

disasterously inhibit the bacterial action of the sludge digestion process. Even when the metal concentration of the raw sewage is low enough for efficient removal, the metals are still concentrated to levels of 1000 - 2000 parts per million in the sludge discarded by the works and retain considerable potential for the wreaking of environmental havoc elsewhere (6), particularly if the sludge is used as a nitrogenous fertiliser for crops or grazing.

Table 1.1 Metal toxicity - lethal limits for fish

Metal	Minimum Lethal Concentration (ppm)
Cadmium	0,01 - 0,9
Chromium (Cr^{6+})	5
Copper	0,02 - 1,0
Lead	0,1 - 2,4
Manganese	50 - 75
Mercury	0,01 - 1,0
Nickel	1 - 30
Silver	0,004
Zinc	0,3 - 0,5
Cyanide (CN^-)	0,05
Cyanate (CNO^-)	50 - 100

Table 1.2 Toxic limits for metals and cyanide in raw sewage subject to sludge digestion

Metal	Range of toxic limits (ppm) quoted
Chromium	0,05 - 5
Cyanide	0 - 2
Copper	0,2 - 1,0
Iron	5,0
Nickel	0,3 - 5
Zinc	2,0

The response of governments to the worldwide threat has been to introduce increasingly strict standards of effluent control. In the United States the Water Pollution Control Act of 1970 sets the zero discharge of pollutants as a long term national goal and the local and foreign standards given in Table 1.3 indicate current requirements (4,7). The degree of effluent treatment required before discharge may be estimated by comparison of Table 1.3 with Table 1.4 which gives details of metal concentrations in typical electroplating plant effluents (4,7).

Table 1.3 Local and foreign limits for effluent discharge (in ppm)

Material	Discharge to waterways			Discharge to public sewers	
	South Africa	U.S.A.		S. Africa	W. Germany
		New plants	Existing plants		
Arsenic	0,5	0,05	0,1	5	
Cadmium	N/S	0,1	0,2	20-50	
Chromium(Cr^{6+})	N/S	0,05	0,1	N/S	0,5
Chromium(tot)	0,5	0,25	0,5	20-50	4,0
Copper	1,0	0,2	0,5	20-50	3,0
Lead	1,0	0,05	0,1	5-50	
Nickel	N/S	1,0	2,0	20-50	5,0
Silver	N/S	0	0,05	N/S	
Zinc	5,0	0,5	1,0	20-50	5,0
Cyanide	0,5			10-20	

Table 1.4 Typical plating waste concentrations

Material	Concentration (ppm)
Copper	6 - 300
Chromium (Cr^{6+})	0 - 500
Chromium (tot)	0 - 600
Iron	1 - 20
Nickel	0,2 - 32
Cyanide	0,7 - 15

There are therefore considerable moral, legislative and economic reasons for minimising pollution by heavy metals. The treatment is likely to be most effective at the source of the pollution, as discharge of untreated or partially treated effluent into public sewer systems merely creates a secondary source of pollution in the form of discarded sludge.

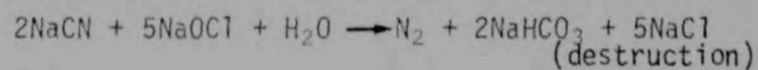
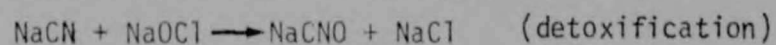
1.2 Techniques for the Removal of Heavy Metal Ions from Solution

1.2.1 Conventional Treatment Method

Electroplating and other wastes containing heavy metals are generally treated in a manner which varies little from place to place (3, 4, 5, 7). The steps of this treatment scheme may be briefly summarised as follows.

- (a) Alkaline chlorination Cyanide wastes must be rendered harmless by oxidation before discharge. The cyanide is completely destroyed with the formation of CO_2 and N_2 or is converted to cyanate which, as may be seen from Table 1.1 is approximately one thousand times less toxic. This conversion or destruction is performed under alkaline conditions using either chlorine gas or hypochlorite.

The reactions with sodium hypochlorite are



- (b) Chromium reduction Hexavalent chromium is not precipitated in the next step of the process and is therefore reduced under acid conditions to the trivalent form. The reducing agents most frequently used are ferrous sulphate, sodium metabisulphite and sulphur dioxide.

- (c) Neutralisation and precipitation After cyanide oxidation and the reduction of hexavalent chromium neutralisation, by means of sodium hydroxide or lime for acid solutions or sulphuric acid for alkaline solutions, takes place. The metal hydroxide precipitates thus produced are then dewatered either by direct filtration or by settling. The resulting sludge (containing 10 - 50% solids) is dried and then is either dumped or incinerated.

The conventional process, which has been proved in numerous applications, has several disadvantages. The handling of the bulky sludge (which initially contains about 99% water) poses considerable problems, as does transport and disposal of the dewatered or dried sludge. A further consideration is that valuable metals are not recovered in a form suitable for recycling. It is also becoming increasingly more difficult to meet effluent discharge standards by precipitation alone, as the limiting concentrations produced by this method are in some cases greater than current or future standards. Considerable attention is therefore being given to alternative treatment methods.

