JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 104–115

A validated mathematical model for a zinc electrowinning cell

G. W. BARTON, A. C. SCOTT

Department of Chemical Engineering, University of Sydney, NSW 2006, Australia

Received 14 November 1990; revised 27 February 1991

A set of (95) equations forming a dynamic, nonlinear model of an industrial pilot-plant scale zinc electrowinning cell fed with high purity electrolyte is presented. Only the solution of the steady-state model is considered in this paper. Values for unknown model parameters have either been obtained from the literature or else estimated using experimental data taken from the pilot-plant cell. Sensitivity studies showed that uncertainties in the temperature dependency of the zinc and hydrogen reaction exchange current densities and the exchange coefficient for the hydrogen reaction have a major effect on the model predictions. Excellent agreement between predicted and experimental results was obtained, provided that cathodic mass transfer effects were included in the model. Both parameter estimation and solution of the steady-state model were carried out using the SPEEDUP flowsheeting package.

1. Introduction

As 80% of the power requirements for an electrolytic zinc refinery are associated with the electrowinning process, it is economically important to run the cellroom as close to optimum operating conditions as possible. Optimum performance of a cellroom is here taken to mean that the energy required per tonne of zinc produced is minimized. As a first step to achieving this objective for the cellroom at the Electrolytic Zinc Company (EZ), Hobart, Australia, a series of experiments were conducted to investigate the major factors affecting the efficiency of zinc electrowinning [1]. These experiments were conducted in 10 litre cells using a high purity industrial zinc sulphate solution. This paper will describe the development and validation of a steady-state mathematical model that accurately describes these experimental data. The steady-state model is, in fact, a special case (i.e. at steady-state, all time derivatives are equal to zero) of a more general dynamic model of the zinc electrowinning cell. A dynamic model of the pilot-plant cell was developed so that an extended version could be used to look at control problems in the EZ circuit. The extended model and various applications, both steady-state and dynamic, will be described in a latter paper.

Various mathematical models have been proposed for copper electrowinning [2, 3, 4] with the latter two authors also applying their models to nickel electrowinning. However, the only previous model of a zinc electrowinning cell reported in the literature is that by Bryson [5]. In all these cases, the complete equation set comprising mass balances, an energy balance, electrochemical equations and physical property correlations, taking into account all major species in the electrolyte, was not solved. For example, although Bryson presented most of the equations required in a mathematical model of a zinc electrowinning cell, he made no attempt to solve the full model but rather restricted himself to a simpler model comprising only a sub-set of his full equation set.

Before describing our model of a zinc electrowinning cell, it is worth pointing out that the reason for developing such a model was to provide EZ personnel with a tool that would allow them to quickly assess changes in plant design and/or operation. The aim was, therefore, to produce a "practical", predictive model. Consequently, the more important (in terms of current efficiency or power required per tonne of zinc produced) a mechanism was known to be, the greater the effort that was made to ensure a realistic description within the model. The less important a mechanism was, the greater the amount of simplification that was felt to be justified.

2. Model development

Before developing the mathematical model, a decision had to be made as to which chemical species to include. The two most important species in the electrolyte are the zinc and hydrogen ions. Both are involved in reactions occurring at the cathode:

$$\mathrm{Zn}^{2+} + 2e^- = \mathrm{Zn(s)} \qquad E_e^0 = -0.763\,\mathrm{V} \tag{1}$$

$$2\mathrm{H}^+ + 2e^- = \mathrm{H_2(g)} \qquad E_e^0 = 0.0\,\mathrm{V} \tag{2}$$

The E_e^0 values given above are the standard equilibrium potentials for the two half reactions. In this paper, symbols will be defined where they are first used in the model development.

Generally, about 90% of the cathodic current is used in the production of zinc by Reaction 1.

