Main reaction:

\[
i_{\text{R}} = i_{R,\text{ref}} \exp \left( \frac{a_{\text{R}}F}{RT} \eta - \frac{C_{\text{R,ref}}}{C_{\text{R}}} \exp \left[ \frac{-a_{\text{R}}F}{RT} \eta \right] \right)
\]

Side reaction:

\[
i_{\text{S}} = i_{S,\text{ref}} \exp \left( \frac{a_{\text{S}}F}{RT} \left( \eta - \Delta U \right) \right) - \exp \left[ \frac{-a_{\text{S}}F}{RT} \left( \eta - \Delta U \right) \right]
\]

in which the \( \Delta U \) term takes into account the difference between the rest potentials of the main and side reactions. Provided therefore that the value of \( \eta \) does not become much more positive than about \(-100\) millivolts the assumption, made in deriving the mathematical model, of a negligible anodic contribution to the partial current densities remains valid.

5.2.4.1 Effective of Variations in Nickel Concentration on Cell Performance and Overall Current Efficiency

The effect of varying nickel concentrations on the overpotential profile is shown in Figure 5.9(a) for constant conditions of current, flowrate and \( pH \). With decreasing nickel concentrations the solution conductivity drops rapidly and this has the effect of markedly increasing both the potential gradient and the potential itself at the free solution interface \((X = 0)\). In the 50 - 100 parts per million range the overpotential at the current feeder \((X = 1)\) is virtually unaffected by large changes at the other face of the electrode: as the nickel concentration drops further the effect on the overpotential at the current feeder becomes more marked.

Corresponding current efficiency profiles are given in Figure 5.9(b). All the profiles exhibit a maximum value which corresponds to the position at which the local over-
FIGURE 5.9. OVERPOTENTIAL AND LOCAL CURRENT EFFICIENCY PROFILES FOR NICKEL REMOVAL SHOWING THE EFFECT OF VARYING NICKEL CONCENTRATION.
FIGURE 5.9: OVERPOTENTIAL AND LOCAL CURRENT EFFICIENCY PROFILES FOR NICKEL REMOVAL SHOWING THE EFFECT OF VARYING NICKEL CONCENTRATION.
potential for the limiting current density for nickel deposition has just been reached. At higher potentials the current efficiency inevitably falls as the side reaction, which is not subject to significant mass transfer limitations, becomes predominant. At lower overpotential values the current efficiency is again less than the maximum value, this time as a consequence of the combined effect of different beta values for the main and side reactions and of the \( \exp(n\Delta U) \) term in the partial current density expression for the side reaction, which has a larger value than the \( \exp(n) \) term in the expression for the main reaction.

The effects mentioned in the preceding paragraphs are clearly shown in Figure 5.10, which gives the current density profile for the packed bed electrode at three different values of the nickel concentration and which shows the contributions of the individual partial current densities to the total. It may be seen that the major part of the overall electrode reaction takes place in the section of the electrode immediately adjacent to the free solution interface and that the current at the opposite face of the electrode is smaller by up to three orders of magnitude.

A feature of all the partial current density curves for nickel deposition is the limiting current density plateau at higher values of the overpotential. As may be expected, the values of these limiting currents increase with increasing nickel concentration, from about \( 4 \times 10^{-7} \) amperes per square centimetre at ten parts per million to nearly \( 4 \times 10^{-3} \) amperes per square centimetre at one hundred parts per million. In each case the \( X \) co-ordinate at the start of the limiting current plateau corresponds very closely to that of the maximum of the current efficiency profile in Figure 5.9(b).

The concentration dependence of the overall current efficiency for nickel deposition in the packed bed electrode is illustrated in Figure 5.11 with cell current and catholyte flowrate as parameters. Figure 5.11(a) shows that at lower flowrates the current efficiency is more or less linearly dependent on the nickel concentration. At the larger flowrates
Figure 5.10. Current density profiles for nickel removal showing the effect of varying nickel concentration.
FIGURE 5.11: DEPENDANCE OF THE OVERALL CURRENT EFFICIENCY FOR NICKEL REMOVAL ON THE NICKEL CONCENTRATION.
the current efficiencies are greater as a consequence of the increased limiting current densities for nickel deposition. These curves initially also demonstrate an approximately linear dependence on the nickel concentration but do flatten off considerably once overall current efficiencies in excess of $\xi_{Ni} = 0.8$ are reached.