1.2.2. Alternative Treatment Methods

Three membrane processes, namely ultrafiltration, reverse osmosis and electrodialysis are available for the recovery of metal values from waste solutions (7 - 10). Ultrafiltration and reverse osmosis rely on the application of pressure to a dilute solution. This causes the solvent to permeate a membrane and results in the treated solution emerging from the apparatus depleted of solvent and at a considerably higher concentration. The applicability of the reverse osmosis technique to the treatment of certain heavy metal waste solutions is limited by the fact that the membranes

suffer from an inability to reject cyanide complexes which pass through into the treated solution. In the electrodialysis method the reverse situation applies, with the charged solute species being removed from the solution under the action of a potential gradient. Operating costs for electrodialysis tend to be lower than for the other two techniques.

Two further methods which are frequently employed in treating solutions are the closely related techniques of ion exchange and solvent extraction (5, 7, 11). Ion exchange is most applicable to solutions of concentration 200 parts per million or lower while solvent extraction is better suited to the treatment of more concentrated wastes. Capital costs for ion exchange are high but the long term economics do appear to be changing in its favour as a result of the capacity of this technique for water recycling (7).

Cementation of some heavy metals from solution onto scrap iron is still practised (5, 7) but the operation does not produce sufficiently low metal concentrations. A further consideration is that all metals are not completely removed but rather that iron is merely substituted for other, more objectionable, materials. Other less well known methods which may be used are foam fractionation (11), complexing of metal ions with polyelectrolytes (11) and the absorption of metal ions as organo-metallic complexes on activated carbon (8 , 11).

1.2.3 Electrolytic Methods

All the methods of metal ion removal considered thus far, while they might succeed in producing a treated effluent of sufficiently high quality, suffer from a common drawback, namely that in no case can the metal be completely recovered from the waste stream without further treatment. At best a high degree of

concentration is achieved and in the worst case a useless sludge, which itself creates a considerable pollution problem, is produced. This leaves electrolysis as the only method currently capable of producing metal directly from effluents in a form suitable for recycling.

The conventional flat plate electrochemical cell has been used for many years for treating fairly concentrated solutions. Silver is routinely recovered from photographic wastes (5) and in the electroplating industry such cells are used for the oxidation of cyanides and the regeneration of chromic acid (4, 5, 9). Both the electrowinning and electrorefining of nickel make use of such cells. Below concentrations of about two grams per litre, however, plating efficiency drops dramatically and unless the current density is progressively reduced competing reactions eventually dominate.

The poor performance at low concentrations of conventional cells is due to mass transfer limitations. As the current density is increased more and more reactant is consumed, until a point is reached where the concentration of the reactant at the electrode surface becomes zero. The rate of deposition then becomes limited by the rate of diffusion to the electrode and any further increase in current density or decrease in reactant concentration must result in some competing reaction (usually that of hydrogen evolution) becoming significant. The designer of a cell intended for operation at low concentrations must therefore either specify a very low current density (and consequently a very high surface area) or must reduce the resistance to mass transfer by stirring or by some other means.

The packed bed electrode cell, in which the conventional plate electrode is replaced by a three dimensional fixed (12-55, 108-127) or fluidised

(24, 25, 41, 44, 47, 48, 56-62, 128-132) bed of conducting material satisfies both requirements. The surface area per unit volume can be very large and mass transfer from the solution pumped through the bed is enhanced by the very nature of the cell construction. The cell current is supplied to the bed by a current feeder which may be either a backing plate or a wire grid inserted into the bed. Problems associated with the low electrical conductivity of certain dilute solutions are minimised by the very short paths available to the cell current within the particulate electrode.

The packed bed electrode cell, while a fairly recent development, has been used with success in the removal of a number of metals from dilute solution. These include copper (13-23, 132), silver (24 - 27), antimony (28), cobalt (115), lead and mercury (26, 123). The feasibility of electrolytic oxidation of cyanides in this type of cell has also been demonstrated (10, 29, 30). Development of the packed bed electrode technique remains far from complete, however, and many areas of theoretical and practical uncertainty still exist.

1.3 Motivation for this Research Project

With the standards for removal of heavy metals from dilute waste streams becoming stricter the conventional treatment method of neutralisation and precipitation is becoming increasingly less attractive. Of the alternative methods available, only the packed bed electrode technique has the demonstrated potential of meeting both current and future effluent standards and of additionally recovering valuable metals in a convenient form for recycling.

At the time this investigation was started little progress had been made on the subject of electrochemical deposition of metals in packed bed electrodes occurring simultaneously with a competing electrochemical reaction. In particular, with the possible exception of preliminary investigations of lead removal (26, 123), no detailed and systematic

investigation of the removal from dilute solution of a metal less noble than hydrogen had been reported. In such a case the extent of the inevitable hydrogen evolution reaction is of critical importance as the competing reaction can, under certain conditions, completely prevent any removal of the metal itself.

It was therefore decided that the removal of nickel ($E^0-0,23V$) from dilute solution would form the subject of a detailed theoretical and experimental investigation.

A packed bed electrode in which current flow and electrolyte flow are at right angles (flow-by electrode) would be used for the experiments, as this is the electrode configuration most suitable for application in industrial packed bed electrolytic reactors. The objective throughout would be to develop the simplest possible engineering model which would adequately describe the experimental results and which would be suitable for the design of industrial electrochemical reactors for metals removal from dilute solution.

