A noticeable difference from the corresponding results for the nickel cell is that the overpotentials and potential gradients shown in Figure 5.24(a) are much smaller. As the metal undergoing reduction is now more noble than hydrogen and as the reaction can penetrate further into the bed on account of the higher solution conductivity, there is a complete reversal in the side of the bed at which the major overpotential changes take place. These now occur at the face adjacent to the current feeder \((X = 1)\) and relatively large overpotential changes here are accompanied by considerably smaller changes at \(X = 0\).

As the copper concentration falls so does the limiting partial current density for this reaction. The partial current density for the hydrogen evolution reaction must therefore increase if the cell current is to remain the same. This increase can only be achieved at a more cathodic overpotential, as may be observed in the profiles plotted in Figure 5.24(a). The combined effect of the increased overpotential and reduced limiting current density, caused by decreasing copper concentration, on the local current efficiency profiles is shown in Figure 5.24(b).

The total current density profiles of Figure 5.25, particularly at the higher copper concentrations, are much flatter than those for nickel reduction and indicate a far greater penetration of the electrochemical reactions into the bed. The values of the limiting current densities for copper reduction show the expected decline with falling copper concentration, and at 6.5 parts per million the partial current density for copper reduction is at its limiting value over the entire thickness of the bed.

Similar behaviour may be observed in Figures 5.26 and 5.27 for varying flowrates at constant copper concentrations. The overpotential and local current efficiency profiles react in the same way to changes in the limiting current density for copper reduction, which in this case is now influenced by changes in the flowrate instead of in the copper concentration.
FIGURE 5.25 . CURRENT DENSITY PROFILES FOR COPPER REMOVAL SHOWING THE EFFECT OF VARYING COPPER CONCENTRATION.
FIGURE 5.26. OVERTOTENTIAL AND LOCAL CURRENT EFFICIENCY PROFILES FOR COPPER REMOVAL SHOWING THE EFFECT OF VARYING FLOWRATE.
FIGURE 5.27. CURRENT DENSITY PROFILES FOR COPPER REMOVAL SHOWING THE EFFECT OF VARYING FLOW RATE.
5.4 Validity of Assumptions

The validity has already been discussed in earlier sections of the assumptions made in deriving the mathematical model. Some aspects have, however, not been considered and these form the subject of this section.

It might be expected that a model which, in essence, treats the porous electrode as a superposition of two continua will fail when a length characteristic of the microstructure becomes comparable to a length characteristic of the electrode as a whole (34). The particle diameter/bed thickness ratios of 0.58 and 0.28 in the electrodes used for nickel and copper removal respectively, do indicate that such a model, when applied to the results reported in this investigation, will be stretched to its limits. The effects of bed anisotropy, wall effects and channelling are indeed significant and have been discussed in the appropriate sections. The mathematical model does, nevertheless, still provide a good fit to the experimental results for both nickel and copper removal from dilute solution.

Catholyte transport through the packed bed electrode was assumed to take place by plug flow, with complete lateral mixing and negligible axial dispersion. This is a valid approximation for turbulent flow in reactors of length greater than approximately fifty times the particle diameter (133). In both experimental cases considered in this work the Reynolds numbers ranged from 35 to 408, which is well above the value of \( Re = 10 \) at which well developed turbulent flow already exists (52, 121), and the length/diameter ratio ranged from 320 to 445, thus satisfying the requirements of the plug flow assumption.

Further support for the assumption of negligible axial dispersion is furnished by the work of Sioda (49) and of Ateya and Austin (53) who have found that significant axial diffusion takes place only at values of a dimensionless parameter \( \frac{D}{uy} \) (the reciprocal of the Peclet number) greater than \( 10^{-3} \sim 10^{-2} \). The corresponding values for the lowest flow-rates in the nickel and copper cells were approximately
$4 \times 10^{-2}$ and $3 \times 10^{-4}$ respectively, clearly indicating that axial diffusion and dispersion effects may be neglected for the purposes of this investigation.

