULAE

Many throwing power formulae have been proposed but the most popular formula is that attributed to Field:

\[
T.P. = \frac{(K-M) \times 100}{(K+M) - 2}
\]

where K is the ratio of distance from anode to cathode and M the ratio of weight of metal deposits (or cathode current) for the two cathodes.

The popularity of the above formula is due to the convenient range where +100 is for the best throwing power and -100 for the poorest throwing power.

The table below shows some other well known 'throwing power' formulae and compares the throwing power index.
<table>
<thead>
<tr>
<th>M</th>
<th>( (K-M)x100 )</th>
<th>( (K-M)x100 )</th>
<th>( (K-M)x100 )</th>
<th>( (K-M)x100 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \frac{K-M}{K} )</td>
<td>( \frac{K-M}{K-1} )</td>
<td>( \frac{K-M}{K+M-2} )</td>
<td>( \frac{K-M}{M(K-1)} )</td>
</tr>
<tr>
<td>1</td>
<td>80</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
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<td>60</td>
<td>75</td>
<td>60</td>
<td>37.5</td>
</tr>
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<td>40</td>
<td>50</td>
<td>33.3</td>
<td>16.7</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>-38.5</td>
<td>-12.5</td>
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<tr>
<td>100</td>
<td>-1900</td>
<td>-2375</td>
<td>-92</td>
<td>-23.75</td>
</tr>
</tbody>
</table>

### 5.10 PANEL CALIBRATION

The Hull cell panel (cathode) is plated non-uniformly where several areas on the panel can be distinguished. The area A is dark and rough; area B is dull; area C is bright and area D little or not deposit, Figure 16. The borderlines 1 and 2 curve towards the low current density end. This is due to interruption of the flow of solution along the cathode by the bottom of the cell.

Results are taken half way up the panel represented by a dotted line in the figure. The appearance of the panel under test should be noted in a handbook; there are codes for convenience and simplicity, see Appendix 1. Tests should be repeated at least twice for convincing results. Interpretation of the test panel is then carried out with the aid of a diagram or scale to correlate current density, Figure 17.

If the purpose of the test is to evaluate the effect of addition agent concentration, the total current used should be that which will give the widest possible bright or levelled range.
If presence of agitation is vital, then a stirrer should be placed near the cathode with moderate agitation. According to W. Nohse, movement of the solution near the anode is less desirable since anode polarization is usually much higher than that of the cathode and hence it is easier to maintain a constant current density by the recommended methods.
It was found that the research work needed to be extended from laboratory to workshop. For this purpose a portable rotating rig was required. The portable rotating rig must satisfy the following conditions.

a) light enough to be carried around easily  
b) compact enough to fit in the back of a car  
c) easy access to all parts with minimal maintenance required.

This rig can be divided into the following five sections: power unit, bearing house, electrical contacts, frame and auxiliary equipment.

6.1 POWER UNIT

A standard electrical motor with variable speed control model Citenco KQ 1.5-7, 1200 rpm, was used.

An electric motor can rotate an electrode in two ways, directly or indirectly. In the former case the shaft of the motor needs to be coupled to the shaft of the electrode. As the motor must be electrically isolated from the electrode, this is necessary to prevent any current being drawn into the motor during electroplating, a non-conductive joint must be used in between the two shafts. Alternatively in an indirectly coupled method, two pullies and an "O" ring are used. Here there are two advantages: (i) a simple way of isolating the motor and (ii) by using a combination of pullies with different diameters, various ranges of speed and power can be obtained. On this basis the second arrangement was used (see Plate 1).
6.2 BEARING HOUSE

It is crucial to have the electrode rotated absolutely concentric. This is only possible if the rotating shaft is concentric. Therefore a bearing house was constructed. It consisted of a true shaft which connects the motor shaft to the electrode shaft and two sets of bearings at either rear ends of the shaft. The bearings were set in the bearing house firmly and the shaft passed through them. Sealed bearings were used as they are maintenance free and the possibility of leakage of any grease is minimal. To reduce corrosion problems, the shaft was made of stainless steel and the bearing house sealed.

6.3 ELECTRICAL CONTACTS

It is necessary for the electrode to be connected to an electrical power supply. In doing so the contact between power supply and the rotating electrode is made by using a slip ring and a couple of brushes. The slip ring was mounted on top of the rotating shaft and two brushes made the required contact. Although only one of the brushes was connected to the power supply, another brush is needed to make contact on the opposite side of the slip ring in order to balance the force that the other rush is exerting on the shaft. A good contact between the slip ring and the brushes is essential at all times. This is ensured by using a spring to push the brush against the slip ring (see Plate 1).

To minimise Ohmic drop in this circuit the slip ring was silver plated and the brushes were made of an alloy of carbon and silver. This resulted in a circuit resistance of less than 0.5 Ohms.

6.4 FRAME

The frame was made of iron tubes with square cross-section. This reduced the total weight of the frame considerably. All joints were welded and the final finish was painted thoroughly in order to protect the structure from any corrosion. The base dimensions were
51 x 51 cm, the cross-section of the tubes 2.5 x 2.5 cm and a height of 70 cm. These dimensions were chosen so that the structure was small enough to fit in a car yet there was enough room for the operator to work comfortably. Also the wide base gave a very good stability to the whole frame (see Plate 2).

6.5 AUXILIARY EQUIPMENT

i) Tachometer
A volt generating tachometer was connected to the rotating shaft by means of two identical pullies and an "O" ring. With an increase in rotation rate, the tachometer generates a greater voltage. This voltage was measured with a voltmeter. From a graph of voltage versus rotation rate, the required rpm was set by adjusting the speed of the motor, to give the wanted voltage. The relationship between rpm and voltage was established by the following method.

A disc of about 11 cm in diameter was cut out of an aluminium sheet. Seventeen holes of 0.6 cm diameter and equidistant from each other were drilled near the edge of the disc. The disc was connected to the rotating shaft along its axis so that it rotated concentrically. Next an infra-red light unit, which transmitted and received infra-red light, was placed above the disc, also directly over the path of the holes when the disc was rotating. The optimal distance between the light source and the disc was 4 mm. During operation the infra-red light receiver received signals that were reflected from the surface of the aluminium disc. When one of the holes passed by, the infra-red light passed through the hole and no signal was received. A digital tachometer collected the data received from the infra-red unit and displayed it every 10 seconds. Therefore the value displayed by the tachometer can be converted to rotation rate by dividing this value by 10 x 17. Meanwhile the voltage shown by the voltage tachometer was noted. Figure 18 shows the relationship between rotation rate and voltage generated by the tachometer. Finally Figures 19 and 20 show the portable rotating electrode rig.
CHAPTER 7
EXPERIMENTAL

7.1 APPARATUS

7.1.1 Design Considerations
The objective of this research work was to design and operate a cell which would give a controllable agitation rate in conjunction with the Hull cell effect over the length of the cathode. Therefore the cell's geometry was designed in such a manner that it would result in a variation of overpotential along the cathode, hence variation of current density along it.

I. Agitation
By rotating one of the electrodes along its axis by means of an electric motor, the agitation requirement was fulfilled. The rate of agitation was controlled by controlling the rotational speed of the motor. The speed range used was from 10 to several hundred rpm, depending on the type of rotating electrode used.

II. Hull Cell Effect
Where one end of a cathode is plated more in preference to the other end, this effect is known as the Hull cell effect. The effect is due to variation of primary current distribution which in turn depends on the geometry of the cell.

Several cells were designed in such a way that the distance between the anode and cathode varied in a linear fashion. This was achieved by ensuring that the electrodes were at an angle to each other. This requirement was fulfilled in three different ways:

1. One electrode was used as a rotating cylinder electrode, placed at the centre of the cell, and the other electrode was placed at an angle of about 45° against the wall of the cell, see Figure 21 and Plate 4.
2. As above but the anode was set at an angle of 52° and below the rotating cylinder electrode, Figure 22 and Plate 5.

3. The cathode was machined in the shape of a cone from a stainless steel bar with an apex angle of 52°. Two electrodes were made in such a way, one upright and the other inverted, Figure 23 and Plate 6. The anode was placed against the upright wall of the cell.

7.1.2 Choice of Materials for Cell Construction
This was divided into two groups: metals and polymers. The metals group consists of steel, aluminium, copper, stainless steel galvanic steel. From this selection of metals only copper is easy to form and solder.

The polymer group consisted of perspex which is expensive, acrylic sheet, polypropylene and PVC. From this group PVC seems to be the best choice as the sheets are formable and joining is done quite simply by means of a welding rod and a hot torch. Since the cell needs to be non-conductive, metals would need to be painted with a non-conductive paint which would also resist a highly corrosive environment. Thus PVC seemed the best choice as a non-conductive and heat resistant material. However, the bottom section of the RHC also needs to satisfy all the above conditions, yet it has to be very rigid and very precisely constructed; therefore the required part was machined from a solid block of perspex.

7.1.3 Choice of Material for Electrodes
The choice of anode was simple. Since most of the research was carried out in copper-sulphate solution, in order to maintain the copper concentration in the solution for as long as possible, a copper anode was used. During electroplating the copper anode slowly dissolves and thereby replaces the copper ions used up in plating.
In choosing the cathode material the following points were considered:

1. conductive material
2. sulphuric acid resistance
3. machinable
4. not too expensive
5. resistance to nitric acid which is used to remove copper from the cathode surface.

By considering all of the above factors, all working electrodes were machined from stainless steel 316 rods/bars.

7.1.4 Reference Electrode
The reference electrode used throughout the experiments was mercurous sulphate with saturated potassium sulphate as the salt bridge electrolyte. This type of reference electrode was chosen because of the absence of chloride ions which are present in more common reference electrodes such as the calomel electrode.

7.1.5 Luggin Tube and Reference Electrode
To minimise the distance between the reference electrode and the working electrode, especially when only a small portion of the working electrode is under examination, a luggin tube was constructed. It consisted of a flexible tube of about half a metre long with a small glass frit fitted at one end and the other end connected to the reference electrode. The bridge solution was made of saturated potassium sulphate.

7.1.6 Power Unit
In all the experiments that were carried out, the power unit needed to satisfy two functions:

i) keep the potential between the reference electrode and the working electrode constant irrespective of the cell condition i.e. under potentiostatic control; or
ii) maintain a constant current irrespective of the cell potential i.e. under galvanostatic control.

Therefore three different kinds of ministats were used depending on the power output required. Power up to 1.2 amp/28 volts: a Thompson's precision potentiostat was used; power up to 12 amps/18 volts: the E series of Thompson ministat was used and finally for experiments requiring up to 30 amps/20 volts the Chemical Electronics 20V/50A potentiostat was used.

Conversion of a ministat from a potentiostat to a galvanostat was straightforward. This was achieved by replacing the reference electrode with a resistor of say 1 ohm across the reference electrode terminal and the working electrode terminal. Here the working electrode terminal is taken from the reference electrode. This arrangement causes the ministat to maintain the potential across the resistor constant and since the resistance of the resistor is constant, hence a constant current flows through the circuit.

7.1.7 Monitoring Units
The monitoring equipment was as follows:

i) several digital voltmeters (DVM) were used to measure voltage and current up to 10 amps
ii) ammeter used for currents of greater 10 amps
iii) chart recorder to plot polarization curves
iv) tachometer to monitor the rotational speed of the working electrode
v) sweep unit used to increase the potential of the cell at a constant rate for polarization purposes.

A typical arrangement of the apparatus is shown in Plate 3.
7.1.8 Electrochemical Solutions
In all the experiments the same basic electrochemical solution was used. This solution consisted of copper sulphate CuSO$_4$.5H$_2$O and sulphuric acid H$_2$SO$_4$. However the concentrations of both the constituents were altered in order to see the effect of copper ions and the conductivity of the solution on the experiments.

7.2 EXPERIMENTAL TECHNIQUES

7.2.1 Kinematic Viscosity
The kinematic viscosity is defined as the dynamic viscosity divided by the density of the liquid. The dynamic viscosity in turn is defined as the shear stress divided by the rate of shear for steady flow of the liquid.

The kinematic viscosity changes from one solution to another and is highly dependable on the temperature. Therefore in order to calculate the Reynolds number for different concentrations of copper sulphate, it was necessary to obtain the kinematic viscosity of each solution at a particular temperature.

7.2.2 Determination of the Kinematic Viscosity of Copper Sulphate Solution
For this purpose a U-tube viscometer size A was used, Figure 24. The appropriate acid copper solution was charged in the dry, clean viscometer until the bottom of the meniscus reached the mark G. Next the tube was mounted and immersed in a water bath which was maintained at a specific temperature at all times. After about 30 minutes of settling time by applying suction, the liquid level was brought up passing the mark E. Suction was released and the flow time taken for the bottom of the meniscus to pass from the top of mark E to the top edge of mark F. The measurement was repeated several times until two successive flow times agreed within 0.2%. The experiment was carried out for 0.014M Cu, 0.07M Cu and 0.1M Cu solutions. This procedure was also repeated for distilled water at 21°C. The kinematic viscosity of distilled water at 21°C is given
as \(0.00979 \text{ mm}^2/\text{sec}\). Therefore in order to obtain the kinematic viscosity of a solution \(X\) the following formula was used:

\[
\nu_x = \frac{t_x}{t_w} \times 0.00979 \text{ at } 21^\circ C
\]

where \(t_x\) is the flow time of solution \(x\) and \(t_w\) is the flow time for water which was found to be 516 sec. The results obtained are tabulated below:

<table>
<thead>
<tr>
<th>Solution</th>
<th>(t_x) sec</th>
<th>(t_x) sec</th>
<th>(t_x) sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.01\text{M Cu}^{1/2}) (\text{H}_2\text{SO}_4)</td>
<td>538.4</td>
<td>540.7</td>
<td>544.0</td>
</tr>
<tr>
<td>(0.07\text{M Cu}^{1/2}) (\text{H}_2\text{SO}_4)</td>
<td>543.1</td>
<td>546.8</td>
<td>544.3</td>
</tr>
<tr>
<td>(0.1\text{M Cu}^{1/2}) (\text{H}_2\text{SO}_4)</td>
<td>544.0</td>
<td>544.9</td>
<td>543.7</td>
</tr>
<tr>
<td>(0.01\text{M Cu}^{1/2}) (\text{H}_2\text{SO}_4)</td>
<td>538.5</td>
<td>540.0</td>
<td>541.5</td>
</tr>
<tr>
<td>(0.01\text{M Cu}^{1/2}) (\text{H}_2\text{SO}_4)</td>
<td>538.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mean Value G for each solution is given as follows:

- \(0.01\text{M Cu}^{1/2}\) \(\text{H}_2\text{SO}_4\): 538.4 mm\(^2\)/s
- \(0.07\text{M Cu}^{1/2}\) \(\text{H}_2\text{SO}_4\): 540.7 mm\(^2\)/s
- \(0.1\text{M Cu}^{1/2}\) \(\text{H}_2\text{SO}_4\): 544.0 mm\(^2\)/s

* The density of water at \(21^\circ C\) is taken as 1 g/ml (0.998 g/ml).