The mathematical model would also be tested against the results of an earlier experimental investigation into copper removal (11).

It is worth noting that an investigation into simultaneous copper and cobalt ($E^0-0,28V$) deposition on a one-dimensional (parallel current and electrolyte flow) packed bed electrode has recently been reported (115). In view of the fact that the analysis was for a simple one-dimensional reactor and the fact that the significant contribution made by the hydrogen evolution reaction to the overall cell reaction was ignored this investigation has little bearing on the present work.

The results reported here have proved to be suitable for application to the design of industrial electrochemical reactors for the treatment of electroplating effluents (108).

1.4 Scope and Objectives of the Investigation

The objectives of this work are thus:

- (a) To investigate the feasibility of nickel deposition from dilute, poorly conducting solutions in a fixed bed electrolytic cell.
- (b) To develop a mathematical model applicable to the two-dimensional flow-by packed bed electrode for use in cell design. The model would be based on conventional electrochemical kinetic theory, would account for multiple electrode reactions and would allow for mass transfer limitations. The general model equations would be simplified wherever possible to provide the most basic model which would still adequately describe the experimental results.
- (c) To determine the values of the electrochemical kinetic parameters which provide the best fit of the mathematical model to the experimental results for the nickel system.
- (d) To independently verify and account for the values of any fitted parameters significantly different from values recorded in the electrochemical literature.
- (e) To further confirm the validity of the electrode model by comparison with the result of Young's investigation (11) of copper removal from strongly supported electrolyte.
- (f) To demonstrate the applicability of the mathematical model to the design of an electrochemical packed bed reactor system.

2 GENERAL THEORY

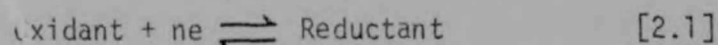
2.1 Basic Electrochemistry

2.1.1 Introduction

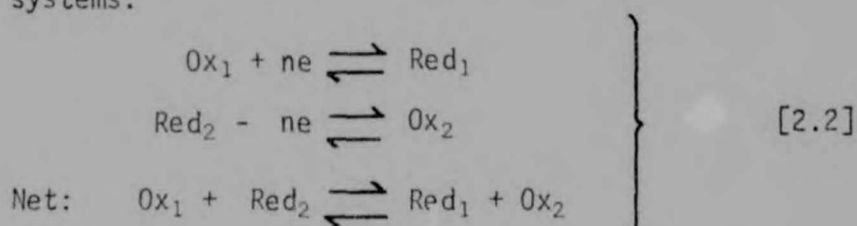
The purpose of this section is to provide a broad outline of basic electrochemistry and electrochemical kinetics. Detailed discussions and derivations are generally not included as these may be found in any of the many textbooks on the subject (12, 63 - 70).

2.1.2 Electrochemical Reactions

Electrode reactions are oxidation - reduction processes of somewhat unusual type which obey the scheme



where ne represents the transfer of n units of electrical charge. The uniqueness of electrochemical reactions lies in the fact that the individual oxidation and reduction processes may be separated and conducted at separate electrodes, at which electrons are either supplied or absorbed. In the general net chemical redox reaction (equation [2.2]), the contributing processes are coupled and it is not possible to isolate either of the two individual systems.

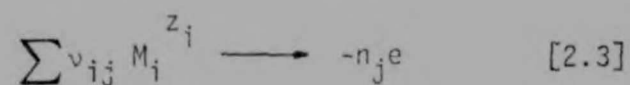


2.1.3 Faraday's Laws and Current Efficiency

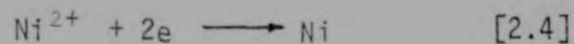
The two laws which express the relationship between the quantity of products formed during electrolysis and the quantity of current passed were discovered by Faraday in 1834. These can be combined in the following statement :

The passage of 96487 coulombs through an electrochemical reactor produces a total of one gram equivalent of products at an electrode. This quantity of electricity is called a Faraday and is designated by F .

Consider the general electrode reaction



in which the stoichiometric coefficients v_{ij} (the coefficient of the component i when involved in the j th reaction) are positive for oxidised components and negative for reduced components. The following example should clarify the usage of this notation. In the reaction



the various values are as follows

$$n_j = 2$$

$$M_1^{z_1} = \text{Ni}^{2+} \quad v_{1j} = 1$$

$$M_2^{z_2} = \text{Ni} \quad v_{2j} = -1$$

For a single reaction j the number of moles of the product i produced by the partial current I_{ij}

flowing for t is given by

$$N'_{ij} = \frac{v_{ij} I_{ij} t}{n_j F} \quad [2.5]$$

If the component i is produced or consumed in more than one electrode reaction the total number of moles produced is

$$N_i' = \sum_j N_{ij}' = \frac{t}{F} \sum_j \frac{\nu_{ij} I_{ij}}{n_j F} \quad [2.6]$$

The total current to the reactor is given by the sum of all the partial currents

$$I = \sum_i \sum_j I_{ij} \quad [2.7]$$

and the current efficiency for the production of a given species i is defined by

$$\xi_i = \frac{\sum_j I_{ij}}{I} \quad [2.8]$$

If this component is only produced or consumed in one of the j reactions the subscript j may be dropped for simplicity and equations [2.8] and [2.5] combined to give

$$\xi_i = \frac{N_i'}{\nu_i i t / nF} \quad [2.9]$$

which indicates how current efficiency may be calculated from experimental measurements of the number of moles produced or consumed.