"Pure" EZ electrolyte also contains significant amounts of the ions manganese, magnesium and ammonium. Typical values for these three com-

0021-891X/92

ponents are 12.2, 4.6 and 2.5 g dm^{-3}, respectively. Although these ions have no effect on current efficiency, they do affect the solution conductivity, and hence the cell voltage. Therefore, these three ions are included in the pure solution model. The other two species modelled are the sulphate ion and water. The sulphate ion is the major negative ion in the electrolyte and is required in the model to maintain electrical neutrality. Water is included since it is the solvent, and a water balance is required in order to calculate the concentrations of all ionic species. Water also takes part in an anodic reaction:

$$H_2O = 2H^+ + 2e^- + 0.5O_2(g) \qquad E_c^0 = -1.229\,V \qquad (3)$$

The reaction of manganese ions at the anode (resulting in the deposition of a manganese dioxide scale) is assumed to be negligible.

Combining Reactions 1 and 3 gives the desired overall reaction:

$$Zn^{2+} + H_2O = Zn(s) + 2H^+ + 0.5O_2(g)$$
$$E_c^0 = -1.992\,V \qquad (4)$$

The equations comprising the mathematical model of the zinc electrowinning cell can be divided into five main sections, each of which will be examined in turn;

(i) mass balance equations
(ii) energy balance equations
(iii) thermodynamic and kinetic relations
(iv) electrochemical equations
(v) conductivity and density correlations.

Wherever possible, a mechanistic modelling approach is employed with equations used to mathematically describe actual processes occurring in the cell. In some cases this is not possible. For example, the model includes correlations based on experimental data to describe electrolyte conductivity and density (see § 2.5 and § 2.6).

2.1. *Mass balance equations*

Each of the seven chemical species assumed to be present in the electrolyte is the basis of a dynamic (i.e. unsteady-state) mass balance of the following form:

$$[\text{ACCUMULATION}] = [\text{INPUT}] + [\text{GENERATION}] - [\text{OUTPUT}] - [\text{CONSUMPTION}] \qquad (5)$$

Once again, note that at steady-state, all derivatives in the model equal zero.

The ACCUMULATION term is the time derivative of the amount of a species in the cell. For a constant volume, well-mixed cell (such as that used by Scott [6]) the accumulation term is given by

$$[\text{ACCUMULATION}] = V\frac{dy_j}{dt} \qquad (6)$$

where V = cell volume (in dm^3) and y_j = concentration of species j in the cell electrolyte (M).

The INPUT term is the product of the volumetric flowrate of the feed (Q_f in dm^3 s^{-1}) and the concentration of species j in the feed (x_j in M).

$$[\text{INPUT}] = Q_f x_j \qquad (7)$$

The GENERATION term accounts for any reactions where one of the chemical species is produced:

$$[\text{GENERATION}] = r_{\text{gen},j} \qquad (8)$$

where $r_{\text{gen},j}$ = rate of generation of species j (mol s^{-1}).

Of the seven species in the model, the only one generated is H^+ which is produced at the anode by Reaction 3.

The OUTPUT term accounts for the amount of species j leaving the system. There are two possible outputs, the overflow of the spent solution leaving the cell and any loss due to evaporation:

$$[\text{OUTPUT}] = Q_d y_j + r_{\text{evap},j} \qquad (9)$$

where Q_d = volumetric flow leaving the cell (dm^3 s^{-1}) and $r_{\text{evap},j}$ = rate of evaporation of species j (mol s^{-1}).

Evaporation is included in the model, since in industrial cells it can cause a reduction in electrolyte volume and hence a corresponding increase in species concentrations. However, its effects are small (of the order 2–3% of the water entering a cell evaporates at cell temperature 35° C) and a simple mathematical description is quite adequate. It is assumed that only water is lost through evaporation, with the rate of evaporation being described by an equation similar to that presented by Coulson and Richardson [7]:

$$r_{\text{evap},H_2O} = K_{\text{evap}} A_s (p_s - p_w) \qquad (10)$$

where K_{evap} = evaporation constant (mol m^{-2} s^{-1} (mm Hg)$^{-1}$), p_s = saturated vapour pressure (mm Hg), p_w = working (or atmospheric) vapour pressure (mm Hg), and A_s = surface area of the air-electrolyte interface (m^2).