7.2.3 Individual Electrode Method

For this method, the concentric rotating electrode was used. The cathode consisted of seven independent electrodes along the wall of the cell. A thin wire was soldered on to the back of each electrode. The wires were plugged into a resistor box. The resistor box consisted of seven resistors, each of a value of 1 ohm. The resistors were connected to one end of the electrodes and to the working terminal of a potentiostat at the other end. By means of a switch, it was possible to measure the voltage drop across any of the resistors with a voltmeter without affecting the rest of the circuit. Using Ohm's Law \(V = IR\), the current through each electrode was found owing to the high conductivity of the electrolyte and the
very low resistance of the rest of the circuit. The circuit is shown in Figure 25.

In this experiment the anode was set to rotate at different rotational rates and various currents were passed through the circuit and the voltage drop across each resistor was measured.

7.2.4 Blocking Methods

To determine the secondary current distribution in CRC, the potential between the strip and cathode was kept at zero by adjusting the variable resistance and the current was determined from the milliammeter. This current supplied by the cell was the amount required to maintain equal potential on the strip and the cathode plate and was therefore a measure of C.D. on the strip. By moving the copper strip along the cathode and adjusting the variable resistance to give zero potential at that point, the current at that point could be determined, Figure 26.

In order to maintain constant total current a galvanostat was used and the experiment was repeated at different total current and anode rotational rates.

7.2.5 Travelling Reference Electrode Method (TRE)

A Luggin tube was mounted on an arm of a helical screw thread drive which was driven by a motor. The Luggin tube was connected to a reference electrode (mercury/mercury sulphate). This apparatus was set up in such a way that the Luggin tube could travel at different speeds along and close to the Rotating Cylinder Electrode which enabled monitoring of the surface potential of the RCE over its length, Figure 27.

In this section the Rotating Hull Cell (RHC) was used in which the RCE was made of stainless steel and used as a cathode. The solution used consisted of 0.014M CuSO₄ and 0.5M H₂SO₄. A solution with lower conductivity was used in order to reduce the throwing power and therefore create a better Hull cell effect. In this method a
constant total current was supplied by a galvanostat where the cathode was rotated at a pre-set speed. By means of the TRE, the potential difference between the reference electrode and working electrode was noted.

7.2.6 General Polarization Curves

Polarization curves were obtained by the following method:

i) with the help of a reference electrode and a potentiostat the rest potential of the solution was found. The equilibrium state may be established after several minutes;

ii) the potentiostat was set at the rest potential and the circuit is closed. At this stage there was no net current flow;

iii) by means of a sweep unit, a constant rate of voltage was applied across the electrodes. Hence a net current flowed between the working electrode and the auxiliary electrode. The rate of increase of voltage was generally between 1 to 10 mV/sec depending on the nature of the experiment;

iv) a chart recorder was connected across a 1Ω resistor which in turn was connected in series with the auxiliary electrode. The chart recorder recorded the voltage drop across the resistor. Using Ohm's Law (V = IR) this voltage drop was related to the current flow. The horizontal axis of the chart recorder denotes the current and the vertical axis denotes time. Noting the feed rate of the chart paper and the sweep rate, the time axis can be converted into voltage (overpotential);

v) the overpotential was increased until the hydrogen evolution reaction (HER) was commenced.

The significance of the polarization curves is that, they show the relationship between the total current (hence C.D) and the
overpotential. From this the limiting current \( I_L \) can be found. There are several definitions for the limiting current\(^{46}\). Figure 28 shows a typical polarization curve, and \( I_L \) is described in the following manner:

1. \( I_L = \frac{I_1 - I_2}{2} \)

2. \( I_L \) is where \( \frac{dI}{dE} \) is a minimum

3. \( I_L \) is where \( E_L \) is set potentiostatically on the basis of \( E_L = \frac{E_1 + E_2}{2} \).

The sweep rate is dependent on the type of experiment carried out. The chosen rate must be fast enough not to allow the electrode surface to roughen yet slow enough to be able to see any rapid changes in the current behaviour.

7.2.7 Polarization Curves for the Rotating Cones

In the previous section, the general method of obtaining polarization curves was outlined. That method is useful for electrodes such as RDE and RCE where the surface of the electrode has a uniform potential. However for the rotating cone, greater attention needs to be given to the reference electrode on two counts:

1. The RE (the luggin probe) needs to be as near as possible to the WE, as there may have been some variation in the overpotential alone the cone.

2. Due to hydrodynamic considerations, the luggin probe must be as slim as possible in order to keep its effect on the flow pattern, which is created by the rotating cone, to a minimum.
The procedure of obtaining polarization curves was basically as follows: first the RE was placed as near to the edge of the cone as possible. The rest of the procedure is described in the previous section. For each curve obtained, a different rotation rate was used. However, after each experiment the cone was removed from the solution, cleaned in 50% nitric acid and rinsed. This ensured that each test had the same starting point.

Next, the luggin probe was moved up in increments of 1 cm, and the above procedure was repeated. This procedure was carried out for both the inverted and upright cones. Figure 29 shows the layout of the apparatus for the above work.

7.2.8 Constant Voltage Method

A typical solution used consisted of 0.014M CuSO₄ and 0.5M H₂SO₄. A reference electrode was connected to a luggin tube and it was placed half way and along the working electrode at an approximate distance of 4 mm. The RE consisted of mercurous sulphate with saturated potassium sulphate. The rest potential was noted at 0.42V and the limiting region between 0.8 and 0.5 overpotential.

The potentiostat was set so that the potential between RE and WE was at 0.9V, this ensured that the experiments were carried out under limiting current region. Next the electrode was rotated at different rotation rates and at each rotation rate the total current was measured. Before increasing the rotation rate, the working electrode was removed and thoroughly cleaned. This ensured that no roughness was produced on the cone as the deposition increased. Also the fresh substrate was a reference point for each experiment.

The above procedure was carried out for the RCE, the inverted cone and the upright cone. In the two latter cases the copper concentration in the solution was increased from 0.014M, 0.07M and 0.1M with acid concentration of 1/2 molar.
7.2.9 Coulometric Measurement

A conventional method of determining the thickness of a deposit layer is to cut the specimen into segments, and measure the weight before and after electrodeposition. From the weight gain and the measured cross-sectional area, the thickness of the deposit can be estimated. Since this measurement is a destructive method, it was not a practical method to use for the conical electrode. An alternative method is the coulometric measurement. Basically after electrodeposition is carried out (copper in this case) five cell rings are placed along the slant height. A cell ring consists of a spongy ring with an inner diameter of 1.2 cm, about 5 mm thick with sticky bottom.

Each cell was filled with acid copper solution (the same as the electrolyte used to plate copper). The cone was connected to the positive terminal (AE) of a galvanostat and a small strip of stainless steel was immersed in the cell solution and connected to the working electrode terminal. Next a known current of several milliamperes was passed through the circuit. This resulted in depositing copper ions from the cone on to the working electrode. The time taken to remove all the copper from the cone was noted. Using Faraday's Law:

\[
\frac{w}{It} = \frac{A}{nF}
\]

where \(n = 2, A = 63.5 \text{ for Cu, } F = 96500, w = \text{weight of copper.}

From

\[
w = v \rho = a s \rho
\]

where \(v = \text{volume, } \rho = \text{density } s = \text{thickness and } a = \text{area.}

Therefore

\[
w = \frac{\text{It}_e}{96500} = \text{It}_e = Q_e
\]

(1)
e for copper, valency 2 = 0.3294
\[ p = 8933 \text{ kg m}^{-3} = 8.933 \times 10^{-3} \text{ g mm}^{-3} \]
a = cell area = \( \pi r^2 = \pi (6)^2 = 113 \text{ mm}^2 \)

Hence the thickness of copper is given by

\[ s = \frac{w}{\rho a} \]

so

\[ w = 1.01s \quad (2) \]

From 1 and 2:

\[ Q_e = 1.01s \]

\[ s = \frac{0.3294 \times 10}{1.01} Q \]

\[ s = 0.326 \times 10^{-4} q \text{ mm} \]

where \( q = \frac{It}{a} \)
or

\[ s = 0.0326q \mu m \]

Therefore by knowing \( q \), the thickness \( s \) is obtained in \( \mu m \).

In order to establish the time taken to remove all the copper from the cone a reference electrode was placed in the cell with a chart recorder connected between the reference electrode and the stainless steel cone. Since the rest potential between the copper and stainless steel was quite different, when all the copper was removed from the cone the voltage between the reference electrode and the cone changes which denotes the end of the test. This method was far more reliable than depending on the visual changes of the surface.

7.2.10 Scanning Electron Microscopy (SEM)
The SEM is a device which produces images of surfaces at magnifications of up to 50,000 times with a resolution of down to 100 Å. Basically an electron beam is accelerated and scanned across the specimen surface. A picture of the specimen is built up on a
cathode ray tube as a result of the reflectance and absorption of electrons on the surface of the specimen.

The surface needs to be conductive, therefore for non-conductive materials the specimen must be coated with a thin layer of usually gold or carbon. As this conductive layer is of an order of several hundreds of angstroms thick, it does not change the morphology of the specimen.

Most of the information given by the SEM is topographical. No information on composition can be obtained by this system. With the aid of a camera a picture of the surface structure can be obtained and analysed later.

In order to examine the morphology of the deposits on the RCE in the concentric cell, a copper sheet was made into a sleeve to fit the cylinder. The edges of the sleeve were electron beam welded in order to maintain a smooth surface finish. Next copper was deposited on the sleeve at a total current of 3 amps (43 A/dm²) for 5 minutes whilst the RCE was rotating at a rate of 400 rpm. The electrolyte consisted of 0.014M CuSO₄ + 0.5M H₂SO₄. After a thorough rinse the sleeve was removed and cut into sections, ready for SEM examination.

SEM examination was also carried out for the inverted cone. In this case it was not possible to obtain a sleeve for the cone. Instead the cone was polished with metal polish and a smooth cloth until a mirror like image was obtained. The cone was electroplated at 400 rpm for 3 minutes with a current density of 6 A/dm², in 0.7M CuSO₄ + 0.5M H₂SO₄. Next, the cone was removed, carefully rinsed and the deposit film was peeled off the cone surface. Finally small sections of the film were cut out and examined under SEM.

Also a few photographs were taken from the inverted and upright cones showing the deposition of copper on them. The upright cone was in the following condition: \( i = 4 \text{ A/dm}^2 \), solution consisting of 0.014M CuSO₄ + 0.5 M H₂SO₄, and rotation rates of 0, 10, 30, 50, 90,
150, 200, 250 and 400 rpm for 3 minutes. The inverted cone was used under similar conditions, but the current density was reduced to 1.3 $\text{A/dm}^2$ with rotation rates of 30, 50, 70, 150 and 200 rpm.

7.2.11 **Atomic Absorption Analysis**

Atomic absorption spectrometers (AAS) are used to determine:

1. impurities in plating solution and in electrodeposits, particularly gold electrodeposition
2. the concentration of known elements in solutions.

In AAS the sample must be converted into atomic vapour. This atomic vapour is formed by spreading the required solution onto a hot flame. The atoms will be excited to higher energy levels and when they return to lower energy levels, they generate light. The primary source of radiation is the hollow cathode lamp consisting of a cathode of the material of the element to be determined with tungsten cathode. Light of an equivalent wavelength which is generated from the hollow cathode tube can absorb this light which is emitted by the atomic cloud. A photodetector will measure the degree of absorption.

For the AAS studies the rotating Hull cell was used. The cathode was rotated at various designated speeds, whilst being plated with copper for a given time and current. Next copper was removed from the cathode by immersing the cylinder in 50% nitric acid, in increments of 1 cm. This resulted in seven solutions with various amounts of copper. By comparing the AAS count from the standard solution (4 mg/l copper) with that of unknown solution, the copper concentration in the unknown solution was estimated.

7.2.12 **X-Ray Fluorescence Analysis (XRF)**

Prior to any thickness measurement by XRF, the following steps must be taken:
1. The substrate (the uncoated metal) is placed under the X-ray so that the background emission is noted. This reading will be used by the computer for any correction needed during thickness measurement;

2. A standard, consisting of the coated metal with a known thickness on a similar base as the cathode is measured by the XRF for calibration purposes.

Basically, after the electrodeposition has taken place, the cathode is rinsed, dried and place on an adjustable table in the X-ray chamber. By moving the table up or down the object is focused which can be seen through a television monitor. Next the X-ray is emitted for several seconds (depending on the degree of accuracy needed). The measured thickness is shown on a secondary monitor. Furthermore by moving the table sideways a measurement of different sections of the specimen can be made and an average reading noted.

The computer can construct a profile from the thickness measurement and produce some statistics.

The accuracy of the XRF type Fisherscope XM 1500 is down to two decimal points of a micron. However the longer the exposure of the specimen to the X-ray the greater the accuracy of the thickness measurement. When the object is in focus the X-ray beam covers surface of about 0.2 mm².

The following tests were carried out:
<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>Plating Condition</th>
<th>Rotation Rate, rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IA</td>
<td>t_{min}</td>
</tr>
<tr>
<td>Indirect cathode</td>
<td>0.5 5</td>
<td>300, 400 PS</td>
</tr>
<tr>
<td></td>
<td>1.0 3.6</td>
<td>0, 200, 300, 400, 500</td>
</tr>
<tr>
<td>RHC</td>
<td>1.0 14</td>
<td>0, 50, 100, 200</td>
</tr>
<tr>
<td></td>
<td>3.0 3</td>
<td>50, 200, 300, 400 PS</td>
</tr>
<tr>
<td>Upright cone</td>
<td>2.0 10</td>
<td>50, 100, 200, 250</td>
</tr>
<tr>
<td></td>
<td>5.0 10</td>
<td>0, 50, 100</td>
</tr>
<tr>
<td></td>
<td>5.0 5</td>
<td>50, 100, 150, 200 PS*</td>
</tr>
<tr>
<td>Inverted parallel</td>
<td>2.0 15</td>
<td>0, 50, 100</td>
</tr>
<tr>
<td>cone</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3A 3</td>
<td>100, 200, 300</td>
</tr>
<tr>
<td>Inverted cone</td>
<td>0.5 30</td>
<td>50, 100, 300</td>
</tr>
<tr>
<td></td>
<td>1 20</td>
<td>100, 150, 200, 250</td>
</tr>
<tr>
<td></td>
<td>1.5 20</td>
<td>100, 150, 200, 250, 300, 400</td>
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<td>2 15</td>
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</tr>
<tr>
<td></td>
<td>3 6</td>
<td>0, 50, 100, 200, 300</td>
</tr>
<tr>
<td></td>
<td>5 10</td>
<td>50, 100, 200, 300 PS</td>
</tr>
<tr>
<td>Hull cell</td>
<td>0.5 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 6</td>
<td></td>
</tr>
</tbody>
</table>

* PS = prop-i eto1 solution
CHAPTER 8
RESULTS

The results will be presented according to the separate cell designs investigated and are in the following order:

8.1 The Hull cell
8.2 The rotating anode (or inclined cathode)
8.3 The rotating Hull cell
8.4 The inverted cone
8.5 The upright cone
8.6 Micrographs.