A further assumption was made that the length of the electrode in the direction of solution flow is such that the amount of reaction taking place does not greatly influence the solution concentrations and that the concentrations might therefore be taken as uniform throughout the electrode. This assumption can never be entirely valid as long as any reaction at all is taking place. In the case of the copper removal experiments (11) the concentration changes over the length of the electrode were up to fifty per cent of the initial value at the entrance to the cell. In the nickel experiments the concentration changes ranged from less than one part per million, at low current and high flowrate, to about forty per cent of the initial value under conditions of low flowrate and high current density. Significant pH changes also took place between entry and exit during nickel removal runs, as may be seen from the experimental results given in Appendix A. Certain errors must therefore have been introduced by taking the mean of the inlet and outlet concentrations as applying throughout the cell when fitting the mathematical model. The concentration changes were generally much smaller, however, than the extreme values mentioned above. Since the fit of the model in the case of larger current changes is not much different to the fit where the assumption of uniform concentration is most nearly true, it may still be assumed that any errors caused by the averaging of concentrations are not excessively great.

In the numerical solution of the model equations it was assumed that the effective matrix phase conductivity is much greater than the effective solution phase conductivity and that the $\frac{1}{c}$ term can be dropped from the expression
b = \left( \frac{1}{2} + \frac{1}{3} \right). If it is assumed that the electrical conductivity of the bed particles, whether copper or nickel coated, is approximately equal to that of the pure lead substrate then the specific conductivity ratios for the experiments were

\[ \frac{\sigma_0}{\kappa_0, \text{max}} = \frac{4.35 \times 10^{-1} \, \text{ohm}^{-1} \, \text{cm}^{-1}}{0.8 \times 10^{-1} \, \text{ohm}^{-1} \, \text{cm}^{-1}} = 5.4 \times 10^7 \]

Nickel : \[ \frac{\sigma_0}{\kappa_0, \text{max}} = \frac{4.35 \times 10^{-1} \, \text{ohm}^{-1} \, \text{cm}^{-1}}{0.8 \times 10^{-1} \, \text{ohm}^{-1} \, \text{cm}^{-1}} = 3.41 \times 10^6 \]

Copper : \[ \frac{\sigma_0}{\kappa_0, \text{max}} = \frac{14.0 \times 10^{-2} \, \text{ohm}^{-1} \, \text{cm}^{-1}}{3.1 \times 10^{-2} \, \text{ohm}^{-1} \, \text{cm}^{-1}} \]

Even when allowance is made for the effect of bed voidage on the effective specific conductivities, by means of one of the many expressions which are available \((91)\), the bed conductivity is still vastly greater than the solution conductivity and the assumption is well justified. In view of the high matrix conductivities the assumption of a negligible potential drop in the matrix phase is also justified, although small potential drops have been observed \((45)\) with beds of bronze or graphite \(\sigma_0 = 7.3 \times 10^{-2} \, \text{ohm}^{-1} \, \text{cm}^{-1}\) plated with nickel and gold.

It was pointed out earlier that existing data for hydrogen evolution on nickel indicate that limiting current effects are only likely to become noticeable at current densities greater than approximately 1.0 A/cm². As may be seen from the current density profiles presented earlier in this Chapter, the maximum experimental values for the local current densities were approximately \(10^{-1} \, \text{A/cm}²\) for nickel and \(10^{-2} \, \text{A/cm}²\) for copper removal, thus justifying the assumption of negligible limitations on the rate of the hydrogen evolution reaction.
5.5 Application of the Porous Electrode Model to a Reactor System

5.5.1 Introduction

The purpose of this section is to show how the one dimensional mathematical model for the porous electrode may be used to predict the performance of an integrated flow system which incorporates a packed bed electrochemical reactor. The system might operate on a once-through basis, or there might be continual recirculation of solution as was the case for the program of nickel removal experiments.