2.1.4 Electrode Potentials

For the simple case of a metal dipping into a solution of its own ions an equilibrium of the form



will eventually be established at its surface. The metal electrode will adopt a potential whose value is a function of the equilibrium position of reaction [2.10]. This

potential is the equilibrium electrode potential.

The potential at equilibrium and the activities of the species involved may be related by means of the Nernst equation

$$E_{eq} = E^0 + \frac{RT}{nF} \ln \frac{a_{OX}}{a_{RED}} \quad [2.11]$$

This is a thermodynamically derived equation and can only apply when dynamic equilibrium exists and there is no net flow of current. The standard electrode potential E^0 is defined (at unit redox activity : $a_{OX} = a_{RED} = 1$) relative to the standard hydrogen electrode, whose E^0 value is fixed at the arbitrarily chosen value of zero volts.

If a potential $E \neq E_{eq}$ is applied to the electrode the shift away from the equilibrium potential creates a driving force for current flow between the electrode and solution. The difference between the applied potential and the equilibrium potential is the overpotential, η , defined by

$$\eta = E - E_{eq} \quad [2.12]$$

A cathodic current, which conventionally is assigned a negative value, creates a negative overpotential. The reverse applies for an anodic current.

2.1.5 Electrochemical Kinetics

The form of the relationships between overpotentials, ionic concentrations and current densities is the subject of electrochemical kinetic studies. Since 1905 when Tafel first introduced his empirical equation a vast body of literature has grown on the subject : possibly the best single book on the subject is that by Vetter (66) whose results are quoted extensively in this and subsequent sections.

It was implied in the earlier discussion that overvoltage only results if an electrode process is in some way hindered. If this were not the case the electrode reaction would be completely reversible, equilibrium would always be maintained and even the passage of very large currents would not require any potential driving force. A number of different processes, none of which can be perfectly reversible, may take place at an electrode and each gives rise to a specific kind of overpotential.

- (a) The fundamental electrode process is that of charge transfer, in which charge carriers (ions or electrons) are transferred across the electrical double layer at a phase boundary. The rate of charge transfer is determined by the potential difference across the double layer. Any hindrance of this process gives rise to a charge transfer overpotential η_t .
- (b) It is possible that a chemical reaction, occurring homogeneously in the electrolyte or heterogeneously at the surface, may be involved in the electrode reaction. The rate constant of this reaction is, by definition, independent of potential. If the electrode reaction in any way hindered by the progress of the chemical reaction then a reaction overpotential η_R may arise.
- (c) Finally, in the case of metal / metal ion electrodes, there is the crystallisation process in which atoms are incorporated into, or removed from, the crystal lattice. Hindrance of this process leads to crystallisation overpotential η_c .

Reaction and crystallisation overpotentials are either nonexistent or insignificant in the systems investigated in this project and do not feature in any further discussion.

In addition to the partial processes already mentioned there is a transport process involved in the overall electrode reaction. Mass transport of substances formed or consumed in the electrode reaction must take place

between the bulk electrolyte and the electrode surface. Limitations on the rate of mass transfer give rise to a diffusion overpotential η_d .

In electrode kinetics, as in conventional chemical reaction kinetics, the slowest partial reaction is rate-determining for the total reaction. The magnitude of the overpotential is therefore governed by the slowest partial reaction. In particular:

- (a) when there is no limitation on mass transfer the rate of reaction is entirely controlled by charge transfer overpotential and,
- (b) if mass transfer to or from the surface is the slowest process taking place then pure diffusion overpotential will be encountered.

2.1.5.1. Charge Transfer Overpotential

The occurrence of charge transfer overpotential at metal / metal-ion electrodes is caused by the hindrance of the transfer of the metal ions from the electrolyte to the electrode and vice versa. This hindrance is caused by the activation energies for the transfer of charged species across the electrical double layer at the electrode surface. A quasi-thermodynamic treatment of the system may be employed to yield the well known Butler-Volmer equation

$$i = i_0 \left[\exp\left(\frac{\alpha z F}{RT} \eta\right) - \exp\left(-\frac{(1-\alpha) z F}{RT} \eta\right) \right] \quad [2.13]$$

In this equation the current density i is related to the overpotential η by means of the kinetic parameters i_0 and α .

The exchange current density i_0 arises from the fact that at equilibrium there is no net flow of current. The rates of the anodic partial reaction and cathodic partial reaction at an electrode

(the first and second terms within the square brackets respectively) are equal and the relationship

$$i_+ = -i_- = i_0 \quad [2.14]$$

holds. If the potential is shifted away from its equilibrium value one or other of the partial reactions increases in rate and a net current flows in accordance with equation [2.13]. The value of i_0 depends on concentration and temperature. The precise form of the concentration dependence will be given in a later section when the equations for the mathematical model of the packed bed cell are derived.

The transfer coefficient may take on any value between zero and unity but for a single electron transfer process the value is usually of the order $\alpha = 0,5$.