8.1 THE HULL CELL

Figures 37 and 38 show the data obtained by the coulometric method for the Hull cell. The Hull cell panel was plated for 3 minutes with plating current of 1 amp and again for 6 minutes with plating current of 0.5 amps. The plating solution consisted of 0.014M CuSO₄ and 0.5M H₂SO₄. The gradient at 0.5A gives slightly lower value than that at 1 amp. Figures 39 and 40 show the relationship between the coating thickness and the slant height obtained from the XRF method. The slant height being the distance from the edge of the panel starting at the high current density area. It is clear that the logarithmic relationship is a much better fit than the linear one.

Each graph consists of two sets of data which represent different plating conditions: one with a plating time of 6 minutes and a total current of 0.5A, the other with a plating time of 3 minutes and a total current of 1A.

Finally Figures 41 and 42 show the theoretical results plotted using the Hull equation originally derived for the 267 ml cell.
8.2 THE ROTATING ANODE

Figures 43 and 44 show the relationship between current density distribution and the distance between the anode and working electrode for which a constant current of 60 mA was used. The data were gathered by using seven independent electrodes, rather than a long cathode. This graph indicates that as the distance between the individual electrodes increases with respect to the rotating anode, the current density decreases. However, the effect of agitation is not clear. There is a significant scattering of data at a distance of 65 mm.

Figures 45 and 46 show the same relationship as described above. However the technique used here was different. The current distribution was determined by the blocking method, whilst the anode was rotating at a predetermined speed (0, 500 and 1000 rpm). A plating current of 0.1A was used. Although the rotation increases the enhancement, nevertheless the role of the agitation is not clear. The data obtained for the rotation rate of 500 rpm are above that of the 1000 rpm rotation rate.

Figure 47 shows the results obtained from the inclined cathode cell where the plating time was 3.6 minutes and the plating current of 1A (5.5 A/dm²). It is clear that as the distance between the working electrode and the auxiliary electrode increases, the thickness of the copper deposits on the working electrode decreases. The slopes of 200, 300, 400 and 500 rpm are roughly equal whereas that of 0 rpm is much less. Also the data for 0 rpm is well scattered in comparison to the other data obtained. There is an enhancement effect when the rotation rate is increased to 400 rpm. Above this agitation rate the effect of rotation on enhancement is not clear. There is also an edge effect apparent at 1 cm slant height.
Figure 49 is obtained by using the proprietary solution with a constant current of 0.5A (2.8A/dm²) for 5 minutes. The data obtained for 300 and 400 rpm show a wide scattering and therefore it is difficult to come to any concise conclusions.

8.3 THE ROTATING HULL CELL

Figure 49 shows the relationship between the amount of copper deposited on the RCE and its distance from the anode detected by the AAS. Due to shortage of data and the wide spread of data, it is difficult to come to any solid conclusions. The gradient of the 200 rpm indicate that the copper thickness decreases with increase in distance. If the last point on the 400 rpm is disregarded the same results as above can be obtained. Finally at 0 rpm when the last data is also disregarded, the result shows that the copper content on the RCE increases with distance.

Figure 50 shows the current distribution on the RCE where the total current was 0.5 Amps (0.72 A/dm²). The graph shows that, as rotation rate is increased, the variation in current distribution on the cathode increases. The 200 and 400 rpm have similar slopes whereas the 600 rpm has lesser gradient and 1000 rpm has the greatest gradient fall. In all cases the data fits the lines very well. Figure 51 is a repeat of the above experiment. Here the total current was maintained at 1 Amp (1.4 A/dm²) and rotation rates of 400, 600 and 1000 rpm were used. At 400 rpm the data obtained in the first half is scattered, but at other speeds the data fits the lines well. This graph shows that as the rotation speed increases, the enhancement factor increases. All the lines have more or less equal gradient.

Figure 52 shows the mass transfer relationship for the RCE. The points lie on a straight line with a gradient of 0.64. This graph shows that as the rotation speed increases, so does the mass transfer.
Figure 53 shows again the mass transfer relationship for the RCE. The figure compares the data obtained from the top of the cylinder to those obtained at the bottom. The top section of the cylinder is further away from the anode. The gradient for the top slope is 0.54 and for the bottom line 0.58.

Figure 54 is obtained under similar conditions as above, however the limiting current is estimated from the polarization curves for the rotating Hull cell, the gradient for both top and bottom of the cathode is almost the same at a value of

Figure 55 shows the results obtained by the XRF method. The plating time was 14 minutes with a constant plating current of 1A (1.45 A/dm²). At 100 rpm the copper thickness decreases with increase in slant height whereas at 200 rpm the reverse is apparent.

Figure 56 is a repeat of the experiment described above with rotation range of 0, 50, 100 and 200 rpm. The slopes of 50 and 200 rpm are parallel to each other, but the scatter of data is much wider in the former case. The gradient of 50 rpm is much less than the other two rotation rates described above. Finally there is an opposite trend in the 100 rpm data, that is, an increase in coating thickness with increase in the slant height. There is also some edge effect apparent in all rotation rates.

Figure 57 is obtained by using the proprietary solution. Plating time was 3 minutes with constant current of 3 amps (4.3 A/dm²). The data obtained for 50 rpm is very scattered and indicates an increase in copper deposit with increase in slant height. The slopes of 200, 300 and 400 rpm show a decrease in copper with an increase in the slant height. If the last three points of these rotation rates are disregarded it will result in three parallel slopes for 200, 300 and 400 rpm.
DAMAGED TEXT IN ORIGINAL
8.4 THE INVERTED CONE

In the following experiments the relationship between slant height and measured coulomb level was under investigation, as a function of agitation rate.

Figure 58 shows the above relationship for agitation rates of 0, 30, 50, 100, 200 and 300 rpm where a total current of 1.75A was used for 3 minutes under galvanostatic control. The solution consisted of 0.014M copper sulphate and 0.5M sulphuric acid. The gradient of zero rpm is very low, whereas for the other agitation rates the gradient is much greater. The slopes of 30, 100 and 200 rpm are almost parallel to each other so are the slopes of 50 and 300 rpm, but with much greater gradient. The data presented shows that

i) increase in agitation rate increases the enhancement
ii) measured coulomb level, hence copper deposited, depends on the slant height i.e. increase in slant height results in a decrease in copper deposited.

Figure 59 shows a similar relationship as described above. Here the total current was increased from 1.75A to 3A. The data obtained for 0 rpm is very scattered, but at higher agitation rates this scatter is reduced. The gradient increases sharply above 100 rpm. Further, the overall amount of copper deposited is much greater than the previous graph. However this increase in enhancement is not as expected in Figure 60. Although in this case the total current is increased to 5A, the enhancement is reduced to a similar level as in Figure 58, where a total current of 1.75A was used. Nevertheless all the slopes at different rotation rates are more or less parallel to each other. The slope of 200 rpm is above 300 rpm which is unusual.

Figure 61 is again as a result of similar experiments that have been described above. Here the ion concentration of copper was increased from 0.014M to 0.07M and a total current of 3A was used. It may be assumed that the gradients of 0, 30, 50 and 100 rpm are equal but
much less than those of 200 and 300 rpm. Again the data from 200 rpm is greater than that of 300 rpm. When comparing this graph to those described above, it is clear that an increase in copper ions has resulted in a greater deposition.

Finally Figure 62 was obtained under similar conditions as described above. Here the total current was increased to 5A. This graph shows the slopes of zero and 200 rpm are parallel to each other, but at much less gradient than the slopes of 30, 50, 100 and 300 rpm which are also more or less parallel to each other.

In the following experiments the inverted cone was plated for a specific amount of time (3 minutes) and current, under galvanostatic control. The relationship between the rotation rate and the coulomb measured at specific slant heights was considered.

Figure 63 shows the relationship described above when a total current of 1.75A was used. The acid copper solution consisted of 0.014M copper and 0.5M sulphuric acid. The graph shows that any increase in rotation rate results in an increase in coulomb level measured irrespective of the slant height. However, at a given rotation rate any decrease in slant height increases the amount of copper deposited. It may be assumed that all the slopes obtained are parallel to each other.

Figure 64 was obtained under similar conditions as described earlier, but the total current was increased from 1.75A to 3A. This graph is similar to the previous one. Nevertheless there is a slight decrease in gradient but an overall increase in the measured coulumb.

Figure 65 is again similar to the above graph, although the total current was increased to 5 amps, but there is a marked decrease in the overall measured coulumb level and in the gradient when compared to Figure 63.
Figure 66 shows the above relationship for a plating current of 3A with a copper concentration of 0.07M. When comparing this Figure to Figure 56, it is evident that there is an increase in the overall measured coulomb level with a similar gradient. The data obtained from the slant height of 60 mm shows an inverse relationship between \( q \) and \( \text{rpm} \). This may be due to experimental error.

Figure 67 shows the same experimental work as for the previous section, but with a total current of 5A. Again the general pattern is repeated, that is any increase in rotation rate results in an increase in the measured coulombs; furthermore any increase in slant height results in a decrease in the copper content on that point.

Figure 68 shows the relationship between the copper content on the inverted cone at specific slant heights. This measurement was repeated for different rotation rates i.e. 0, 50, 100, 200 and 300 rpm. The plating current was 2A (1.33 A/dm\(^2\)) and its duration 15 minutes. The plating solution level which consisted of 0.014M copper sulphate and 0.5M sulphuric acid in the cell was much greater than the minimum amount required. Therefore the distance between the vertex of the cone and the bottom of the cell was about 5 cm.

The slopes of 50, 100 and 300 rpm are similar, that is the copper coating thickness on the cone decreases with increase in slant height. At 200 rpm it seems that the thickness of the copper is constant along the cone. At 0 rpm this indicates that the copper content increases with slant height. Figure 69 is a repeat of the above experiment.

Figure 70 shows similar results as above where the total current was increased to 3A but the plating time reduced to 6 minutes. Here the slopes of 50, 100, 200 and 300 were more or less parallel to each other. Again at 0 rpm this pattern is not applicable.
The effect of solution level may be apparent in Figure 71 where the plating condition was as described above, but the solution level was maintained at its minimum level so that the distance between the vertex of the cone and the bottom of the cell was no more than a couple of millimetres. Here the 100 and 300 rpms have equal decreasing gradient whereas at 200 rpm this trend is reversed. The slope of 400 rpm is much greater than the others.

Figure 72 shows the effect of hydrogen evolution reaction. It compares the data obtained at 50 rpm where the plating current was 2A and 1A for 15 minutes. The graph clearly shows that at higher current where vigorous HER takes place, the data is much more scattered. The graph also shows that at 100 rpm the copper deposited is more or less independent of slant height i.e. constant thickness over the whole surface.

Figure 73 is an extension to the above graph. The plating current was maintained at 1A for 20 minutes. Rotation rates of 100, 150, 200 and 250 rpm were used and in all cases it is apparent that the thickness of the copper coating decreases significantly with increase in the slant height, from 3.5 μm at 0.5 cm slant height to an average of 1.5 μm at 7 cm slant height. It is also apparent that rotation rate has not much effect on the enhancement.

Figure 74 shows the effect on plating when the plating time is increased to 30 minutes and the current reduced to 0.5A for rotation rates of 50, 100 and 300 rpm. Again similar to Figure 71 all slopes are parallel to each other and there is no apparent effect of rotation rate on coating thickness. At plating current of 1.5A for 20 minutes it seems that rotation rate has a marked effect on deposition as shown in Figure 75. The gradient increases as rotation rate increases from 100 to 400 rpm. It seems that the copper coating has a constant thickness at a slant height of about 3 cm irrespective of rotation rate. The graph also shows that the influence of the edge effect becomes more significant as rotation rate increases.
Figures 76 and 77 show the effect of slant height on coating thickness when a proprietary solution was used. The solution consisted of 75 ml/l CuSO₄ + 125 ml/l H₂SO₄ + additives. The plating time was 10 minutes with a current of 5A. Again the graphs show that the coating thickness is almost independent of rotation rate. It seems that this solution is very sensitive to the distance between the two electrodes, increase in slant height results in much lesser deposition of copper on the rotating cone. For example at a slant height of 7 cm the copper thickness is about 3 µm yet at a slant height of 1 cm the coating thickness has increased to about 7.5 µm.

Figure 78 shows again the relationship between copper thickness deposited and slant height. Unlike the previous experiments, where the plating current was kept constant, here the overpotential between the cathode (WE) and the reference electrode was maintained at 0.8 volts, irrespective of surface condition. The graph shows that up to 200 rpm, there is a constant coating thickness along the cone. However above 200 rpm, the thickness of the copper deposited does depend on its distance from the anode. Further, the graph shows the effect of agitation rate on enhancement. Under constant conditions, a thicker film of copper is produced when the rotation rate is increased. Above 200 rpm the edge effect is also more significant than at lower speeds.

The following graphs show the mass transfer behaviour for the inverted rotating cone. They show the relationship between the limiting current and the rotation rate. All the experiments were carried out in 0.014M copper sulphate and 0.5M sulphuric acid solution.

Figure 79 shows the above relationship when the reference electrode was placed at 31 mm slant height. The graph indicates that there are three distinct regions. The first region has a gradient of 0.49, the second region a gradient of 0.60, and finally the last region a
gradient of 1.17. The graphs show that any increase in rotation rate results in an increase in the limiting current.

Figure 80 shows the above relationship and it compares the effect of position of the reference electrode on the values of limiting current obtained. Any increase in the slant height i.e. increase in the distance between the RE and the auxiliary electrode, will reduce the limiting current. Again two regions are shown on the graph. The first region has a slope of 0.44 and the second an average gradient of 0.89.

Figure 81 is a repeat of the above experiment. The first region has a gradient of 0.43 and the second 0.96. However, the limiting current is greater at the slant height of 48 mm than at 10 mm.

Figure 82 shows the two regions with gradients of 0.46 and 0.79 respectively. Figure 83 gives an average gradient for region one of 0.46 and for region two of 0.79. Although the limiting currents of different slant heights have been found, they do not show any relationship between the limiting current and slant height. Figure 84 gives average gradients of 0.45 and 0.66 for the two regions where the slant heights were 1 mm and 55 mm.