The second case, that is a system with recirculation of the catholyte, has been chosen for demonstration purposes as there are experimental results available for comparison with the theoretical predictions. The aim is to show how the model may be used to reproduce the concentration versus time, current efficiency versus time and pH versus time curves measured in an actual experimental run (Run 13). The induction period during which the mean catholyte pH was less than pH 4 is not considered as definite information on the value of the kinetic parameter $k_2$ is not available in this range. From pH 4 upwards the value of $k_2$ at any intermediate pH is calculated from a cubic spline curve fitted to the data points of Figure 5.7.

Appropriate simplifying assumptions are made wherever necessary and certain approximations are introduced, particularly with regard to hydrogen ion transport processes through the anion exchange membrane dividing the anode and cathode compartments of the cell. A rigorous treatment of diffusion and migration through the membrane is outside the scope of this investigation, as this in itself would probably provide sufficient material for a complete research project.

In view of these uncertainties a rather crude numerical solution is used in solving the reactor system equations but a good correspondence with the experimental results is still obtained.

5.6.2 Development of the Equations and Computer Program for the Reactor System

The flow system is shown in Figure 5.28 and the electrochemical reactor is shown schematically in Figure 5.29.
FIGURE 5.28. GENERAL FLOW ARRANGEMENT IN THE REACTOR MODEL.

FIGURE 5.29. SCHEMATIC REPRESENTATION OF A SECTION OF A PACKED BED ELECTROLYTIC REACTOR.
This system of batch electrochemical reactor with continuously recirculating electrolyte has been the subject of rigorous analyses by Pickett (12, 159, 160) and Walker and Wragg (161). These authors point out that the form of the equations used in this section and also in Chapter 3 are only strictly valid for the case of a) Reservoir volume >> Reactor volume.

b) Small conversion per pass.

In the experimental runs for nickel removal the volume ratio in (a) above ranged from 31 to 99 (generally the latter) and conversion per pass was generally less than 20%. The conditions for the use of simplified forms of the concentration-time expression for the reactor system are therefore well satisfied and application of the equations in this work should lead to results of quite acceptable engineering accuracy.

The investigations mentioned above were concerned only with single reactions conducted at limiting current density, with an explicit concentration dependence for the electrochemical reaction rate. Such analytical solutions for the complex kinetics of the multiple electrode reactions encountered during the process of nickel removal from dilute solution are not possible and recourse must be made to a numerical calculation scheme.

Even though a number of processes are involved in the overall side reaction (see Table 5.3), the hydrogen ion concentration-time relationship may be formulated as if the only side reaction is that of hydrogen evolution, since the Faraday's law expression for hydrogen ion reaction is identical for all the partial processes.

A component mass balance for the catholyte yields

\[
\frac{dC_{Ni,0}}{dt} = \frac{51}{2F} \quad \text{[5.10]}
\]

\[
\frac{dC_{H,0}}{dt} = \frac{(1-c)1 + N_H}{F} \quad \text{[5.11]}
\]

Where \( V \) is the system volume, \( C_{Ni,0} \) and \( C_{H,0} \) (mol/l) are the bulk concentrations of \( \text{Ni}^{2+} \) and \( \text{H}^+ \) respectively.
and \( N_H \) (mol/Sec) is the rate of back migration of hydrogen ions from the anode compartment to the cathode compartment. The anion exchange membrane serves to prevent any loss of \( \text{Ni}^{2+} \) ions to the anolyte.

Component mass balances over the packed bed reactor give

\[
\frac{Q}{60} (c_{N,0} - c_{N,1}) + \frac{I_\xi}{2F} = 0 \quad [5.12]
\]

\[
\frac{Q}{60} (c_{H,0} - c_{H,1}) + \frac{I(1-\xi) + N_H}{F} = 0 \quad [5.13]
\]

Provided \( \xi \) and \( N_H \) can be calculated these equations are sufficient to define the concentration versus time performance of the reactor system. The current efficiency depends on the concentrations of both species and for the purposes of numerical calculation the concentration changes of the components may be approximated by

\[
\frac{dC_{N,0}}{dt} = \frac{C_{N,0}(t+\Delta t) - C_{N,0}(t)}{\Delta t} \quad [5.14]
\]

\[
\frac{dC_{H,0}}{dt} = \frac{C_{H,0}(t+\Delta t) - C_{H,0}(t)}{\Delta t} \quad [5.15]
\]

for a sufficiently small time interval \( \Delta t \).