In Figure 2.1 the dependence on the charge transfer overvoltage of the total electrode current density and the partial anodic and cathodic current densities is shown as calculated from equation [2.13] with $\alpha = 0,5$ and $z=1$. It is apparent that the anodic partial current density has dwindled into insignificance by the time a cathodic overpotential of approximately -100 millivolts has been attained. The converse also applies for large anodic overpotentials.

At large cathodic overpotentials ($\eta \ll \frac{-RT}{zF}$) equation [2.13] may therefore be simplified to give

$$\eta = \frac{RT}{(1-\alpha)zF} \ln i_0 - \frac{RT}{(1-\alpha)zF} \ln |i| \quad [2.15]$$

which is of the same form as Tafel's empirical equation

$$\eta = a + b \log|i| \quad [2.16]$$

A plot of the logarithm of the current density against overpotential therefore produces a straight line of slope

$$b = \frac{2,303 RT}{(1-\alpha)zF} \quad [2.17]$$

which, when extrapolated to zero overpotential gives the value of the exchange current density. A typical plot of this type is shown in Figure 2.2. At low current density the relationship between current density and overpotential is no longer exponential and the Tafel curve deviates from the straight line. The current-overpotential relationship at low overpotentials is, in fact, linear and is given by

$$i = i_0 \frac{zF}{RT} \eta \quad [2.18]$$

The linear and exponential sections of the polarisation curve may be clearly distinguished in Figure 2.1

Equation 2.13 only holds for charge transfer in the presence of a large excess of indifferent electrolyte. Under these circumstances the zeta potential of the diffuse double layer at the electrode surface is effectively zero. If the zeta potential across the diffuse double layer is not zero then the current density at an electrode is given instead by (16)

$$i = i_0 \left[\exp \left(\frac{\alpha z F}{RT} \eta \right) - \exp \left(- \frac{(1-\alpha) z F}{RT} \eta \right) \right] \\ \times \exp \left[\frac{-(z_R + \alpha z) F (\zeta - \zeta_0)}{RT} \right] \quad [2.19]$$

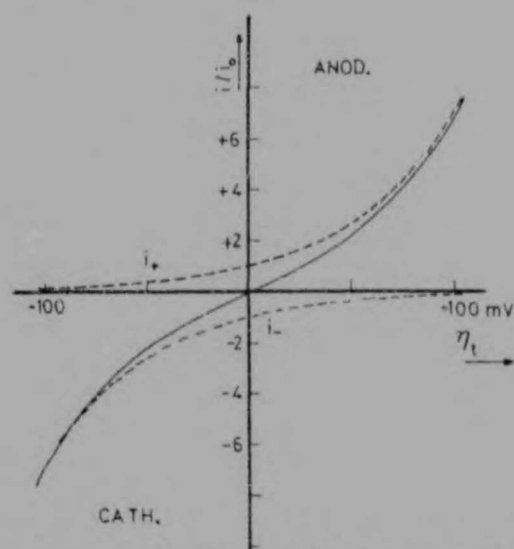


FIGURE 2.1. DEPENDENCE OF TOTAL AND PARTIAL CURRENT DENSITIES ON CHARGE TRANSFER OVERPOTENTIAL.

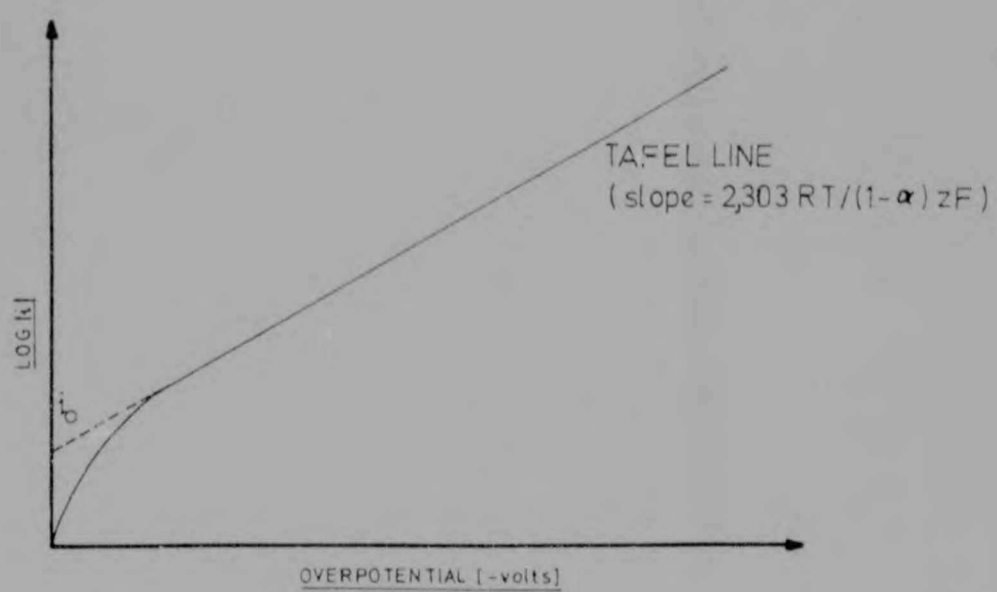


FIGURE 2.2. TYPICAL CATHODIC TAFEL PLOT.