The concentration dependence of the overall current efficiency at varying currents is less clear cut. The dependence is more or less linear at high cathodic currents whereas lower currents, as may be seen from Figure 5.11(a), result in current efficiencies which are essentially independent of concentration at values greater than about thirty parts per million. The curves also indicate the existence of a current density - concentration relationship which maximises the overall current efficiency.

5.2.4.2 Effect of Variations in Cell Current on Cell Performance and Overall Current Efficiency

Figure 5.12(a) shows the effect of increasing cell currents on the overpotential profile in the packed bed electrode. Because of the limited solution conductivity a rapid rise in the overpotential and in the potential gradient in the section of the bed close to the free solution interface is apparent. At the low current of 1.0 amperes the potential is more or less uniform across the bed. As the current increases there is very little change in the interior of the bed and the major changes are in the region $X = 0$ to $X = 0.2$. In this region the transition between current flow taking place mainly in the matrix phase and current flow in the solution phase takes place, together with the major part of the electrochemical reaction.

The effects of the overpotentials on the local current efficiencies, shown in Figure 5.12(b), are similar to those previously discussed for varying nickel concentration. Maxima are once again apparent at the point in the bed where the limiting current density for the main reaction is first attained.
FIGURE 5.12. OVERPOTENTIAL AND LOCAL CURRENT EFFICIENCY PROFILES FOR NICKEL REMOVAL SHOWING THE EFFECT OF VARYING CELL CURRENT.
The current density profiles in Figure 5.13 show a general upward shift as the cell current is increased. Limiting currents for nickel deposition are reached at five and fifteen amperes but not at one ampere. This observation clearly accounts for the concentration independence at low cell currents which has already been mentioned, since only once the concentration is lowered or the cell current is raised to a point where a limiting current plateau is established can further concentration changes shift the position of that plateau and significantly affect the overall current efficiency of the electrode.

Values of the overall current efficiencies for the packed bed electrode at varying currents are plotted in Figure 5.14 with catholyte flowrate and nickel concentration as parameters. These curves clearly show that optimum cell currents exist for each nickel concentration (as was predicted in the previous subsection) and also show a similar maximum in the current efficiency versus current curves for various flowrates. The implication is therefore that each concentration – flowrate combination is associated with an optimum current which will maximise the overall current efficiency of the electrode.

5.2.4.3 Effect of Variations in Flowrate on Cell Performance and Overall Current Efficiency

Changes in flowrate, as may be seen in Figure 5.15(a), have a relatively minor effect on the potential profile in the packed bed. The changes which do occur may be ascribed to lower limiting currents being obtained for the nickel deposition reaction at the lower flowrates. These, in turn, require higher overpotentials in order to sustain the cell current by means of increased rates for the hydrogen evolution reaction. Once again maxima are observed in the local current efficiency profiles at X co-ordinates corresponding to the start of the limiting current plateaux. As would be expected the values of the maximum current efficiency increase with increasing flowrate, since the mass transfer coefficient and hence the limiting current density also increase with increasing flowrate.

The current efficiency profiles in Figure 5.16 show the
FIGURE 5.13. CURRENT DENSITY PROFILES FOR NICKEL REMOVAL SHOWING THE EFFECT OF VARYING CELL CURRENT.
FIGURE 5.14 - DEPENDANCE OF THE OVERALL CURRENT EFFICIENCY FOR NICKEL REMOVAL ON THE CELL CURRENT.
effect of increasing flowrate on the limiting current density for the nickel deposition reaction. This increases from $1.1 \times 10^{-3}$ amperes per square centimetre at 1.0 litres per minute to $3.3 \times 10^{-5}$ amperes per square centimetre at 8.0 litres per minute and is balanced by a corresponding decrease in the partial current density of the side reaction.