Figures 85 and 86 show the limiting current distribution on the inverted rotating cone. The solution consisted of 0.014M copper sulphate and 0.5M sulphuric acid. These graphs represent the value of limiting current obtained at various slant heights at specific rotational rates. Figure 85 shows the rotation rates of 0, 20, 50, 80, 120 and 160 rpm. All the slopes are more or less parallel to each other. The average change of the limiting current is no more than 0.05 A/dm² over the whole surface. Figure 86 indicates that above 200 rpm any increase in rotation rate results in an increase in the gradient. However it must be noted that the data obtained for 400 rpm is well scattered and therefore less reliable.
Another important implication of agitation is the enhancement factor, both Figures 85 and 86 show that any increase in rotation rate results in an overall enhancement.

The flow pattern of cones was discussed in Section 3.6 in some detail. In this section, the effect of peripheral speed of the cone was of prime importance. Since the radius of the cone increases linearly, so does the velocity at the periphery. Therefore at the apex where the radius of the cone is almost zero, there is no peripheral speed, yet at zero slant height (at the edge), the cone experiences the greatest peripheral speed. Although the electrolyte is driven from the apex towards the edge due to this imbalance of peripheral speed, it was important to see whether there is any peripheral plating at the edges due to speed differentiation. For this purpose it was important to maintain a constant distance between the cone and the anode. The inverted cone was chosen to investigate this effect.

Figure 87 shows the results obtained when a sheet of copper was formed into a cone and used as anode where the inverted cone placed in the middle. It is difficult to explain these results. When there is no rotation, the copper deposited has uniform thickness over half of the cone, towards the apex the copper deposits become a function of slant height. It may be argued that near the apex there is an edge effect i.e. a concentration of current density which results in a greater plating. However at 50 rpm the data obtained show exactly opposite results.

In Figure 88 the rotating Hull cell's anode was used in order to maintain a constant distance between the cone and the anode. Since the width of the anode (4 cm) is much less than the length of the cone (7 cm) this results in an increase in the distances between the two electrodes at either end of the cone. Therefore any data obtained above the slant height of about 6 cm and below 2 cm should be disregarded.
The variation of the thickness of the copper deposit with slant height is not very much, about 0.2 m over a distance of 4 cm. The most accurate results were obtained when both ends of the cone (above 6 cm and below 2 cm slant height) were lacked so that the areas which did not have an equal distance from the anode were not influencing the experiment in any way. This experiment was carried out at a total current of 3A (7.5 A/dm²) for 3 minutes. The results are shown in Figure 89. If the first and last two points are disregarded then the overall thickness of the copper deposit remains almost constant over the cone. The figure also shows that as the rotation rate increases from 100 to 300 rpm then the thickness of the film decreases slightly.

8.5 THE UPRIGHT CONE

The results obtained here are an extension to those described in the previous section and under similar conditions. The following figures show the relationship between coulomb level i.e. copper deposited and slant height at different rotation rates.

Figure 90 shows that for rotation rates less than 100 rpm, there is no effect on the rate of deposition of the copper in the upright cone. Here a total current of 3A was used. It is clear that any increase in slant height results in a decrease in measured coulombs.

Figure 91 is obtained by increasing the current to 5A. Again the effect of rotation rate is only apparent after it is increased above 100 rpm. Any increase in rotation rate above 100 rpm seems to increase the gradient.

Figure 92 shows the effect of ion concentration. In this case the concentration of copper ions was increased from 0.014M to 0.07M. This resulted in a greater deposition of copper in comparison to Figure 90. Also the gradient has increased but the effect of rotation rate is not as clear as before. The total current used was 3A.
Finally Figure 93 is obtained by increasing the current to 5A. The data obtained here is much more scattered, to such an extent where it is difficult to establish any pattern. Although an increase in rotation rate results in a greater deposition of copper, the effect of slant height and its slope is not clear.

The following sets of data were obtained by considering the effect of rotation rate on measured coulombs for the cathodic deposition of copper. Figure 94 shows the above relationship obtained under the following conditions: total current 3A, plating time 3 minutes, 0.014M Cu$^{2+}$ as sulphate. It is clear that any increase in rotation rate results in an increase in coulombs measured. It may be assumed that all the slopes are more or less parallel. Further, the graph shows that the measured coulombs are also dependent on the slant height position that is, nearer to the anode, the greater the deposition. It is also interesting to note that values of q obtained at 30 rpm, are greater than those at 50 and 100 rpm irrespective of the slant height. This may be due to the edge effect.

Figure 95 shows a similar relationship as described above. The total current was increased from 3A to 5A in this case. There is a slight increase in coulombs measured at slant heights of 11 and 29 mm when compared with the previous figure, yet values obtained at 35 and 59 mm show no change. There is also much less evidence of the edge effect.

Figure 96 represents results obtained under similar conditions as those obtained in Figure 94, but here the concentration of copper ions was increased from 0.014M to 0.07M. This change has a significant effect; firstly the number of coulombs measured has increased by over 200% and secondly the slopes for 12, 25 and 37 mm slant height have decreased.
Figure 97 is a repeat of the above experiment where the total current was increased from 3 to 5A. Comparing this figure to the previous one it is clear that the gradients have increased; furthermore they are parallel to each other. As expected the values of coulombs measured are greater as well.

The following graphs show the relationship between the limiting current and the rotational rate of the upright rotating cone. Furthermore they also show the effect of slant height on the reference electrode. The plating solution consisted of 0.014M copper sulphate and 0.5M sulphuric acid.

Figure 98 shows the above relationship when the reference electrode was positioned at 38 mm slant height and only about 2 mm away from the cone. There are two distinctive slopes present on the graph. The lower region has a gradient of 0.39 and the upper one 1.05.

Figure 99 shows the different data obtained by changing the position of the reference electrode. The reference electrode positions were at 6, 23, 40 and 59 mm slant height. As above the average slope for the low region is 0.45 and the upper region has an average slope of 0.76.

Figure 100 exhibits gradients of 0.68 and 0.96 for the lower and upper regions respectively. This graph shows that the limiting currents obtained at a slant height of 60 mm are greater than those obtained at 7 mm slant height.

Finally Figure 101 is a repeat of the above experiment. The average slopes for the lower and upper regions are 0.41 and 0.96 respectively. Here the limiting current values at slant height 17 mm are greater than those of 57 mm slant height in the lower region. At the upper region the reverse is true.
Figures 102-104 show the relationship between the limiting current and slant height for the upright cone. The solution consisted of 0.014M copper sulphate and 0.5M sulphuric acid. It seems that the limiting current is constant all over the cone, at zero and 20 rpm. However at higher rotation rates the values obtained for the limiting current show that they increase with increase in slant height, i.e. the gradient increases. The gradients obtained for 120, 160, 200, 250 and 300 rpm are more or less constant. The other fact that emerges from these data is that an increase in agitation increases the enhancement.

Figure 105 shows the relationship between coating thickness and the slant height. The plating current used was 2A for 10 minutes and the solution consisted of 0.014M CuSO$_4$ + 0.5M H$_2$SO$_4$. The rotation rates were 50, 100, 200 and 250 rpm. If the entry length or edge effects are ignored for the time being, the graph shows that coating thickness remains constant along the cone for rotation rates of up to 100 rpm. Above this the copper coating reduces in thickness with increase in slant height. At 250 rpm the edge effect has a marked effect on the thickness especially at slant heights less than 1 cm and greater than 5.5 cm.

When the above experiment was repeated at a lower plating current of 1A for 15 minutes, quite a different set of results were obtained. These results are shown in Figure 106 where the rotation rates of 50, 100 and 150 rpm were used. In all three cases, the thickness of the copper coating is increased by over 100% from a slant height of 6 cm to 0.5 cm. However the effect of rotation on enhancement is not clear, nevertheless all slopes have equal gradient.

Figure 107 was obtained under similar conditions as described above. However instead of the normal simple copper sulphate solution a proprietary solution was used (75 g/l CuSO$_4$ + 125 ml/l H$_2$SO$_4$ + additives). The experiment was carried out for 10 minutes at a plating current of 5A (4.5 A/dm$^2$). Zero rpm shows that the coating thickness is almost constant at about 5 $\mu$m over the whole surface.
At 50 rpm the coating thickness increases from 2 μm at a slant height of 6 cm to 8 μm at a slant height of 0.5 cm. At 100 rpm, the coating thickness at 6 cm is about 5 μm. The gradient of this slope is much less than that of 50 rpm. Also there is no edge effect apparent for any of these agitation rates.

Figure 108 shows a repeat of the above experiment but the plating time was reduced from 10 minutes to 5 minutes. Here the rate of decrease in coating thickness with increase in the slant height is almost constant for all the rotation rates used i.e. 50, 100, 150 and 200 rpm. In contrast to the previous graph there is an edge effect near the apex i.e. slant height of 6 cm and over. This effect seem to increase with increase in rotation rate.

Figure 109 is obtained from experiments that were carried out under potentiostatic control where the overpotential between the upright cone and the reference electrode was kept constant at 0.8 volts. The plating time was 10 minutes and the rotation rates used were 50, 100, 150 and 200 rpm. It is apparent that under such plating control the effect of agitation is in the enhancement. The average thickness of the coating at 50 rpm is about 0.55 μm where the current used was 0.65A. Increasing the rotation rate to 200 rpm resulted in an average coating thickness of 0.95 μm with a plating current of 0.98A. The thickness of the coating is almost constant and independent of slant height, however near the apex there is an edge effect apparent.

Figure 110 shows the relationship between the total current and the rotation rate for the inverted cone under potentiostatic control. The overpotential between the working electrode and the reference electrode were kept constant at 1.1V. At specific rotation rates the plating current was noted. This graph shows that by increasing the ion concentration a greater current is obtained at the constant overpotential for a given rotation rate. For instance at 100 rpm the total currents for 0.014M, 0.05M and 0.1M copper concentration are 0.6, 1.4 and 2.3 A/dm² respectively.
Figure 111 shows the effect of overpotential on the plating current. In this case where the copper concentration was 0.014M it shows that by increasing the overpotential by a fraction (0.9 to 1.1) increases the plating current by as much as 100%. It is clear from this figure that the rate of increase of the current decreases with increase in the rotation rate. For instance, in the case of $V_{\text{ref}} = 0.9$ the current has not increased significantly above 100 rpm.

Figure 112 is the corresponding result obtained for the upright cone. Similarly Figure 113 shows the effect of ion concentration on the upright cone. The results are very similar to those discussed for the inverted cone.

Before examining the results obtained for the upright cone, it is important to note that due to the size of the cone, it was not possible to fit the cone into the XRF chamber. Therefore sheets of stainless steel were cut and placed over the upright cone. After each experiment the sheet was removed and examined by the XRF. The main shortcoming of this technique was that the two ends of the sheet did not flush. This resulted in some extra drag in the solution.

Figure 114 shows the mass transfer relationship for the inverted and upright rotating cones. $K_L/K'_L$ is the enhancement effect which is defined as the ratio of the limiting current obtained by rotation and the unrotated limiting current. This is plotted against $\omega \sin \alpha / v$. The graph shows that at lower $\omega \sin \alpha / v$ values the enhancement of the inverted cone is greater than that of the upright cone. However the two curves converge at higher values of $\omega \sin \alpha / v$.

Figure 115 is an extension to the above graph. Here the relationship between rotation rate of the inverted cone and the diffusion layer thickness is shown. The values of the diffusion layer thickness are calculated from $i_L = nFCD / \delta$. As expected, the
diffusion layer thickness decreases rapidly with increase in the agitation rate. Figure 116 shows the above relationship for the upright cone.

8.6 RESULTS OF SEM

Plate 7 shows the micrographs obtained with SEM for the concentric rotating cell (Rotating Hull Cell). (i) and (ii) show the morphology at 7 and 5 cm from the bottom respectively at magnifications of 1.2K and 6K; (iii) and (iv) are at magnifications of 1 and 5K at a distance of 3 and 1 cm from the bottom of the cylinder where the current density was higher. The effect of current density is clearly shown in these micrographs. As the distance between anode and cathode is reduced, there is an increase in the current density, as a result the surface becomes rougher. (iii) and (iv) show dendrites formed on the surface.

Plate 8 shows the morphology of the inverted cone at 1 and 5K at a distance of 0.7, 4.2 and 6.4 cm from the edge. Again the closer to the edge, the higher the current density. The effect of current density is shown in this series of micrographs.

Plate 9 shows the copper deposits on the upright cone, where it is deposited at 4 A/dm² for 3 minutes. This series of photographs show the effect of rotation on the deposit. Although it is not very easy to distinguish between different bands of deposits on the cone, nevertheless the photographs show a gradual change in the colour of the deposit.

Plate 10 is obtained in a similar manner to the above procedure where the inverted cone was plated at 1.5 A/dm² for 3 minutes. Again the change in colour of the copper deposits indicates the different types of deposition on the cone.

In all the above colour photographs the lighting of the room, film exposure time and speed of the camera were kept constant.
9.1 INTRODUCTION

In the electroplating industry it is important to know the current density range at which metal can be deposited within a specific requirement. These requirements, which are set by the customer, may be: the minimum and maximum thickness, hardness of the deposit, porosity etc. One of the most important criteria which is required is the brightness of the coating. Even though further coatings may be needed, such as gold on nickel, the brightness of the coating usually indicates a satisfactory deposit i.e. low porosity of certain hard metals. Unfortunately the current density at which bright deposits are deposited has a narrow range and therefore it is important to be aware of the minimum and maximum current density range. Therefore a Hull cell is used to estimate these optimum current densities in only one or two tests since the current density along the cathode varies considerably. With one glance the required current density can be estimated from the deposits. It is important to note that the Hull cell test is a static test, whereas the actual electroplating may be barrel, reel to reel, jet etc where the conditions at which plating are performed is quite different. Often some sort of agitation is used in the Hull cell in order to provide a more realistic test similar to that of shopfloor tests, but there are no precise rules at which the agitation is achieved. The agitation rate in the Hull cell depends on experience of the operator and the rule-of-thumb.

It was thought that this problem may be overcome by designing a conical cell which provides a wide range of current densities along its slant height. Furthermore by rotating the cone along its axis a well defined agitation can be obtained at any given rotation rate. This idea has been the basis of this research work and thesis. It may be noted briefly that other attempts have been made to institute
a "dynamic" Hull cell, by means of air agitation, pumped flow etc but none have proved to be generally acceptable to the industry.

9.2 THE LIMITING CURRENT

The performance of cells can be estimated in many ways but regarding both mass transfer and deposit quality under rapid rates of deposition the limiting current approach has been used because it indicates the maximum rate of effective electrodeposition and also responds systematically to the use of differing means of agitation or stirring in the solution.

The limiting current is estimated from the polarization curve and has been discussed in Chapter 7.