Provided also that the concentration changes over the reactor or section of the reactor are not too great, the effective current efficiency for the entire reactor may be calculated at the mean concentrations

\[
\xi_N = \frac{C_{N,0} + C_{N,1}}{2} \quad [5.16]
\]

\[
\xi_H = \frac{C_{H,0} + C_{H,1}}{2} \quad [5.17]
\]
The logic diagram for calculation of the reactor system is given in Figure 5.30. Stepwise calculations are made at small time increments, with the results for the end of the preceding time interval being used to start the calculation for a new interval.

At the start of any interval the current efficiency at the end of the previous interval is used in equations [5.10] and [5.11] to calculate \( \frac{dC_{H_2}^0}{dt} \) and \( \frac{dH_2O}{dt} \). The bulk concentrations at the mid-point of the new time interval are then estimated by using these values of the concentration gradients in equations [5.14] and [5.15] for \( \Delta t' = \Delta t \). With inlet concentrations to the reactor at the mid-point of the time interval now known, these concentrations and an estimated current efficiency are then applied to calculate outlet concentrations using equations [5.12] and [5.13].

The estimates of the inlet and outlet concentrations to the reactor at the mid-point of the interval are used to calculate \( \xi_N \) and \( \xi_H \). The current efficiency at these mean concentration values may then be calculated by means of the computer program for solution of the porous electrode equation (Appendix C). The calculated value is compared with the assumed value used in the preceding calculations and if the two current efficiencies are in close enough agreement the bulk concentrations at the end of the current interval are calculated and the entire process is then repeated for the next time interval. Initially, however, the current efficiencies are usually not in close enough agreement. The latest calculated value is therefore used as a new estimate and the entire cycle of calculation of concentrations at the interval mid-point, calculation of reactor outlet concentrations, calculation of mean concentrations and revision of the current efficiency estimate is repeated a number of times until successive current efficiency estimates do not change significantly.

A problem arises in defining the value of \( N_H \), which according to the general flux equation is given by

\[
N_H = \frac{D_H \phi_C H - Z_H u_H FC_H}{\Delta} [5.18]
\]
Figure 5.3 Simplified logic diagram for calculation of the performance of a complete system incorporating a packed bed electrochemical reactor.
where the terms on the right hand side are for diffusion and migration respectively. The diffusion term may be calculated by means of the results in Appendix E, but the migration term is less tractable as information on the potential gradient across the anion permeable membrane is not available.

An empirical approach was therefore adopted for prediction of the hydrogen ion back migration rate. This approach is based on the consideration that the diffusion component of the flux is likely to remain relatively constant over the range of interest and that variations in the $\gamma_2$ term are the controlling influence on the value of $N_H$. According to equation [E.3] the diffusion fluxes at an anolyte pH of 1.6 and at catholyte pH values of 4 and 8 are

$$\text{pH} 4: J_H = 1.927 \times 10^{-9} \text{ moles/cm}^2 \text{ sec}$$

$$\text{pH} 8: J_H = 1.935 \times 10^{-9} \text{ moles/cm}^2 \text{ sec}$$

As these values differ by less than 0.5 per cent the assumption of a constant diffusion flux is quite justified.

The potential gradient across the membrane is governed, in part, by the conductivity of the solution phase. An expression of the form

$$N_H = F_1 - F_2 < \text{[5.19]}$$

may therefore be used as an approximation to equation [5.18]. This is a purely empirical equation which merely indicates that as the conductivity increases the rate of back migration decreases. The $F_1$ term bears no relation to the diffusion flux as such. A better representation of reality might possibly be given by an equation of the form

$$N_H = F_3 + F_4 < \text{[5.20]}$$

but this was not tried as equation [5.19] gave quite acceptable results. The values of the empirical constants are determined by mass balances at the start and end of the experimental run chosen for demonstration purposes. The
back migration rate is thus given by

\[ N_H = 9.74 \times 10^{-5} - 0.144 \times \text{mhos/sec} \]

At \( \kappa = 400 \times 10^{-6} \) mhos per centimetre the total rate of hydrogen ion back migration is thus \( 4 \times 10^{-5} \) moles/sec of which pure diffusion, according to equation \[ E.3 \], accounts for only about ten per cent.