The dependence of the overall current efficiency on the catholyte flowrate is shown in Figure 5.17, in which current efficiency is plotted against flowrate with nickel concentration and cell current as parameters. Except at the lowest flowrates the current efficiency at a nickel concentration of 100 parts per million is independent of flowrate, which indicates that the limiting current density for this reaction has not yet been reached at the higher flowrates. At ten and fifty parts per million there is a gradual increase in current efficiency with increasing flowrate, with the overall value at 8.0 litres per minute being approximately double the value at 1.0 litres per minute. Below a flowrate of 1.0 litres per minute, which corresponds to a Reynolds number of 51, there is a very marked decrease in current efficiency as the transition from turbulent to laminar flow at around $Re = 10$ (52) is approached.

The current efficiency versus flowrate curves of Figure 5.17(b) exhibit a similar behaviour, in that the current efficiencies at 5.0 and 15.0 amperes at 8.0 litres per minute are approximately double their values at 1.0 litres per minute. The current efficiency at 1.0 amperes is essentially independent of flowrate, indicating once again that the limiting current density for nickel deposition at a concentration of fifty parts per million has not yet been reached.

5.2.4.4 Effect of Variations in pH on Cell Performance and Overall Current Efficiency

The pH of the flowing catholyte might be expected to have a twofold influence on the cell performance. The first effect is that changes in pH alter the solution conductivity,
FIGURE 5.15. OVERPOTENTIAL AND LOCAL CURRENT EFFICIENCY PROFILES FOR NICKEL REMOVAL SHOWING THE EFFECT OF VARYING FLOWRATE.
CURRENT DENSITY PROFILES

a - 1.0 l/min

CURRENT DENSITY PROFILES

b - 3.0 l/min

CURRENT DENSITY PROFILES

c - 8.0 l/min

FIGURE 5.16 CURRENT DENSITY PROFILES FOR NICKEL REMOVAL SHOWING THE EFFECT OF VARYING FLOWRATE.
FIGURE 5.17. DEPENDANCE OF THE OVERALL CURRENT EFFICIENCY FOR NICKEL REMOVAL ON THE FLOW RATE.
although these changes, under the near-neutral conditions, of the experimental runs, are of far smaller magnitude than are the variations with changing nickel concentration. The more important influence of pH is on the kinetic parameter $k_2$ for the overall side reaction, which takes on different values throughout the pH range and which changes most rapidly in the range pH4 - pH6.

The combined effect of these two factors on the overpotential profiles and local current efficiency profiles in the packed bed electrode are shown in Figure 5.18. Fairly large increases in the overpotential take place between pH4 and pH5 and between pH5 and pH6, with very much smaller changes being predicted over the remainder of the range. Similar comments apply to changes in the local current efficiencies.

The relative magnitudes and positions of the current efficiency peaks in Figure 5.18(b) are consistent with these variations in conductivity and in the value of $k_2$. In particular, the considerably lower peak value at pH4 is due to the greater extent of the competing side reaction, which results from a considerably larger $k_2$ value for the reaction under acidic conditions. A slightly reduced value of the mass transfer coefficient for nickel deposition by the main reaction has a contributory effect. This lowering of the effective mass transfer coefficient comes about as the result of considering the acid as acting as a supporting electrolyte in the nickel deposition reaction. By means of this assumption, the validity of which is discussed in Appendix C, the results of Appendix F as plotted in Figure 2.4 may be applied to estimating the degree of mass transfer enhancement for the nickel reaction in the weakly supported electrolyte. Even the very small concentration of acid in solution at pH4, as may be seen from Figure 5.19, does have a noticeable effect on the limiting current density which is therefore slightly lower than at the more alkaline pH values.

The effect of varying $k_2$ values shows up most clearly in the values of the partial current density for hydrogen evolution at $X = 0$. Even though the $\text{e}^{\delta_xh}$ term of the partial
FIGURE 5.18. OVERPOTENTIAL AND LOCAL CURRENT EFFICIENCY PROFILES FOR NICKEL REMOVAL SHOWING THE EFFECT OF VARYING pH.
FIGURE 5.19. CURRENT DENSITY PROFILES FOR NICKEL REMOVAL SHOWING THE EFFECT OF VARYING pH.
current density expression at pH8 has a value which is 5.7 times as large as the value at pH4, the simultaneous decrease in $k_2$ results in a partial current density which is only 1.1 times greater.