Figure 30 shows the polarization curve obtained for the static Hull cell. The three curves correspond to the position of the reference electrode and its distance from the anode. These graphs show that, as the potential was increased there was no current flow until the potential reached 0.75V. At this voltage a slight increase in the voltage resulted in a surge in the current. This potential is known as the discharge potential. The delay in the current flow is due to activation polarization. Referring back to Figure 30, it is clear that any further increase in the voltage does not result in an increase in the current up to a voltage of about 1V. This limit in the magnitude of the current is due to the limitation of metal ion in the catholyte. The ions in the diffusion layer are used up as soon as they arrive from the bulk of the solution. In other words the ion concentration in the diffusion layer is near zero. Thus the current does not increase any further. However it is possible to increase the ion migration from the bulk to the diffusion layer i.e. by reducing the diffusion layer. This is achieved in two ways:

1. Increase in agitation which reduces the diffusion layer as shown in Figures 31-33. Figures 31 and 32 show that although the reference electrode was kept constant relative to the electrodes
a greater current was registered as the rotation rate of the cathode was increased. Figure 33 shows that the limiting current also depends on the position of the reference electrode relative to the anode and the type of cone used. This depends on the RE increasing with increase in the rotation rate. For the upright cone, $i_L$ increases with increase in the slant height but the reverse is true for the inverted cone.

2. Increase in metal ion concentration in the electrolyte. Since more metal ions are present in the solution, more charge can be transferred from the catholyte to the cathode. This effect is shown in Figures 34 and 35.

Figure 36 shows the effect of plating time on the current at a constant potential (1.1V) around the limiting region. These graphs show that the magnitude of the current gradually increases with increase in time. This rise in current is due to development of a rough surface on the cone, as the deposit grows, thereby increasing the number of eddies generated by the fluid flow. These eddies reduce the diffusion layer thus an increase in the current is noted.

9.3 THE HULL CELL

Figure 42 shows the current distribution on the cathode predicted by Hull using the following formula:

\[
\text{c.d. at any point} = I (5.1 - 5.24 \log L)
\]

where the current density is in amp/dm$^2$, $I$ is in amperes and $L$ in cm with the limitation of $0.6 < L < 8.1$. This limitation is to avoid the edges where the current lines converge and give a greater current density than predicted.

In order to compare the results obtained with XRF and coulometric methods to theory, it is necessary to convert the thickness and the coulombs into current in the following manner:
\[ W = Sa \rho \]

where \( W \) = weight of deposit in g
\( \rho \) = deposit density = 8.23 g/cm\(^3\)
\( a \) = electrode area = 5 cm\(^2\)
\( S \) = deposit thickness in cm

From Faraday's law

\[ W = \frac{ItA}{nF} = 3.29 \times 10^{-4} \text{ It} \]

or

\[ I = 135714 \left( \frac{S}{t} \right) \]

where \( t \) is the plating time. If \( t = 180 \text{s} \) then

\[ I = 754 S \]

or

\[ I = 0.0754 S \text{ where } S \text{ is in } \mu \text{m} \]

The current density is now given by:

\[ i = \frac{I}{A} = \frac{0.0754}{0.5 \times 0.1} S \]

or

\[ i = 1.51 S \text{ amp/dm}^2 \]

To convert the measured coulombs into current a similar procedure may be taken. Alternatively

\[ q = it \]

where \( q \) is the measured coulombs (amp sec/dm\(^2\)), \( t \) is the plating time and \( i \) is the current density.

Thus

\[ q = 180i \]

\[ i = q/180 \]
Using these simple formulae, the current density distribution may be estimated as shown in Figure 117. This figure compares the results obtained from various methods mentioned above. In all cases the plating current was maintained at 1 amp. It is clear that the coulometric and the XRF results are quite different from those of XRF proprietary and theory. The XRF result from the proprietary solution is in good agreement with the theory. The proprietary solution was operated at 100% efficiency whereas the solution used for the XRF and the coulometry was very low in efficiency. The home made solution consisted of 0.014M CuSO₄ + 1/2M H₂SO₄, which is very low in metal ions. The coulometric result is worse than the XRF result. This discrepancy is due to the problems caused by the coulometric method which was explained earlier (e.g. solution leakage etc).

From these results one may conclude that in order to estimate the current distribution on the rotating cones it is best to use the data obtained from XRF and the proprietary solution rather than dilute acid copper solution and/or coulometric methods.

9.4 THE INCLINED CATHODE CELL

The results obtained by resistance measurement, Figure 43, suggest that the current distribution over the cathode decreases with increase in distance between the two electrodes. Furthermore it shows that the effect of agitation on current distribution is minimal. Only at 500 rpm is there a sign of an agitation effect. At this rotation rate, the gradient of the trend is greater, indicating that the area where the cathode is nearest to the anode, there is a concentration of current lines at the expense of the area of cathode furthest from the anode. This may be due to sudden reduction of the boundary layer at the high current density area since this end being closer to the rotating anode benefiting most of the turbulences generated by it.
The results from the blocking method are very interesting, although the results obtained by this method show similar relationships between current density and electrode distance which was obtained with the previous method but the effect of agitation is mysterious. Figure 45 shows that agitation does affect the current distribution. During the three different rotation rates that were used the total current was maintained at 0.1A (45 A/dm²). Each value plotted was an average of 10 readings. However close examination of these graphs show that there is a net gain in the overall current registered at 500 rpm and 100 rpm relative to 0 rpm and the values of 500 rpm are greater than those of 1000 rpm.

Let us consider Figure 47 which shows the relationship between copper thickness and slant height. Here the gradients of 200, 300, 400 and 500 rpm are almost equal, showing a linear relationship between the two variables. Near the high current density end the thickness of the copper deposited is four times greater than that at the low current density end. It is possible to compare Figure 45 with Figure 46. Although in Figure 47 the graph shows the relationship between copper thickness and slant height, the slant height values are easily converted to distance from the anode by the following formula:

\[
\text{Distance from anode} = (\text{Minimum distance from the two electrodes}) + (\text{Slant height} \times \sin 52.7)
\]

Also from Faraday's law

\[
W = \frac{itZ}{nF}
\]

Thus the copper thickness is directly proportional to current density. This enables us to compare the two gradients without any difficulty. The gradient of Figure 47 is about 0.12 and that of Figure 45 is about 0.08. Bearing in mind that the experiments were completely different from each other, 25% difference in gradient is not too great a discrepancy.
Figure 48 shows an odd relationship between slant height and coating thickness. The slopes of the 200 rpm and 400 rpm lines are opposite to each other. Even though the experiment was repeated twice, the same result was obtained. Due to a high degree of scatter of the data in both cases, it is not right to pay too much attention to these results.

9.5 THE ROTATING HULL CELL

Figure 49 shows the results obtained with Atomic Absorption Spectroscopy. The work carried out with the AAS was very limited. This was partially due to the drifts in the AAS readings, thus causing great difficulty in reproducability of the results. Also there were practical problems in stripping the copper off the cylinder. A solution of 50% nitric acid was used to dissolve the copper deposits, but accurate measurement of the area where copper was removed was very difficult due to the surface tension of the solution which resulted in dissolving some of the copper above the solution level.

Let us consider the data obtained with the XRF method first. Figure 55 shows two opposite trends for the relationship between the coating thickness and slant height. Although the data for 100 rpm is scattered, the trend is as expected. However the data obtained for the rotation rate of 200 rpm shows that the copper thickness at the high current density area is less than the area which is further away and therefore at lower current density. Referring to Figure 56 this was obtained under the exact plating conditions as above. The 100 and 200 rpm trends are the opposite to what they were before. Here the 0, 50 and 200 rpm data are as expected, decrease of deposit thickness with increase in slant height i.e. decrease in current density. The 100 rpm data is very scattered. The 0 and 50 rpm data show a well defined trend and one can assume that these results are obtained under the laminar flow region, between 100 and 200 rpm there may be a transition which causes the scattering of data at these rotation rates. Above 200 rpm the flow enters into the
turbulent region. The 200 rpm trend in Figure 56 is well defined. The coating thickness at this rotating rate is much greater than those obtained at 0 and 50 rpm. This is probably due to the mass transfer enhancement in the turbulent region.

Figure 57 clearly verifies the fact that above 200 rpm the flow region is fully developed turbulence. The 300 and 400 rpm data show a clear relationship between the coating thickness and the slant height. It is interesting to note that when the x axis is plotted in logarithmic form the data fit in a straight line. In this graph the 50 rpm data is scattered and has an ill-defined trend. Therefore it may be possible to assume that the transition starts at around 50 rpm rather than 100 rpm.

Figures 50 and 51 are obtained by the polarization method. In brief the method is as follows: the surface potential of the working electrode is monitored and noted during plating. Next, from the polarization curves the local current is found from the corresponding voltage. Figure 50 shows that the trend lines of the 1000 rpm is below 700 which in turn is below 600 and 200 rpm's. Nevertheless the gradient of 1000, 600 and 400 rpm's are between 0.6 and 0.5 i.e. almost parallel to each other whereas the 200 rpm's slope is slightly out (0.3). These facts may be explained in the following manner: for each rotation rate there is a corresponding polarization curve; however the polarization curves are quite different from one another. It is difficult to reproduce a polarization curve exactly, this is mainly due to the substrate condition and the way in which the deposit grows. During polarization, the overpotential is increased to a great degree before any substantial current flows (Figure 28). This break away point is at around 0.65V. If this break away occurs slightly earlier, or later, consequently it will affect the value of current obtained for a given potential.
To check the accuracy of this method it is sufficient to find the average current value at each rotation rate. This average value should correspond to the total current. In Figure 50 the average currents are 0.195, 0.32, 0.5, 0.5 amps for 1000, 400, 600 and 200 rpm respectively. In Figure 51 the average currents obtained for 400, 600 and 1000 rpm are 1.01, 1.06 and 1.3 amps respectively. It should be 1A exactly - this error is significant but not serious when the procedure is considered.

9.6 THE CONICAL ELECTRODES

In this section the discussion on the conical electrodes is divided into four subsections:

9.6.1 The parallel electrode
9.6.2 The edge and entry effects
9.6.3 The inverted cone
9.6.4 The upright cone.

9.6.1 The Parallel Electrodes
The objective of this experiment was to establish the effect of the peripheral speed, if any, on the electrodeposition of metal ions on the cones.

In the experiment section this section was discussed in detail. Figures 88 and 89 were obtained by using the rotating Hull cell anode. Greater attention should be paid to Figure 89 rather than Figure 88 since in the latter case the unwanted areas of the cone were masked off (see the results section for more details), thus giving a more accurate result. Here the variation of the deposit thickness is very small, 0.2 μm if the first and last two points are disregarded. The greater deposition at both ends is thought to be due to the edge effects and perhaps the entry effect. Therefore it may be assumed that the overall effect of the peripheral speed on plating is minimal.
9.6.2 The Entry and Edge Effect
In the results section each figure was discussed in brief. The data obtained by the XRF show some interesting results. In almost all figures which are from the inverted cone and upright cone, there is a sharp change in the data trend at both ends representing the apex and the edge. These sharp changes may be explained as the edge and entry effects.

1) Entry effect or entrance effect (length) is defined as the distance which it takes for a flow to stabilise in a semi confined space such as a tube, channel etc. As the flow enters the confined space the flow rate near the walls slows down considerably until a parabolic velocity profile is formed. The distance before the parabolic velocity profile is formed is called the entrance length.

For example according to Sparrow\textsuperscript{48} the entrance length for a channel of width \(w\) with a distance \(B\) between the electrodes leads to the result:

\[ l_e = 0.0064 \frac{d_e}{Re} \]

where \(d_e\) is known as the hydrodynamic diameter. For a channel \(d_e\) is defined as \(\frac{2wB}{w+B}\) and for a tube with a diameter of \(D\) is \(D\).

The flow pattern of a RCE was described in Section 3.5.1 in some detail. However it is important to bring in some results obtained by other investigators.
At low rotation rates where the flow is laminar-axial, flow causes the fluid to move in a helical rather than tangential manner and with rapid axial flow, the pattern approaches that of pipe flow. Here the entrance length effect is clearly apparent. In order to minimise this effect, Walsh used long and thin cylinders (d << 1) in conjunction with PTFE caps at either end of the electrodes. This argument of flow pattern may be taken further and used for the rotating cone electrodes. The flow pattern may be considered similar to that of an infinite open channel. An entry length effect may be assumed to be present around the apex for the inverted cone and at the edge of the upright cone. However it is possible that the edge effect due to current distribution is superimposed on the entry length effect.

ii) Edge effect. The edge effect is defined as the irregularities in deposition at the edges of the cathode (anode) due to variation in current distribution. This effect is well presented on Hull cell panels. In practice, the plating section at either end and the bottom part of the panel is disregarded due to edge effects. Similarly Walsh used PTFE caps on the RCE in order to minimise this effect.

The cause of edge effects is the high concentration of current lines. If the edge of the cathode is not confined some current lines will go round the edge and cause an increase in the current density.
In the case of the rotating cones (upright and inverted), this edge effect is present at the apex and the edge. By studying these two effects on the cones it is clear that in order to avoid these effects on the electrodeposition it is necessary to disregard the data obtained at slant heights of 0 to 1.5 and 6.5 cm onwards.

9.6.3 The Inverted Cone
Figures 85 and 86 show the effects of rotation and slant height on the limiting current obtained for the inverted cone. As expected, any increase in rotation rate results in an increase in the limiting current. This is due to the reduction of the diffusion layer. From the Nernst diffusion equation

\[ i_L = \frac{niFCD}{\delta(1-t)} \]

it can be concluded that if C and D are constant, then by reducing the diffusion layer (by agitation) the limiting current is increased. For example in Figures 85-86 the average limiting current at 0 rpm is about 0.15 amp/dm² yet at 400 rpm the limiting current is increased to 1.15, an increase of 760%. These graphs show that the slant height has some effect on the limiting current. The slopes at 0, 50, 80, 120, 150 and 200 rpm's are more or less equal. There is a slight increase of limiting current with decrease in the slant height. This increase is not more than 0.05 A/dm² i.e. maximum of 10% increase. Above 200 rpm the effect of slant height is much more apparent. At 400 rpm the limiting current has increased from 0.95 at the apex to 1.29 at the edge, an increase of 35%.

Let us consider Figures 73 and 74, where the coulombs used were 1200 and 900 As respectively. The latter graph shows a lesser degree of scattering of the data. The increase in scattering of data in Figure 73 may be due to greater plating current that was used. At the higher current HER takes place. When hydrogen bubbles are evolved, they increase the agitation of the solution. Thus decreasing the diffusion layer further when compared to the diffusion layer
resulted due to rotation only. This may explain the well scattered data of 50 rpm when plating current was 2A in Figure 72. When the plating current is reduced to 1A although the scattering of the points is reduced, the average thickness of the deposit is also less. When the rotation rate is increased to 100 rpm the scattering of the points is reduced further.

Figures 73 and 74 show that the agitation has not much effect on the deposition thickness. However Figure 75 shows that greater agitation results in a steeper gradient.