### 5.5.3 Results and Discussion

A comparison of the calculated curves with the experimental data points from Run 13 is given in Figure 5.31. An excellent correspondence with the concentration versus time curve is obtained over a period of thirty five minutes and there is good agreement with the current efficiency versus time curve. As might be expected from the approximate nature of the hydrogen ion back migration term the pH results show a fair degree of deviation, particularly towards the end of the fitted range. Even though the current efficiency is fairly insensitive to pH changes, as may be seen in Figure 5.20, these deviations do have a cumulative effect and result in slightly low values being calculated for the overall current efficiency and these, in turn, result in slightly high values for the bulk nickel concentration.

The reactor model failed in the 50-52.5 minute time interval when a negative value was calculated for the hydrogen ion concentration at the reactor outlet. As may be seen from Figure A.13 the actual outlet pH was greater than 8.0 by this time. The model attempts to calculate this very small outlet concentration by taking the difference between two much larger terms, namely the hydrogen ion back migration term and the hydrogen ion consumption term and, since the value of the back migration rate is only approximate, it is not surprising that the computer program can no longer cope.

The agreement between the flow system model and the experimental results is nevertheless more than acceptable over a considerable period of time, particularly when the admitted crudities inherent in the iterative solution are taken into
FIGURE 5.31. COMPARISON OF POINTS CALCULATED BY THE REACTOR MODEL WITH THE EXPERIMENTAL RESULTS OF RUN 13.
account. Where rapidly changing hydrogen ion concentrations are not a factor, such as in the very strongly acidic system used for copper removal, even better results should be obtained. Under such circumstances the mass balances need only be written for the principal reactant and an even simpler solution is obtained.

A similar iterative treatment may obviously be applied to an electrochemical reactor operating on a once-through basis. Instead of a time increment being used the solution would be based on incremental length elements, with the outlet concentrations from one element forming the inlet concentrations to the next. The current efficiency calculated for one element is the natural choice as an initial estimate for the current efficiency in the next. The actual value is then obtained by iteration, with each successive iteration yielding a value closer to the true current efficiency.
6. FUTURE WORK

This investigation has shown up a number of areas of interest in which future work would be justified.

(a) This investigation has demonstrated that a complicated set of side reactions, involving both hydrogen evolution and oxygen reduction, may be lumped and described over a wide range of conditions by Pseudo-Tafel electrochemical kinetics. The finer details of the exact combinations of species concentration, polarisation and mass transfer coefficient for which this description is valid were, however, not investigated and could well form the basis for a future detailed study. A similar approach might also have application to other systems of practical interest.

(b) The lack of detailed information on the rates of diffusion and migration of hydrogen ions from the anode compartment to the cathode compartment through the anion exchange membrane resulted in problems being encountered in the application of the mathematical model to the prediction of the performance of a complete system for nickel removal. If adequate information were available, rigorous calculations for systems incorporating electrochemical reactors of the type used in this investigation operating with one or both of the streams at near-neutral conditions would then be possible. Such knowledge would also then allow the determination of the conditions required to establish and hold the pH at an optimum value.

(c) Mathematical models of varying complexity have been developed to the point where the performance of a packed bed electrode may be predicted with reasonable confidence for a number of systems and over a wide range of operating conditions. The optimisation of complete systems incorporating packed bed reactors has, however, received little or no attention. Investigations in which the interplay between packed bed electrochemical reactor design considerations and the associated capital, pumping and power costs is examined
with a view to producing economical and efficient designs for given duties would therefore be of considerable benefit.