Values of the overall current efficiency versus catholyte pH are plotted in Figure 5.20 with flowrate, concentration and current as parameters. These curves demonstrate the pH dependence of the current efficiency under a wide range of conditions. As might be expected the dependence is strongest in the range pH4 - pH6, for which the changes in $k_2$ are most pronounced. As the catholyte becomes more alkaline the dependence becomes very much weaker.
FIGURE 5.20. DEPENDANCE OF THE OVERALL CURRENT EFFICIENCY FOR NICKEL REMOVAL ON THE pH.
5.3 Application of the Numerical Solution of the Porous Electrode Equation to the Results for Copper Reduction

5.3.1 Introduction

A modified version of the program used in fitting the mathematical model for the packed bed electrode to the results of nickel removal experiments was used to treat the current efficiency results, given in Chapter 4, for experiments on copper removal in a packed bed electrolytic cell. The modifications made allowance for the different cell geometry, particle size, particle shape and transport properties applicable to the system used in these experiments. The electrolyte was strongly supported (1.0 g/l H₂SO₄) and no allowance was therefore made for any effect of ionic migration on the limiting current density for copper deposition. Complications caused by variations in electrolyte conductivity were also absent.

The process of hydrogen gas evolution from the strongly acidic catholyte was assumed to constitute the only side reaction and mass transfer limitations on the rate of the side reaction were assumed to be insignificant, although subject to the qualifications of section 5.2.2.1. The electrolyte in this case was of far better conductivity and the hydrogen ion concentration considerably higher than was the case in the experimental investigation of nickel removal and it was therefore anticipated that potentials in the cell would remain at levels where dissolved oxygen in solution, by virtue of the extremely small exchange current density for the reduction reaction, would not contribute significantly to the overall side reaction.

5.3.2 Fit of the Model to the Experimental Results

A similar technique to that already described for nickel was used in fitting the model to the results for copper reduction. The electrochemical kinetic data in Appendix G indicate that the cathodic transfer coefficients for both copper reduction and hydrogen evolution are of the order \( \alpha_c = 0.5 \). The kinetic parameters \( \beta_1 \) and \( \beta_2 \) were therefore set equal to each other at
A value of $1.35 \times 10^{-3}$ amperes per square centimetre was chosen, on the basis of the data in Appendix G, for the value of the exchange current density for copper reduction at a reference concentration of 0.5 moles per litre. A quadratic interpolation technique was then used in a search for the value of $k_2$ which minimised a sum of squared errors objective function at the chosen values of $\beta_1, \beta_2$ and $k_1$. The best fit was initially found to be at

$$k_2 = -2.34 \times 10^{-8} \text{ A/cm}^2$$

This value of $k_2$ gave reasonably good fits of the current efficiency versus concentration data (Figure 5.21(a)) but gave a far poorer fit to the efficiency versus flow results (Figure 5.21(b)). It was decided that the correspondence between the model predictions and the experimental results was not good enough and, as the discrepancies were greatest in the case of the flow data, that the effect of variations in the mass transfer coefficient on the fit of the model should also be examined.

Numerous correlations for mass transfer in packed beds are available in the literature. The correlation used in this investigation for the mass transfer coefficient ($\alpha$) is based on a critical assessment of the majority of the available data on mass transfer in packed beds. The form of the correlation is

$$\alpha J_d = 0.765 \text{ Re}^{-0.02} + 0.365 \text{ Re}^{-0.36}$$

where $\text{Re}$ is the particle Reynolds number which may range from 0.01 to 15 000 and $J_d$ is the mass transfer factor

$$\frac{k_m \text{ Sc}_{\alpha}}{\nu_{\gamma}}$$

The data upon which the correlation is based, however, vary over a considerable range, as may be seen in Figure 5.22, which gives values of the mass transfer factor over the
FIGURE 5.21. FIT OF MODEL TO COPPER RESULTS (1.0 \times k_m).
CORRELATION FOR MASS TRANSFER COEFFICIENT

\[ \epsilon D^{0.765 \text{Re}^{-0.32}} + 0.365 \text{Re}^{-0.386} \]

FIGURE 5.22: CORRELATION FOR MASS TRANSFER IN PACKED BEDS.
range of Reynolds number applicable to this investigation. The spread of Reynolds numbers for the flowrates used in the experimental investigations of copper and nickel removal is also indicated in this figure.