When comparing the results obtained from simple acid copper solution to those obtained from the proprietary solution, slightly different results emerged. In the proprietary solution the scattering of data is minimal, Figures 76 and 77. Nevertheless the edge and entrance effect is still present. Again these figures indicate that there is no direct relationship between plating thickness and rotating rates. The deposition thickness from the proprietary solution is over 100% greater than that from simple acid copper solution. One reason may be that the HER is completely suppressed and therefore operating at or very near 100% efficiency.

Finally, Figure 78 shows the results obtained at constant overpotential (0.8 volts) rather than constant current. Up to 200 rpm the deposit thickness on cone is uniform under this constant voltage condition, yet above 200 rpm there is a sudden change. The thickness of deposit is much greater near the edge compared to the thickness near the apex. This change corresponds to the turbulent region. Up to 200 rpm the plating was carried out under laminar region. The graph also shows that as the rotation increases so does the plating current verifying the effect of diffusion layer on plating.
9.6.4 The Coulometric Measurement

Before discussing the results obtained from the coulometric method, it is important to appreciate its reliability. The reliability of this method is not very good, thought to be due to the following reasons:

1. It is difficult to establish the precise time for which the deposit is completely removed. This is because the thickness of the deposit is reduced gradually and therefore the film disappears slowly. Special care must be taken in choosing the magnitude of the current that is used. If the current is too high, HER may take place, reducing the efficiency and therefore having an exaggerated measurement.

2. Although during the coulometric measurement the surface potential of the anode was monitored, nevertheless the change in potential from copper to steel was not always reproducible.

3. Inevitably there is a leakage under the cell ring which results in removing copper from a greater area and therefore prolonging the removal time.

4. Since the cell ring is spongy and flexible it is easily deformed and therefore the true area may be difficult to estimate.

5. It is assumed that the electrodeposition is 100% efficient, which is not necessarily true.

With a view to the above points, it is important to look at the coulometric measurements in conjunction with the XRF measurements.

Comparing Figures 58, 59 and 60 with each other, it shows that a greater coulomb level was used up near the edge than near the apex of the cone verifying the fact that the copper thickness is greater towards the edge. These figures also show that the coulomb level measured at 3 amps is greater than at 1.75 amps, but at 5 amps it reduces to the same level as that of 1.75 amps. This shows that
increasing the current from 1.75 amps to 3 amps results in an increase of the deposition of copper, however any further increase in the current reduces the efficiency of the electrodeposition by generating hydrogen gas and perhaps oxygen. However when the ion concentration in the electrolyte was increased from 0.014M to 0.07M, the efficiency of the solution was also increased. Figure 61 shows that this increase in ion concentration increased the deposition by about 30% at a plating current of 3 amps. Furthermore when the current was increased from 3 to 5 amps the coulomb level measured was also increased by a further 30% as shown in Figure 62.

The results from the coulometric measurement were not only plotted against the slant height, but also in a log-log relationship against the rotation rate. Figures 63-67 all have two factors in common:

i) any increase in the rotation rate results in an increase in measured coulomb which can be related to the thickness of the deposit as described earlier.

ii) the rate of increase of the coulomb at each slant height is more or less constant relative to the other slant heights. For example if the coulometric difference between slant height 12 and 62 mm is 25 amps sec/dm² at 30 rpm, this difference has remained more or less constant at 300 rpm. This shows that the mass enhancement was increased over all the cone surface uniformly.

9.6.5 The Upright Cone

The results obtained for the upright cone show a great similarity to the inverted cone.

The XRF results for the upright cone show that when the simple acid copper solution (0.014M Cu + 0.5M H₂SO₄) is used, the thickness of the copper deposit remains almost constant over all the cone surface at low rotation rates up to about 200 rpm. Only then the effect of slant height is noticeable where the deposit thickness gradually
decreases with increase in the slant height. However near the apex there is a sudden increase in the thickness. This sudden increase in the copper deposit near the apex is probably due to the whirlpool effect. Going back to the flow pattern in the case of the upright cone, the radius of the cone gradually increases inwards into the solution. Therefore the pumping action of the upright cone is in reverse to that of the inverted cone. Here the fluid is dropped down below, the pumping action is downwards. This action results in a whirlpool which generates much greater agitation in the near vicinity of the surface of the cone, hence an increase in the copper deposition. There is also the entry effect apparent at lower rotation rates which is superimposed on the whirlpool effect at greater rotation speeds. These effects are illustrated below:

As shown there are two types of mixing present in the upright cone:

i) Vortices created due to the cone where the size of the vortices decrease as slant height decreases. These vortices increase in size with increase in rotation rate.

ii) Another flow pattern exists at the bottom of the cone which creates similar flow patterns to those created by the rotating disc. Although the two flow patterns are independent of each other, nevertheless mixing is inevitable. The second fluid flow has no direct effect on the MT on the cone.
Figures 102, 103 and 104 show that the limiting current increases with increase in slant height, in other words the limiting current is shifted into higher values as the distance between anode and cathode increases which seems very odd since it was shown in the inverted cone section that the reverse is true. Therefore one can conclude that this opposite trend is due to eddies which occur at higher rotation rates. It is important to note the variation of the limiting current from one end to another which is little. In the highest rotation rate used, i.e. 300 rpm, the limiting current change was no more than 4% from its value half way up the cone. The opposite increase in the limiting current should result in an increase in the deposition in that direction too. However from the results obtained from several different conditions, there was no case of this kind. This may be explained as follows. Polarisation curves are obtained by increasing the potential in equal steps and from that the limiting current is estimated. It is important to note that as the slant height increases so does the distance between the working electrode and the auxiliary electrode. The limiting region for each slant height is obtained at slightly higher overpotential related to its distance from the anode. Therefore if the bottom of the cone is at the limiting current region say, then at the apex the overpotential is not high enough to reach its limiting current value, hence thicker coatings at the bottom than at the top. These effects are clearly shown in Figure 105.

Further at lower rotation rates the flow is laminar hence no variation in thickness of the deposition yet this variation is vividly shown at higher rotation rates (above 200 rpm) where the flow pattern is fully turbulent. Figure 107 shows the deposition thickness when the cone was plated for 10 minutes at 5 amps using the proprietary solution. When the time is halved the deposition thickness is also halved which indicates that all the energy is used in electrodepositing copper and no or very little gas is generated, hence operating near 100% efficiency as shown in Figure 108.
Also in Figure 108 it can be seen that the data obtained for 100, 150 and 200 rpm are close together yet there is a gap between them and 50 rpm data. This may be due to laminar/turbulent flow regions.

Figure 109 shows the effect on current when the rotation rate is increased, whilst the overpotential is kept constant at 0.8V. At 50 rpm the total current was 0.65 amps, but above 100 rpm the variation of total current with rotation rate was greatly reduced. When the rotation rate is increased from 100 to 200 rpm the increase in total current is only 11%. This suggests that again between 50-100 rpm the flow region has changed from laminar to turbulent where the diffusion layer is greatly reduced, hence a surge in the current.

Figures 90 and 91 show that there is a noticeable gap between the results obtained for 0 to 100 and for 200 and 300 rpm. These graphs show that there is a great enhancement above 100 rpm indicating the presence of vigorous agitation which increases the mass transfer. However Figures 92 and 93 do not suggest such changes on the MT above 100 rpm. Nevertheless this may be explained as follows. Figures 90 and 91 show the data obtained for acid copper solution consisting of 1/2M H₂SO₄ and copper concentration of 0.014 M. At such a low copper ion concentration the efficiency of the solution is low since at high currents (3A, 5A) a lot of hydrogen gas is generated. Therefore any large reduction in the diffusion layer will increase the mass transfer substantially as shown in these figures. However Figures 92 and 93 do not show such a sudden change in mass transfer at rotation rates between 100 and 200 rpm. This may be due to the fact that the ion concentration in the solution is increased by fivefold to 0.7M. Therefore the solution is operating in a much more efficient state. This suggests that at the total current of 3 amp there is no HER taking place and therefore the effect of rotation is not as great as that shown in Figure 90. However in Figure 93 the total current used was 5 amp. At this current HER was taking place therefore again there is quite a noticeable change in the mass transfer above 100 rpm where the presence of vigorous
agitation was significant in increasing the efficiency of electro-deposition.

Figures 94 and 95 show the relationship between the coulomb measured and the rotation rate. These results are similar to those obtained for the inverted cone. These figures show that the amount of copper deposited on the cone is increased in two ways:

i) increase in the rotation rate, which increases the mass transfer
ii) at shorter slant heights current density is greater.

When the above figures are compared with Figures 96 and 97, it can be seen that the slope of the lines has decreased substantially in the latter case. This points out the already mentioned fact on the efficiency factor.

9.7 THE MASS TRANSFER PHENOMENA

As described earlier, there are two distinct regions in mass transfer. The two indices obtained for the cones, corresponding to the laminar and turbulent flow can be tabulated as shown below:

THE INDICES FOR LAMINAR AND TURBULENT REGIONS

<table>
<thead>
<tr>
<th></th>
<th>Upright Cone</th>
<th>Inverted Cone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Laminar</td>
<td>Turbulent</td>
</tr>
<tr>
<td>0.39</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>0.45</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>0.68</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>0.41</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean value:</td>
<td>0.48</td>
<td>0.93</td>
</tr>
</tbody>
</table>
The complete mass transfer formula for the upright and the inverted cones can be written as follows:

In the laminar region:

\[ Sh = 4.5 \, Re^{0.48} \] for the upright cone
\[ i_L = 4.5nFCD_w^{0.48}l^{1.48} \sin^{0.48}v^{-0.52} \]

\[ Sh = 4.0 \, Re^{0.45} \] for the inverted cone
\[ i_L = 4nFCD_w^{0.45}l^{1.45} \sin^{0.45}v^{-0.55} \]

In the turbulent region:

\[ Sh = 0.04 \, Re^{0.93} \] for the upright cone
\[ i_L = 0.04nFCD_w^{0.93}l^{1.93} \sin^{0.93}v^{0.07} \]

\[ Sh = 0.04 \, Re^{0.88} \] for the inverted cone
\[ i_L = 0.04nFCD_w^{0.88}l^{1.88} \sin^{0.88}v^{0.12} \]

Figure 111 shows the relationship between current and rotation rate on a logarithmic scale for the inverted cone. The two curves indicate that the total current increases at a decreasing rate with increase in rotation rate and that there is a ceiling beyond which agitation does not increase the current. This is shown clearly in Figure 112. Also the effect of copper ion concentration is shown in Figure 110 for the inverted cone and for the upright cone in Figure 113. This phenomena is rather unusual especially when these figures are compared to those for mass transfer figures obtained by the limiting current method. In order to explain this is it important to note the experimental method by which these results were obtained.

The potentiostat was set at an overpotential of 0.9 and later 1.1 volts. These potentials were thought to be in the limiting current region. Next the rotation rate was increased in stages after a few seconds when the new flow pattern was stabilised, the current was noted at each stage and the procedure was repeated. This method is acceptable at a short range of rotation rates as it was used by Makanjuola and Gabe. As explained earlier, when considering the limiting current, the potential at which the limiting current is reached increases with increase in the rotation rate. Therefore if the rotation range is large it may result in overshooting the
limiting current region. This is shown in Figure 111 etc. The preset potential of 0.9 or 1.1V was well within the limiting current region at low rotation rates, but at higher rotation rates the limiting current region had shifted to a higher potential. Therefore the plateau as shown in these figures resulted from the power supply (potentiostat) rather than the mass transfer.

In recent years several papers have been published concerning the mass transfer of cones. Subramaniyan et al plotted mass transfer results in two ways: \( \log \left( \frac{Sh}{Sc^{0.4}} \right) \) versus \( \log(Re) \) and \( \log \frac{K_L}{K_{L_0}} \) versus \( \log \left( \frac{\omega \sin \alpha}{\nu} \right) \).

Figure 114 compares directly the results obtained under current studies to that obtained by Subramaniyan et al. The agreement on the gradient and thus the indices in the laminar region is excellent. Subramaniyan does not show any result for the turbulent region. There is a substantial enhancement shown by Subramaniyan when compared to the present studies. The enhancement \( \frac{K_L}{K_{L_0}} \) is the ratio of the limiting current obtained during the rotation and stationary. This ratio seems to be unreliable since the limiting current on a stationary cone can change from one experiment to another depending on the substrate condition i.e. a small error in estimating the limiting current results in transferring this error to all other results. If an enhancement ratio is required it is best to use the limiting current at a low rotation rate say 50 rpm rather than the limiting current at 0 rpm. The limiting current obtained at a specific rotation rate is much less dependable on the substrate and any variation in the boundary layer, thus the limiting current can be repeatable with greater accuracy.

Subramaniyan et al also show their mass transfer results in the form of \( \log \frac{Sh}{Sc^{0.4}} \) versus \( \log(Re) \). Figure 119 compares these results to the present studies. Unfortunately Subramaniyan does not give any results in the turbulent regime. Nevertheless there is good agreement in the laminar region when the experimental data is considered. Subramaniyan et al show the mass transfer data for the
cones is similar to that of a disc when the apex angle is greater than 40°.

\[
\text{Cone: } \frac{Sh}{Sc^{0.4}} = 0.345 \left(Re_{\text{cone}}\right)^{1/2}
\]
\[
Re_{\text{cone}} = \frac{k^2 \omega \sin \alpha}{\nu}
\]

\[
\text{Discs: } \frac{Sh}{Sc^{0.4}} = 0.345 \left(Re_{\text{disc}}\right)^{1/2}
\]
\[
Re_{\text{disc}} = \frac{d^2 \omega}{\nu}
\]

and that for cones the mass transfer correlation can be shown as:

\[
K_I/K_L' = 0.169 \left(\frac{\omega \sin \alpha}{\nu}\right)^{1/2}
\]

The present studies show that

\[
\frac{Sh}{Sc^{0.4}} = 0.9 Re^{1/2} \quad \text{in the laminar region}
\]
\[
\frac{Sh}{Sc^{0.4}} = 0.001 Re^{0.9} \quad \text{in the turbulent region}
\]

This numerical disagreement is partially due to the much smaller Schmidt number used by Subramaniyan (Sc = 1100, present studies 2000).

The transition from laminar to turbulent flow in the present studies is shown to be at Reynolds number of about 10^5. Kreith et al.\textsuperscript{21} reported that the transition value decreases with decreasing cone angle. This has been confirmed by Kappesser et al.\textsuperscript{20} Kappesser et al. reported the transition value at 1.5 x 10^5 for a cone with an apex angle of 60°, whereas Tien and Campbell\textsuperscript{18} have reported a lower transition value of 10^5, while cones with apex angle greater than 90° show the transition value at 2-2.5 x 10^5.