(d) The extension of the packed bed electrolytic technique to the removal of other noxious materials from dilute solution should be investigated. In particular, the oxidation of cyanides has already been demonstrated as feasible, although little fundamental work of a theoretical nature has been reported, and the technique could probably be applied to the removal of chromium from dilute solutions and for the reduction of hexavalent chromium to the less toxic trivalent form.

(e) Direct measurement of kinetic parameters in packed bed electrodes using the analytical solution described in section 2.3.4 should be possible, provided sufficient care is taken in the selection of experimental conditions which would allow accurate potential measurements to be made.

(f) Although the experimental conditions of this investigation maintained the concentration of the evolved hydrogen below the saturation level for the electrolyte and thus prevented the formation of gas bubbles in significant quantities, considerable gas bubble formation could take place in other packed bed electrode systems. This would influence many of the system parameters, including solution effective conductivity, effective interfacial areas and mass transfer coefficients and therefore constitutes an aspect of porous electrode theory which warrants further investigation.
Successful removal of nickel from dilute solutions in a flow-by porous electrode is possible. Even though nickel is less noble than hydrogen this process takes place at acceptable current efficiencies in the 1 - 100 parts per million range of nickel concentrations. Current efficiencies ranging as high as 0.8 were measured and nickel concentrations of less than two parts per million were readily attained.

The experimental investigation was conducted in very weakly supported solution in order to duplicate as closely as possible the conditions encountered in treating dilute industrial effluents.

The defining equations for a one-dimensional mathematical model for multiple reactions in a packed bed electrode have been derived. New analytical and numerical solutions of the porous electrode equation are described and applied to experimental results for nickel and copper removal from dilute solution. By means of certain reasonable assumptions the applicability of the one-dimensional flow-through model can be extended to include two-dimensional flow-by porous electrodes.

The mathematical model provides a good fit to the experimental results for nickel removal from dilute, weakly supported solution. It was demonstrated that the complex simultaneous side reactions involving hydrogen evolution and oxygen reduction could be lumped into a single overall side reaction, which may be described by pseudo-Tafel electrochemical kinetics with an accuracy adequate for engineering applications.

The validity of the model is further demonstrated by the fact that values of the electrochemical kinetic parameters for the overall side reaction, first predicted by the fit of the mathematical model to the experimental data, were later confirmed by independent experiments at a rotating disc electrode.

Apparent anomalies in the value of the initially determined electrode kinetics underline the importance of obtaining experimental electrode kinetic data for practical industrial electrochemical reactor designs, since impurity effects can be
of considerable significance in an industrial application.

(d) The nickel removal efficiency is strongly dependent on flow-rate, cell current and nickel concentration. Little sensitivity to pH is exhibited above pH6 while very low efficiencies are obtained below pH3.5. Between pH3.5 and pH6 the current efficiency exhibits a gradually weakening pH dependence. A further prediction of the model, which was confirmed by experimental observation, is that an optimum cell current for maximum nickel removal efficiency exists for any given combination of the flowrate and the concentrations of the reacting species.

(e) Existing results for copper removal from dilute solutions in sulphuric acid can also be fitted by means of the numerical solution of the porous electrode equation for multiple reactions. Excellent correspondence is obtained between the experimental results and the predictions of the mathematical model. The calculated values of the electrochemical kinetic parameters for this system are in very close agreement with the existing data available in the electrochemical literature.

(f) The use of the mathematical model in predicting the performance of an integrated flow system incorporating a packed bed electrochemical reactor has been demonstrated. The multiple reaction system treated in this example is more complex than any yet reported in the literature and, although a number of justifiable approximations are made, a good correspondence is still obtained with the set of experimental data chosen for the demonstration.

A full size pilot unit was designed using the engineering model developed in this investigation and has been successfully applied to the removal of heavy metals from mixed industrial effluents.

(g) The limited value of increasing the thickness of porous electrodes in the direction of current flow has been conclusively demonstrated by many investigators. A number of current density profiles are presented in this work which clearly show the limited effectiveness of the interior regions of the electrode and which also demonstrate the strong effect of solution conductivity on the thickness of the electrochemically active part of the electrode.
REFERENCES


42. German Patent 954056 (1956)