It may be seen that many workers have measured values of the mass transfer coefficient that are very much lower than those predicted by equation [5.9] and that the \(0.6\lambda_d\) versus \(Re\) curve still falls within the range of reported measurements. The reasons for the high degree of scatter include uncertainties in the determination of effective particle diameters for non-spherical particles as well as experimental errors due to channelling, back diffusion, and superimposed natural convection.

The packed bed electrode used for copper removal was composed of cylindrical particles with a calculated effective diameter of 0.69 centimeters and had a particle diameter/bed thickness ratio of 0.28. Although this ratio is somewhat better than for the nickel cell, wall effects are still quite significant and could lead to channelling and consequently smaller values of the mass transfer coefficients, such as have been observed elsewhere in thin packed bed electrodes (22,105, 115). The fitting of the packed bed electrode model to the experimental data was therefore repeated using the same procedure as before, but with a reduced mass transfer coefficient based on \(0.6\lambda_d\).

The results of the new fit, which was accepted as definitive, are given in Figure 5.23 and in Tables H.6 and H.7. The fitted value of the remaining kinetic parameter is

\[ k_2 = -2.57 \times 10^{-10} \text{ A/cm}^2 \]

A considerable improvement in the correspondence between the experimental and theoretical results may be noted over that presented in Figure 5.21. The predictions of the packed bed electrode model are now in excellent agreement with the current efficiency versus concentration results and exhibit relatively small deviations from the efficiency versus flow-rate results only at the lower end of the experimental range.
FIGURE 5.23 FIT OF MODEL TO COPPER RESULTS (0.6 × k_m).
5.3.3 Discussion

The values used for the kinetic parameters $\beta_1$, $\beta_2$ and $k_1$ in fitting the porous electrode model to the copper results are based on reliable values from the literature. The value of $k_2$ on the other hand, is obtained in the course of the fitting procedure and it therefore remains to be seen how this calculated value compares with reported experimental measurements.

By definition $k_2$ is given by

$$k_2 = -i_{0S, \text{ref}} e^{-\beta_2 \Delta U}$$  \hspace{1cm} [2.37]

where $\beta_2$ has the assigned value of -19.5 volts$^{-1}$ and $\Delta U$, under the chosen reference conditions ($[Cu^{2+}] = 0.5$ mole/l, $[H^+] = 1.0$ mole/l, $p(H_2) = 1$ atm, $25^\circ C$) has the value

$$\Delta U = 0.000 - (0.330) = -0.330 \text{ volts}$$

The fitted value of the exchange current density is therefore

$$i_{0S, \text{ref.}} = 2.57 \times 10^{-10} \text{ e}^{-0.33}$$

$$= 1.59 \times 10^{-7} \text{ A/cm}^2$$

which is in excellent agreement with the values from the literature given in Table G.4.

As may be seen from Tables H.6 and H.7 the calculated current is within 0.4 - 0.8 per cent of the true value at all the data points. The largest term discarded from the Taylor series in deriving the equations for the numerical solution was found to be between 280 and 2000 times smaller than the next retained term. The discarding of terms in $e_1$ of order 3 and higher is thus quite adequately justified.

A number of profiles are presented in Figure 5.24 for the packed bed cathode under the conditions defined in Table H.6 for the current efficiency versus copper concentration data.
FIGURE 5.24. OVERPOTENTIAL AND LOCAL CURRENT EFFICIENCY PROFILES FOR COPPER REMOVAL SHOWING THE EFFECT OF VARYING COPPER CONCENTRATION.
Author  Dardis K A
Name of thesis  Deposition of Copper and Nickel from dilute solutions in packed bed electrolytic cells  1981

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