Kappesser et al. reported that the data obtained for a series of cones with vortex angles of 30°, 60°, 90°, 120° and 180° show good
agreement with theory. Their study shows that in the laminar flow at high Schmidt numbers the mass transfer is given by

\[
Sh = \frac{0.62048 \, Re^{1/2} \, Sc^{-2/3}}{1 + 0.2980 \, Sc^{-1/3} + 0.14514 \, Sc^{-2/3}}
\]

and in the fully turbulent region

\[
Sh = B \, Re^{1/2} \, Sc^{1/3} - 0.01130 \, Re^{0.9} \, Sc^{1/4} + 0.013 \, Re^{0.9} \, Sc^{1/2}
\]

where \(B = \frac{0.62048}{1 + 0.2980 \, Sc^{-1/3} + 0.14514 \, Sc^{-2/3}}\)

Their results show that:

a) Any increase in the vertex angle extends the laminar region by delaying the transition region at higher Reynolds number

b) In the laminar region the gradient of the Sh-Re relationship is almost constant irrespective of the vertex angle

c) The slope in the turbulent region increases with increase in the apex angle.

Figure 118 shows the mass transfer relationship obtained for this study. It shows that:

a) The difference in mass transfer between the upright and inverted cones is very little

b) The transition occurs at Reynolds number of \(10^5\).

The two straight lines drawn on this graph are the data obtained by Kappesser et al. The two sets of data show quite good agreement on
the gradient of the laminar and turbulent regions. However there is disagreement in the transition region. Kappesser et al shows that this occurs at about Reynolds number of $1.5 \times 10^5$, slightly higher than these studies. It must be noted that Kappesser et al operated at the Schmidt number of 400 whereas these studies were conducted at the Schmidt number of 2000. Also the shape and size of the cell may have contributed towards this discrepancy.

The table below shows the index values for different rotating systems:

<table>
<thead>
<tr>
<th>Rotating System</th>
<th>Re</th>
<th>Index, n</th>
<th>Re_{crit}</th>
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<tr>
<td></td>
<td>Laminar</td>
<td>Turbulent</td>
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<td>RDE</td>
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<tr>
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</tr>
<tr>
<td>Parallel plate</td>
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<td>0.58</td>
<td>2200</td>
</tr>
<tr>
<td>UCE</td>
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<td>0.93</td>
<td>$10^5$</td>
</tr>
<tr>
<td>ICE</td>
<td>0.45</td>
<td>0.88</td>
<td>$6 \times 10^4$</td>
</tr>
</tbody>
</table>
In all the experiments that were carried out such as XRF measurement, coulometric measurement, limiting current etc, certain facts emerged from all totally independent experiments. They are as follows:

1. Increase in rotation increases the limiting current. This is because the limiting current is inversely proportional to the diffusion layer, therefore increasing agitation decreases this layer hence greater current for the same overpotential.

2. Generally increase in slant height that is moving away from the anode along the cathode tends to reduce the copper thickness which is deposited on the cone. This is simply due to primary current distribution, which is a dominant factor in copper sulphate solution. As the distance between the electrodes increases the effect of current in depositing copper diminishes.

3. Increase in metal ions in the solution, results in an increase in the deposition rate. Therefore for a given time the thickness of the copper film is much greater at 0.7M CuSO₄ than at 0.014M CuSO₄. As the ion concentration increases the solution becomes more efficient because the concentration polarization for a given current density is reduced and the hydrogen evolution reaction is suppressed. The current is mostly used to reduce the positively charged metal ions generating hydrogen gas.

4. Results obtained by the XRF method are the most reliable since this method is a direct measurement of a film. However in the case of coulometric measurements there are margins of error and some of these are as follows:

a) Since copper which is deposited on the cone needs to be deposited on another electrode, it is difficult to decide the exact time at which there is no more copper on the cone.
Although by monitoring the surface potential of the cone it indicates the change in potential when all the copper is removed, nevertheless there is difficulty in establishing the moment when the last copper ion is removed.

b) Inevitably there is a leakage under the ring cell where extra copper is removed, hence registering longer times for removal of the copper.

c) The ring cell deforms easily which results in a change in the area when coulometric measurements are taken.

d) One assumes 100% efficiency in depositing copper which is not necessarily true.

5. Results from the inclined cathode experiments suggest that this system is not a reliable and efficient cell. This arises from the fact that the anode is rotating rather than the cathode.

6. The rotating Hull cell shows that the transition from laminar to turbulent occurs at 100-200 rpm.

7. The parallel electrode shows that the overall effect of the peripheral speed on plating is minimal.

8. Due to the edge and entry effect on the rotating cones, the deposits of up to 1.5 cm on either end of the slant height may be disregarded.

9. The transition on the rotating cones is between 50 - 150 rpm.

10. The mass transfer for the upright cone is:
    \[ Sh = 4.5 \ Re^{0.48} \text{ in the laminar region} \]
    \[ Sh = 0.04 \ Re^{0.95} \text{ in the turbulent region} \]
115

11. The mass transfer for the inverted cone is
\[ Sh = 4.5 \text{ Re}^{0.45} \text{ in the laminar region} \]
\[ Sh = 0.04 \text{ Re}^{0.88} \text{ in the turbulent region} \]

SUGGESTIONS FOR FURTHER WORK

1. Measurement of the properties of the deposits.

2. More detail work on different solutions such as concentrated copper sulphate solution.

3. Alloy plating such as tin lead, where the local current density governs the alloy composition. Examination of such deposits will undoubtedly give a better understanding of the variation of the local and overall current density distribution.

4. Effect of different Schmidt number where the Sc number is systematically altered from 400 to 4000 by the use of glycerol type viscosity agents and changes in temperature.

5. Use of the conical electrode system in industrial quality laboratories as a direct simulation and control technique for high speed electrodepositing processes.

6. A rotating ring cone electrode has been designed (see Figure 120) but not yet constructed. It would be valuable to study segmental mass transfer behaviour and as this research shows would be most valuable in the inverted mode. A study using this device would be most useful.
REFERENCES


10. E. Brunner. Z. Phys. Chem., 47 56 (1904); 51 (1905), 95, 58 (1907) 1.

11. R.G. Van Name and G. Edgar. ibid., 73, 97 (1901).


33. Fletcher, Houghton, Gardner.


41. BS 188:1977.

42. J. Heyers. Mat. Tech. Ch. 11, 109-114.
43. CRC Handbook of Chemistry and Physics, Chemical Rubber Co., Cleveland, USA.


* * * * *

The following references were used either indirectly or in a less specific manner.

Rotating Electrodes


Cell Design


Current Distribution, Throwing Power etc


APPENDIX 1

for indicating the appearance of the different areas on test plates. Commonly accepted code according to DIN 50957

- Bright
- Semi-bright
- Dull
- Streaky, patchy
- Pitted
- Blistered
- Rough, Burnt
- Powdery
- Brittle, Cracked
- Uncoated
APPENDIX 2

STANDARD SOLUTION DATA

a) The following data were used to calculate various dimensionless groups:

\[ N = 2 \]
\[ F = 96500 \ A \ cm/mole \]
\[ D = 5.2 \times 10^6 \ cm^2/sec \]
\[ C = 0.014M \]
\[ \nu = 1.027 \times 10^{-2} \ cm^2/sec \]
\[ \omega = \frac{2\pi}{60} \ rpm \ rad/sec \]
\[ \alpha = 52^\circ \]
\[ l_{rc} = 77.5 \ mm \]
\[ l_{urc} = 69 \ mm \]
\[ d_{ic} = 124 \ mm \]
\[ d_{urc} = 128 \ mm \]

b) Nomenclature employed:

\[ K_L = \frac{I}{\pi F C_o} \]
\[ \frac{K_L}{K'_L} = \frac{i_L}{i'_L} \]
\[ Sc = \frac{\nu}{D} \]
\[ Sh = \frac{i_L \ell}{N F C D} \]
\[ Re = \omega \ell^2 \sin \alpha / \nu \]
### APPENDIX 3

**EXPERIMENTAL DATA USED IN GRAPHS**

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<td>1A, 3 min</td>
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### Figure 52

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**Figure 74**

|   | 50  | 2.81 | 2.57 | 2.56 | 2.01 | 1.51 | 1.71 | 1.64 | 1.43 | 1.34 | 1.02 | 0.89 | 0.82 | 0.77 | 0.69 |
|---|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   | 100 | 2.76 | 2.62 | 2.48 | 2.22 | 1.91 | 1.71 | 1.64 | 1.43 | 1.34 | 1.02 | 0.89 | 0.82 | 0.77 | 0.69 |
|   | 300 | 3.42 | 2.92 | 2.32 | 1.98 | 2.48 | 1.62 | 1.09 | 0.97 | 0.70 | 0.95 | 0.54 | 0.74 | 0.48 | 0.69 |

**Figure 75**

|   | 100 | 3.84 | 3.72 | 3.8 | 3.81 | 3.78 | 3.78 | 3.68 | 3.74 | 3.74 | 3.65 | 3.61 | 3.66 | 3.9 | 3.39 |
|---|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   | 150 | 4.39 | 4.27 | 4.17 | 4.06 | 3.95 | 3.79 | 3.74 | 3.65 | 3.47 | 3.37 | 3.13 | 3.05 | 3.03 | 3.31 | 3.28 |
|   | 200 | 4.8  | 4.52 | 4.19 | 4.12 | 3.88 | 3.82 | 3.57 | 3.27 | 2.89 | 1.94 | 2.62 | 2.52 | 2.58 | 2.35 | 2.63 |
|   | 250 | 5.1  | 4.67 | 4.54 | 4.16 | 3.97 | 3.65 | 3.18 | 3.5 | 2.91 | 2.61 | 3.08 | 3.86 | 3.81 | 3.11 | 3.27 |
|   | 300 | 5.2  | 4.69 | 4.36 | 4.24 | 4.0 | 3.88 | 3.08 | 3.04 | 2.34 | 2.14 | 1.83 | 1.98 | 1.80 | 1.52 | 1.57 |
|   | 400 | 5.38 | 4.96 | 4.55 | 4.28 | 3.67 | 3.12 | 2.82 | 3.08 | 1.94 | 2.46 | 1.71 | 2.18 | 1.85 | 1.49 | 2.69 |

**Figure 76**

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**Figure 77**

|   | 50  | 7.82 | 7.45 | 6.9 | 6.48 | 6.1 | 5.73 | 5.33 | 5.05 | 4.69 | 4.92 | 4.11 | 3.84 | 3.52 | 3.18 | 2.82 |
|---|-----|------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|   | 100 | 8.86 | 7.93 | 6.99 | 6.59 | 6.04 | 5.64 | 5.29 | 4.91 | 4.68 | 4.36 | 4.11 | 3.1 | 3.33 | 3.08 | 2.63 |
|   | 200 | 9.33 | 7.89 | 7.14 | 6.48 | 6.18 | 5.64 | 5.29 | 5.0 | 4.49 | 4.24 | 3.92 | 3.6 | 3.24 | 2.98 | 2.39 |
|   | 300 | 9.65 | 7.89 | 7.21 | 6.6 | 6.15 | 5.81 | 5.39 | 5.05 | 4.78 | 4.33 | 3.96 | 3.6 | 3.25 | 2.94 | 2.52 |

**Figure 78**

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Figure 81

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Figure 83

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**Figure 88**

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**Figure 89**

| rpm/SH<sub>cm</sub> | 100 | -   | -   | -   | -   | -   | -   | -   | -   | -   | -   | -   | -   | -   | -   | -   |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 200                  | -   | -   | -   | -   | 2.71| 2.25| 2.96| 2.09| 2.13| 2.15| 2.42| 3.74| -   | -   | -   | -   |
| 300                  | -   | -   | -   | -   | 2.39| 2.15| 2.06| 2.06| 2.05| 2.12| 2.23| 2.42| -   | -   | -   | -   |
|                      | 100 | -   | -   | -   | 2.08| 1.97| 2.0 | 1.94| 2.03| 2.07| 2.17| 2.59| -   | -   | -   | -   |
### Figures 90, 91, 94, 95

**Coulometric Measurements on the Upright Cone**

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### Figures 92, 96

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### Figures 93, 97

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Mass Transfer for the Upright Cone

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<td>3.2</td>
<td>4.4</td>
<td>5.1</td>
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</table>
Fig. 1
Various type of Rotating Disc Electrode

type A

type B

type C
Fig. 2. Overall mass transfer rate (\(\text{NuSc}^{1.3}\)) vs. Reynolds number for laminar, transition, and turbulent regimes. Standard deviations for the Schmidt numbers are 31, 41, 26, 38, and 57 for runs 1 to 5. Runs 3 and 4 involve deposition of copper; the others are reduction of ferricyanide.

A typical flow pattern on a up right cone.

Fig. 3
Fig. 4. Mass transfer results in the laminar regime.

Fig. 5. Mass transfer results at higher Reynolds numbers.
Batch reactor

Plug flow reactor

Product

Backmix reactor

continues feed

continuous removal

Fig. 6
The original Hull Cell (1000ml)

267ml Capacity Hull Cell (US). The British Hull Cell is of the same dimension but of greater depth.

The Gilmont and Walton Cell
Modified Hull Cell

Fig. 8

Hanging Hull Cell

Fig. 9
Fig. 12

Bent Cathode Test

Fig. 13

Haring Cell

$E_1$ = Cathode polarization + solution voltage

$E_2$ = Solution voltage

$E_3$ = Anode polarization + solution voltage
Typical Hull Cell test plate
Fig. 16

267 ml. and 534 ml. Hull Cells

<table>
<thead>
<tr>
<th>Current Density (Amp/ sq ft)</th>
<th>1 Amp</th>
<th>2 Amps</th>
<th>Total Current</th>
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<tbody>
<tr>
<td>0</td>
<td>40</td>
<td>60</td>
<td>100</td>
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</tr>
<tr>
<td>50</td>
<td>1</td>
<td>10</td>
<td>10</td>
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</table>

1000 ml. Hull Cell

<table>
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<th>Current Density (Amp/ sq ft)</th>
<th>3 Amps</th>
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</thead>
<tbody>
<tr>
<td>1 Amp</td>
<td>40</td>
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<tr>
<td>2 Amps</td>
<td>30</td>
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<tr>
<td>3 Amps</td>
<td>10</td>
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</table>

Current density scales for the 267 ml, 534 ml and 1000 ml Hull cells. Current density in amp/sq ft.