Where z_R is the valency of a complex forming substance in the bulk electrolyte which combines with metal ions as they leave the electrode and ζ_0 is the zeta potential at the equilibrium electrode potential. For metal ions the most common complex forming substance is $(H_2O)_x$ and z_R is therefore usually zero.

The capacity, C_d , of the diffuse double layer is very much less dependent on potential than the capacity of the compact layer immediately adjacent to the electrode. Provided the zeta potential is not too great, the equation

$$\zeta - \zeta_0 = \frac{C_D}{C_d} \eta \quad [2.20]$$

where C_D is the overall capacity of the double layer, is a reasonable approximation. An equation similar to [2.13] in terms of an effective transfer coefficient α^* is obtained on substitution of equation [2.20] into [2.19]. The approximate formula for metal/metal ions with reasonably small zeta potential is therefore

$$i = i_0 \left[\exp \left(\frac{\alpha^* z F}{RT} \eta \right) - \exp \left(- \frac{(1-\alpha^*) z F}{RT} \eta \right) \right] \quad [2.21]$$

$$\text{where } \alpha^* = \alpha \left[1 - \left(1 + \frac{z_R}{\alpha z} \right) \frac{C_D}{C_d} \right] \quad [2.22]$$

The charge transfer overpotential of an electrode reaction in the absence of a large excess of indifferent electrolyte may thus be treated in a similar manner to that in strongly supported electrolyte provided the distinction between α and α^* is noted.

It should be noted, however, that changes in double layer properties generally have a more pronounced effect on the exchange current density than on the transfer coefficient.

2.1.5.2 Diffusion Overpotential and Limiting Current

Diffusion overpotential appears when the supply of reactants at the electrode or the removal of the reaction products is rate determining when current flows.

It is a well known fact that a laminar layer of liquid is formed at a solid surface, regardless of whether the liquid is stirred or not. In an electrode reaction the substances which react electrochemically at the surface must diffuse through this layer, the thickness of which may vary from $\delta = 0,05$ cm in stagnant solution to as little as $\delta = 0,001$ cm in a system which is vigorously stirred.

For strongly supported electrolytes, in which migration effects are negligible, transport across the diffusion layer can only take place if a concentration gradient exists. The flux is given by Fick's first law

$$N_i = -D_i \frac{dC_i}{dx} \quad [2.23]$$

where D_i (cm^2/sec) is the diffusion coefficient and $\frac{dC_i}{dx}$ ($\text{mol}/\text{cm}^3 \text{ cm}$)

is the concentration gradient. Combination of this result with Faraday's law (equation [2.5]) gives, with due consideration to sign

$$i \frac{v_i}{nF} = -D_i \frac{dC_i}{dx} \quad [2.24]$$

where i is the current density (amp/cm^2). At steady state and in the absence of homogeneous chemical equilibria within the diffusion layer the flow of any component to or from the surface is a

constant. A linear concentration gradient may be assumed and equation [2.24] may be rewritten as

$$\frac{i v_i}{nF} = D_i \frac{c_i - \bar{c}_i}{\delta} \quad [2.25]$$

where c_i is the concentration immediately at the electrode surface and $\bar{c}_i$ is the concentration in the bulk electrolyte just outside the diffusion layer.

The magnitude of the concentration gradient is proportional to the current density. The concentration gradient attains its maximum value when the substance is completely depleted at the surface ($c_i = 0$); the maximum current which corresponds to this complete depletion of the reacting component is known as the limiting current density

$$i_{d,i} = - \frac{nFD_i}{v_i \delta} \bar{c}_i \quad [2.26]$$

The electrode reaction can take place no faster than the rate determined by this limiting current density. If a higher current is forced through the electrode the potential of the electrode will change to such an extent that another electrode process will take place at the current density $i - i_d$. A typical polarisation curve for an electrode reaction with mass transfer limitation is given in Figure 2.3.

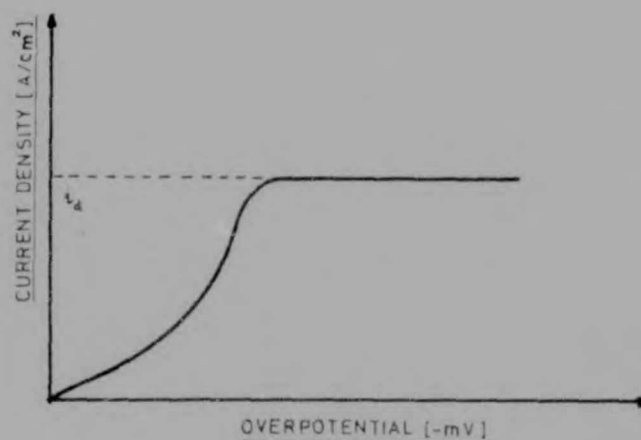


FIGURE 2.3. TYPICAL POLARISATION CURVE SHOWING LIMITING CURRENT DENSITY.