Fig. 17
Fig. 18
Relationship between Tachometer voltage and rotation rate for the portable rotating rig
Fig. 19

- Pulley
- Tachometer
- Drive shaft
- Electric Motor
- "O"ring
- Brushes
- Bearing Housing
- Rotating Shaft
Concentric Rotation Cell

Fig. 21
Fig. 23

ROTATING CONICAL ELECTRODE CELL.
Fig. 24
U-tube viscometer
Power source

Voltmeter

Resistance

Switch

(+)

RCE

(-)

Cathodes

Fig. 25
Fig. 26
Fig. 27
Fig. 28
A typical polarization curve

Overpotential, $E$

Current, $I$

$E_1$

$E_L$

$E_2$

$I_1$

$I_L$

$I_2$
A typical set-up of the apparatus for obtaining polarization curves.
Fig. 30
Polarization curve for the Hull Cell, (0.014M CuSO₄+0.5M H₂SO₄)
Fig. 31
Polarization curve for the upright cone with the slant height of 57mm. (0.014M CuSO₄ + 0.5M H₂SO₄)
Fig. 32
Polarization curve for the Inverted cone with the slant height of 75mm. (0.014M CuSO₄ + 0.5M H₂SO₄)

Legend
- ■ 0 rpm
- □ 20 rpm
- ● 50 rpm
- ○ 100 rpm
- △ 150 rpm
- × 200 rpm
- ▽ 250 rpm

Total current, amps

Potential, volts
Fig. 33(l)
Polarization curves for the Upright cone.
(0.014M CuSO₄ + H₂SO₄)

Legend
- ■ 0.5cm
- □ 2.3cm
- ● 5.0cm
- ○ 7.0cm

Potential, volts

Total current, amps
Fig. 33(ll)
Polarization curves for the Upright cone.
(0.014M CuSO₄+H₂SO₄)

Legend
- ■ 0.5cm
- □ 2.3cm
- ● 5.0cm
- ○ 7.0cm
Fig. 34
Polarization curves for the Inverted cone at different rotation rates. (0.07M CuSO₄+0.5M H₂SO₄)
Fig. 35
Polarization curves for the Inverted cone at a slant height of 10mm. (0.1M CuSO₄ + H₂SO₄)

Legend

- □ 0 rpm
- □ 20 rpm
- ● 40 rpm
- ○ 60 rpm
- △ 80 rpm
- × 100 rpm
Fig. 36
The effect of time on plating current under potentiostatic control. Vref=1.1v

Legend
- ■ 0rpm
- □ 50 rpm
- ● 100 rpm

Total current, amps

Time, min.
Figure 37
Coulometric measurement on the Hull Cell panel (0.014 M O2)

Figure 38
Coulometric measurement on the Hull Cell panel (0.014 M O2)
Fig. 39
Direct coating thickness measurement on the Hull Cell
by XRF. (0.014M Cu+0.5M H2SO4)

Fig. 40
Direct coating thickness measurement on the Hull Cell
by XRF. (0.014M Cu+0.5M H2SO4)
Fig. 41
Current distribution on 267ml Hull Cell panel

![Graph showing current distribution on 267ml Hull Cell panel]

Legend
- □ 1 amp
- □ 3 amp

Distance from the edge (slant height), cm

Current density, amp/dm²

Fig. 42
Current distribution on 267ml Hull Cell panel

![Graph showing current distribution on 267ml Hull Cell panel]

Legend
- □ 1 amp
- □ 3 amp

Distance from the edge (slant height), cm

Current density, amp/dm²
Fig. 43
Current distribution on the inclined panel
Anode rotating, I=60mA

Fig. 44
Current distribution on the inclined panel
Anode rotating, I=60mA
Fig. 45
Current distribution on the inclined panel
Blocking method, anode rotating, I=0.1A

Fig. 46
Current distribution on the inclined panel
Blocking method, anode rotating, I=0.1A
Fig. 47
Direct coating thickness measurement of the inclined cathode by XRF. (3.6 min, 1 A, rotating anode)

Legend
- 0 rpm
- 200 rpm
- 300 rpm
- 400 rpm
- 500 rpm

Fig. 48
Direct coating thickness measurement on the inclined cathode by XRF. (5 min, 0.5 A, proprietary solution)

Legend
- 300 rpm
- 400 rpm
Fig. 49
Copper deposited on the RCE, AAS method

Fig. 50
Current distribution on the RCE, polarization method, I=0.5A
Fig. 51
Current distribution on the RCE, polarization method, I=1A

Legend
- 400 rpm
- 600 rpm
- 1000 rpm

Fig. 52
Mass transfer relationship for the RCE, (with the cover on)

Legend
- 400 rpm
- 600 rpm
- 1000 rpm

Rotation rate, rpm
Fig. 53
Mass transfer relationship for the RCE

Total current density, amp/dm² vs. Rotation rate, rpm

Legend
- Rot at top
- Rot at bottom

Fig. 54
Limiting current distribution for the Rotating Hull Cell (0.014M Cu + 0.5M H₂SO₄)

Limiting current density, amp/dm² vs. Rotation rate, rpm

Legend
- Top
- Bottom
Fig. 55
Direct coating thickness measurement on the RHC by XRF. (14 min, 1A)

Fig. 56
Direct coating thickness measurement of the rotating cathode by XRF. (14 min, 1A)
Fig. 57
Direct coating thickness measurement on RHC by X.R.F. (3 min., 3A, proprietary solution)

Legend
- 50 rpm
- 200 rpm
- 300 rpm
- 400 rpm

Slant height, cm

Coating thickness, um

Fig. 57
Direct coating thickness measurement on RHC by X.R.F. (3 min., 3A, proprietary solution)

Legend
- 50 rpm
- 200 rpm
- 300 rpm
- 400 rpm

Slant height, cm

Coating thickness, um
Fig. 60
Coulometric measurement on the inverted rotating cone (A, 0.014 M Cl)

Legend
- 0 rpm
- 30 rpm
- 50 rpm
- 100 rpm
- 200 rpm
- 300 rpm

Fig. 61
Coulometric measurement on the inverted rotating cone (3A, 0.074 M Cl)

Legend
- 0 rpm
- 30 rpm
- 50 rpm
- 100 rpm
- 200 rpm
- 300 rpm

Slant height, mm
Coulombs, amp-sec/dm²
**Fig. 64**
Coulometric measurement on the inverted rotating cone (3A, 0.014M C3)

**Legend**
- ■ steel height 12mm
- □ steel height 20mm
- ◇ steel height 30mm
- ○ steel height 40mm

**Fig. 65**
Coulometric measurement on the inverted rotating cone (3A, 0.014M C3)

**Legend**
- ■ steel height 12mm
- □ steel height 20mm
- ◇ steel height 30mm
- ○ steel height 40mm
Fig. 66
Coulometric measurement on the inverted rotating cone (5A, 0.074 O)

Coulombs, amp-sec/dm²

Rotation rate, rpm

Legend
- sleet height 1mm
- sleet height 2.5mm
- sleet height 4mm
- sleet height 6mm

Fig. 67
Coulometric measurement on the inverted rotating cone (5A, 0.074 O)

Coulombs, amp-sec/dm²

Rotation rate, rpm

Legend
- sleet height 1mm
- sleet height 2.5mm
- sleet height 4mm
- sleet height 6mm
Fig. 68
Direct coating thickness measurement on the inverted cone by X.R.F. (15 min., 2A)

Legend
- 0 rpm
- 50 rpm
- 100 rpm
- 200 rpm
- 300 rpm

Fig. 69
Direct coating thickness measurement on the inverted cone by X.R.F. (15 min., 2A)

Legend
- 50 rpm
- 100 rpm
- 200 rpm
- 300 rpm
Fig. 70
Direct coating thickness measurement on the inverted cone by X.R.F. (6 min, 3A)

Legend
- 0 rpm
- 50 rpm
- 100 rpm
- 200 rpm
- 300 rpm

Fig. 71
Direct coating thickness measurement on the inverted cone by X.R.F. (15 min, 2A)

Legend
- 100 rpm
- 200 rpm
- 300 rpm
- 400 rpm
Fig. 72
Direct coating thickness measurement on the inverted cone by X.R.F. (15 min.)

Fig. 73
Direct coating thickness measurement on the inverted cone by X.R.F. (20 min., 1A)
Fig. 74
Direct coating thickness measurement on the inverted cone by XRF (30 min., 0.5A)

Fig. 75
Direct coating thickness measurement on the inverted cone by XRF (20 min., 1.5A)
Fig. 76
Direct coating thickness measurement on the inverted cone by X.R.F. (10 min, 5A, proprietary solution)

Legend
- 50 rpm
- 100 rpm

Fig. 77
Direct coating thickness measurement on the inverted cone by X.R.F. (10 min, 5A, proprietary solution)

Legend
- 50 rpm
- 100 rpm
- 200 rpm
- 300 rpm
Fig. 78
Direct coating thickness measurement on the inverted cone by X.R.F. (10 min., V=0.8 V, Pot. cont.)
Fig. 79
Limiting current distribution on the inverted cone 0.014M Cu+0.5M H₂SO₄, RE at 31mm slant height

Fig. 80
Limiting current distribution on the inverted cone 0.014M Cu+0.5M H₂SO₄
Fig. 81
Limiting current distribution on the inverted cone
0.014M Cu+0.5M H2SO4

Fig. 82
Limiting current distribution on the inverted cone
0.05M Cu+0.5M H2SO4
Fig. 83
Mass transfer relationship for the inverted cone
0.014M Cu+0.5M H2SO4

Fig. 84
Limiting current distribution on the inverted cone
0.1M Cu+0.5M H2SO4
Fig. 85
Limiting current distribution on the inverted cone
0.014M Cu+0.5M H2SO4

Fig. 86
Limiting current distribution on the inverted cone
0.014M Cu+0.5M H2SO4
Fig. 87
Direct coating thickness measurement on the parallel inverted cone by X.R.F. (15 min., 2A)

Legend
- 0 rpm
- 50 rpm
- 100 rpm

Fig. 88
Direct coating thickness measurement on the Inverted cone by X.R.F. (15 min., 2A, using RHC anode)

Legend
- 0 rpm
- 50 rpm
- 100 rpm
Fig. 89
Direct coating thickness measurement on the inverted cone by X.R.F. (3 min., 3A, with RHC anode)

Legend
- 100 rpm
- 200 rpm
- 300 rpm

Coating thickness, um

Slant height, cm
Fig. 90
Coulometric measurement on the upright rotating cone (5 A, 0.0144 M Cl)

Fig. 91
Coulometric measurement on the upright rotating cone (5 A, 0.0144 M Cl)
**Fig. 92**
Coulometric measurement on the upright rotating cone \((54 \times 0.07\text{H O}_2)\)

![Graph showing the relationship between coulombs and slant height at different rpm values.](image)

**Legend**
- ■ 0 rpm
- □ 30 rpm
- ● 50 rpm
- ○ 100 rpm
- △ 200 rpm
- × 300 rpm

**Fig. 93**
Coulometric measurement on the upright rotating cone \((54 \times 0.07\text{H O}_2)\)

![Graph showing the relationship between coulombs and slant height at different rpm values.](image)

**Legend**
- ■ 0 rpm
- □ 30 rpm
- ● 50 rpm
- ○ 100 rpm
- △ 200 rpm
- × 350 rpm
Fig. 96
Coulometric measurement on the upright rotating cone (5A, 0.07 M Cl)

Fig. 97
Coulometric measurement on the upright rotating cone (5A, 0.07 M Cl)
Fig. 98
Limiting current distribution on the upright cone
0.014M Cu+0.5M H2SO4, slant height 38mm

Fig. 99
Limiting current distribution on the upright cone, 0.014M Cu+0.5M H2SO4
Fig. 100
Limiting current distribution on the upright cone
0.014 M Cu + 0.5 M H2SO4

Fig. 101
Limiting current distribution on the upright cone
0.014 M Cu + 0.5 M H2SO4
Fig. 102
Limiting current distribution on the upright cone
0.014M Cu + 0.5M H2SO4

Fig. 103
Limiting current distribution on the upright cone
0.014M Cu + 0.5M H2SO4
Fig. 104
Limiting current distribution on the upright cone
0.014M Cu+0.5M H2SO4

Legend
- 100 mm
- 250 mm
Fig. 105
Direct coating thickness measurement of the upright cone by XRF. (10 min., 2A)

Fig. 106
Direct coating thickness measurement on the upright cone by XRF. (15 min., 1A)
**Fig. 107**
Direct coating thickness measurement of the upright cone by X.R.F. (10 min., 5A, Proprietary solution)

**Legend**
- ■ 0 rpm
- ○ 50 rpm
- □ 100 rpm

**Legend**
- ■ 50 rpm
- ○ 100 rpm
- □ 150 rpm
- ● 200 rpm
Fig. 109
Direct coating thickness measurement on the upright cone by X.R.F. (10 min., V=0.8V, Pot. cont.)

Legend:
- □ 50 rpm, h=0.65A
- □ 100 rpm, h=0.85A
- ● 150 rpm, h=0.95A
- ○ 200 rpm, h=0.95A

Coating thickness, µm

Slant height, cm
Fig. 110
Mass transfer relationship for the Inverted cone (Ref. 14)

Fig. 111
Mass transfer relationship for the Inverted cone

Legend
- 0.01M Cu
- 0.05M Cu
- 0.1M Cu

Legend
- Vref 0.9
- Vref 1.1

Rotation rate, rpm
Total current, amp/dm²
Total current, amp/dm²
Fig. 112
Mass transfer relationship on the upright cone

Fig. 113
Mass transfer relationship for the upright cone (Vref 0.9v)
Fig. 114
Mass transfer relationship for the upright and the inverted cone
Fig. 115
Relationship between rotational speed of the inverted cone and the diffusion layer thickness

Fig. 116
Relationship between rotational speed of the upright cone and the diffusion layer thickness
Fig. 117
Current density distribution on the Hull Cell

Legend
- Theory
- XRF
- XRF, proprietary
- Coulometric
Fig. 118
Mass transfer relationship for the upright and the inverted cones

Legend
- ■ upright cone
- □ Inverted cone
- • Kappesser et al
Fig. 119
Mass transfer relationship for the upright and the inverted cone

Legend
- upright cone
- Inverted cone
- Subramaniyan et al
FIGURE 120: THE ROTATING RING CONE ELECTRODE

- Brushes
- Connecting wires
- Stainless steel
- Insulated material
Plate 1

The electrical connection to the portable rotating rig.

Plate 2

The portable rotating rig.
Plate 3

The experimental set up.

Plate 4

The rotating anode cell.
Plate 5
The rotating null cell.

Plate 6
The upright and the inverted rotating cones.
Plate 7

SEM micrographs of the rotating anode electrode at:

(I) slant height of 7 cm, magnification 1.2k 6k

(II) slant height of 5 cm, mag. 1k 5k

(III) slant height of 3 cm, 1k 5k

(IV) slant height of 1 cm, 1k 5k
Semi micrographs of the inverted cone electrode at:

(I) Slant height 0.7 cm, mag. 1k

(II) Slant height 4.2 cm, mag. 1k

(III) Slant height 6.4 cm, mag 1k
Plate 9

The upright cone electrode

Plating conditions: 3 min., 4 A/dm$^2$

0 rpm

50 rpm
plate 9 cont.

200 rpm

400 rpm
Plate 10

The inverted cone electrode.

Plating conditions: 3 min., 1.5 A/dm²

50 rpm

70 rpm
plate 10 cont.

150 rpm.

200 rpm.