For the general electrode reaction the total diffusion overpotential is related to the limiting current densities for each component by

$$\eta_d = \frac{RT}{nF} \sum_i v_i \ln \left(1 - \frac{i}{i_{d,i}} \right) \quad [2.27]$$

Thus far consideration has only been given to the movement of ions through the diffusion layer under the influence of a concentration gradient. In principle the influence of an electric field on the movement of the ions must also be taken into account. This field arises as the result of the limited conductivity of the diffusion layer or of the need to maintain electroneutrality within the layer and gives rise to an additional migration current which is superimposed on the diffusion current. A large excess of an indifferent electrolyte minimises the electric field within the diffusion layer by causing the transport numbers of the reacting components to

become very small.

In the absence of a large excess of indifferent electrolyte Nernst's ionic mobility equation applies.

$$\frac{i v_i}{nF} = -D_i \left(\frac{\partial c_i}{\partial x} + \frac{z_i c_i F}{RT} \frac{\partial \phi}{\partial x} \right) \quad [2.28]$$

where $\frac{\partial \phi}{\partial x}$ is the potential gradient within the

diffusion layer. A further condition is that electroneutrality be maintained

$$\sum_i z_i c_i = 0 \quad [2.29]$$

When equations [2.28] and [2.29] are applied to an overall reaction, $(m+1)$ equations are obtained (for the concentrations c_1 to c_m of the reacting components and for the potential ϕ) which may be solved for the $(m+1)$ unknowns. In the case of a substance which does not appear in the overall reaction (such as the indifferent electrolyte) equation [2.28] still applies with $v_i = 0$ and may be integrated with respect to x from 0 to δ to give

$$c_i = \bar{c}_i \exp \left(- \frac{z_i F}{RT} \Delta \phi \right) \quad [2.30]$$

Equations [2.28] to [2.30] are general equations whose integration in special cases leads to solutions for the complicated diffusion conditions within the layer. Such a calculation is given in Appendix F for a 2:2/1:2 electrolyte (e.g.

$\text{NiSO}_4/\text{Na}_2\text{SO}_4$) and the results are plotted in Figure 2.4. The superimposed effect of ionic migration leads ultimately, in the absence of any indifferent electrolyte, to a limiting diffusion

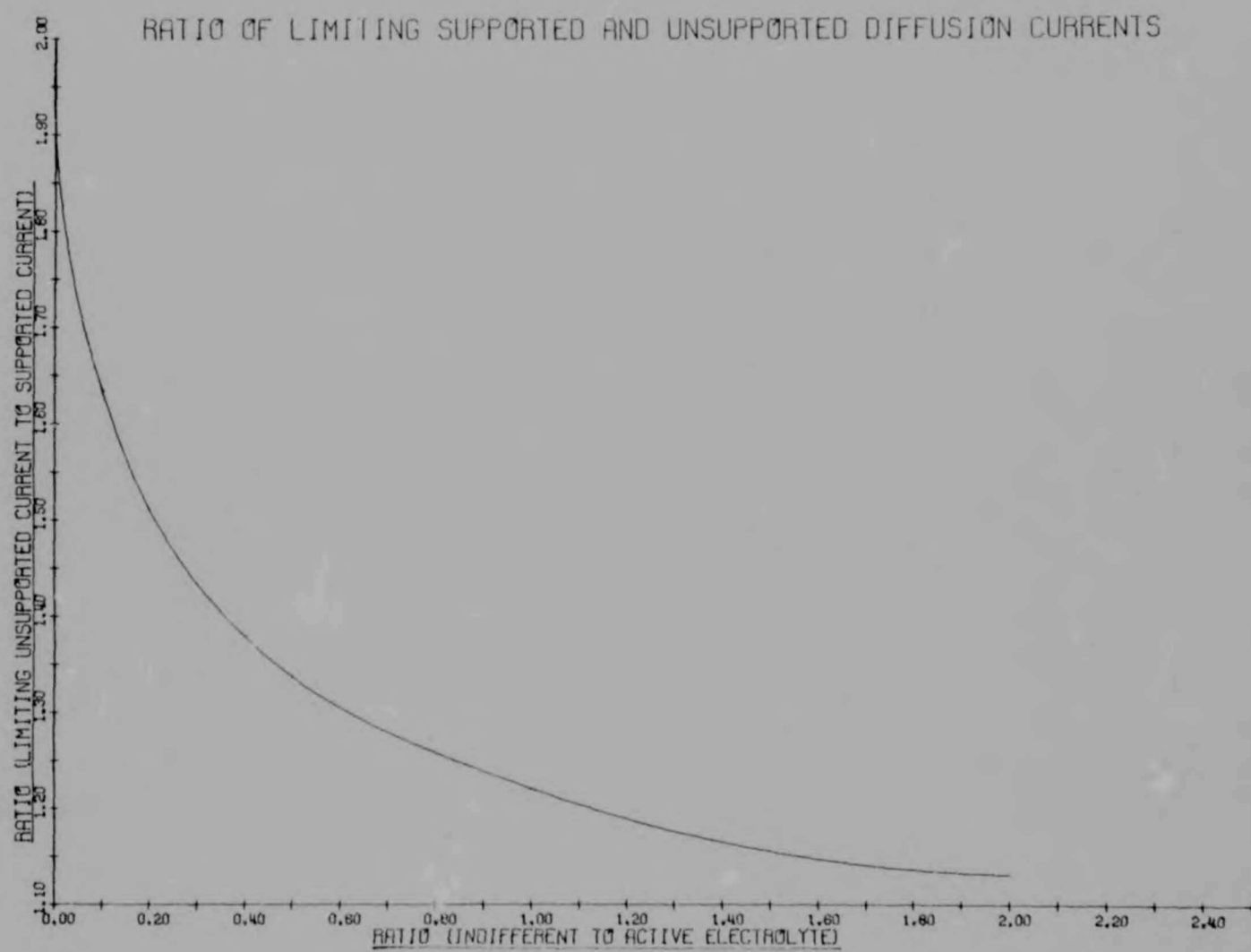


FIGURE 2.4. EFFECT OF MIGRATION ON LIMITING CURRENT DENSITY.

current density which is twice that predicted by equation [2.26] for a strongly supported electrolyte. A relatively small concentration of supporting electrolyte (of the same order as that of the reacting species) has a dramatic effect on the influence of the electric field in the diffusion layer: under these circumstances the limiting current is reduced from 2.0 times to a value of only 1.22 times the limiting current density in very strongly supported electrolyte.

2.1.5.3 Electrochemical Kinetics of Multiple Electrode Reactions

Typical polarisation curves for simultaneous reactions, in this case for metal deposition occurring simultaneously with hydrogen evolution, are given in Figure 2.5. The partial current density for metal deposition is limited by the rate of mass transfer to the electrode: this is generally not the case for the hydrogen reaction for which mass transfer limitations are often less significant. In Figure 2.5 the metal is represented as being less noble than hydrogen and it may be seen therefore that at the minimum potential for metal deposition hydrogen evolution has already been initiated, so that the current efficiency for metal deposition must inevitably be less than unity. For the deposition of a more noble metal on the other hand, there is a range of cathodic overpotential in which only that reaction takes place with one hundred per cent efficiency.

According to the principle of additive combination of all partial processes (first formulated by Wagner and Traud (71)) the total current density is the sum of all the partial current densities. The electrochemical kinetics of the individual reactions are not altered in any fundamental way as the result of the simultaneous occurrence of

other processes. Such changes as might occur (such as, for example, alterations in the nature of the surface by the deposition of a dissimilar metal) may be accommodated by small variations in the kinetic parameters α and i_0 .

A summary of the available electrochemical kinetic data for the systems of interest to this investigation is given in Appendix G. Data on transport properties are also included in this Appendix.

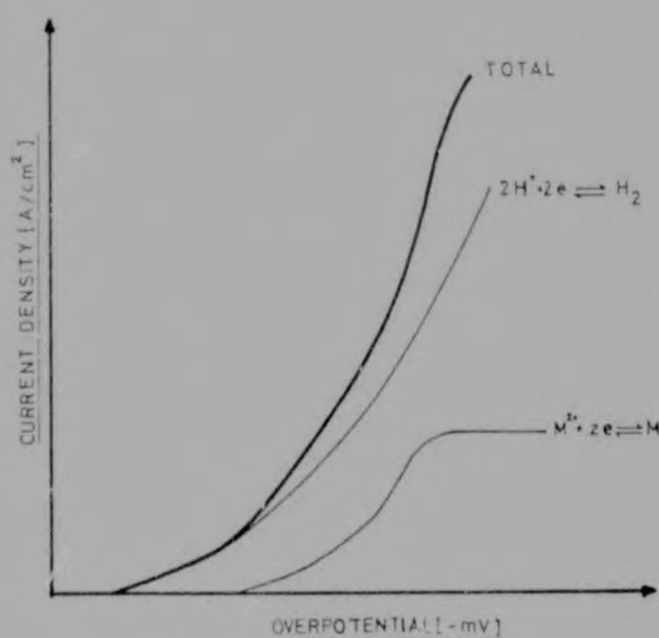


FIGURE 2.5. POLARISATION CURVES FOR MULTIPLE ELECTRODE REACTIONS.

2.2 Fixed Bed Electrode Literature Survey

2.2.1 Introduction

The conventional flat-plate electrochemical cell has many well established applications in electrochemical techniques involving the treatment of concentrated electrolyte solutions (68). At low concentrations of the electrochemically active species however, mass transfer limitations become increasingly more significant and acceptable current efficiencies and space-time yields can no longer be achieved with the conventional apparatus. The cell designer is therefore forced to consider alternative approaches for the treatment of very dilute solutions. Such design approaches generally include mass transfer enhancement (obtained by increasing the relative velocities of electrolyte and electrode) and increased surface area to volume ratios (usually by means of novel cell geometries).

One approach which has been adopted, and which forms the subject of this investigation, is to replace the plate electrode by a three dimensional packed bed of conducting material (11-55, 108-127). This is not a particularly novel concept as such electrodes have been mentioned in work dating back a number of decades and even into the last century (39, 42, 62, 133-135). Some authors have, in fact, drawn attention to the dubious novelty of certain subsequent patent claims (9, 41, 62).

Comparative data for a large number of cell designs are given in Table 2.1 (41, 72). The limiting current values are estimates for a 0.01 molar solution ($n = 2$). In the case of packed and fluidised bed electrodes the limiting current values are related to the projected plane current feeder area: the values related to the actual bed surface area are of the order of six milliamperes per square centimetre.

Author Dardis K A

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