The saturated vapour pressure for industrial strength electrolytes was estimated using the Antoine equation given by Perry and Chilton [8] for a 10% sulphuric acid solution:

$$\log_{10}(p_s) = 8.925 - 2259/T \qquad (11)$$

where T is the solution temperature (K). The relatively small amount of evaporation, together with the dominant effect of temperature (compared with variations in electrolyte concentrations) mean that Equation 11 is quite adequate for the purposes of this model.

The CONSUMPTION term accounts for any reactions which consume one of the chemical species. Zn^{2+} and H^+ are consumed at the cathode (see Reactions 1 and 2) while H_2O is consumed at the anode (see Reaction 3):

$$\text{CONSUMPTION} = r_{\text{con},j} \qquad (12)$$

where $r_{\text{con},j}$ = consumption rate of species j (mol s^{-1}).

Thus, combining Equations 6, 7, 8, 9 and 12 for each species gives a total of seven mass balance equations of the form

$$V\,(\mathrm{d}y_j/\mathrm{d}t) = Q_f x_j - Q_d y_j - r_{\mathrm{evap},j} + r_{\mathrm{gen},j} - r_{\mathrm{con},j} \qquad (13)$$

The anodic reaction produces two moles of hydrogen ions for every mole of water decomposed. This fact is expressed in the final mass balance equation

$$2r_{\mathrm{con,H_2O}} = r_{\mathrm{gen,H^+}} \qquad (14)$$

2.2. *Energy balance equations*

The unsteady-state energy balance for an electrochemical reactor can be derived in an analogous manner to the species mass balance Equation 5:

$$MC(\mathrm{d}T/\mathrm{d}t) = M_{\mathrm{in}}C(T_f - T_{\mathrm{ref}}) - M_{\mathrm{out}}C(T - T_{\mathrm{ref}}) - \sum(\Delta H_i r_i) + IV_{\mathrm{cell}} + q_{\mathrm{loss}} \qquad (15)$$

The term on the left hand side is the time rate of change of enthalpy of the cell contents. In deriving this equation, both the total amount of material in the cell (M in mol) and the heat capacity of the electrolyte (C in J mol^{-1} K^{-1}) have been taken as constant. The first two terms on the right hand side represent the enthalpy flows into and out of the cell, respectively. Note that the inflow (M_{in} in mol s^{-1}) and the outflow (M_{out}) are not assumed to be equal. T_{ref} is an arbitrary reference temperature (K), required as enthalpy is not an absolute quantity. The next term on the right hand side represents the net enthalpy change brought about by all reactions occurring in the cell (ΔH_i is the specific enthalpy change, in J mol^{-1}, for the ith reaction, occurring at a rate r_i in mol s^{-1}). The term IV_{cell} is the heat input rate arising from the passage of a current I (amps) through a cell with a total voltage drop V_{cell}. The final term in Equation 15 accounts for all heat losses from the cell. In the 10 litre cells being modelled here, there were no cooling coils and it was assumed that negligible heat loss occurred through the walls. Thus, the only heat loss (in J s^{-1}) is that associated with the evaporation of water which may be calculated using

$$q_{\mathrm{loss}} = r_{\mathrm{evap,H_2O}} H_{\mathrm{evap}} \qquad (16)$$

where H_{evap} is the specific heat of evaporation for water (J mol^{-1}).

2.3. *Thermodynamic and kinetic relations*

The basis of all thermodynamic calculations for electrochemical processes is the Nernst equation [9] which relates the equilibrium potential (E_e volts) for a half reaction in which n electrons are transferred, to the cell temperature and the activities of the oxidised (a_0) and reduced (a_r) species:

$$E_e = E_e^0 + (RT/nF)\ln(a_0/a_r) \qquad (17)$$

In the above equation, R is the gas constant (equal to 8.314 J mol^{-1} K^{-1}) while F is the Faraday constant (equal to 96 500 C mol^{-1}).

For the zinc electrowinning process, this equation is used to calculate the equilibrium potential for the two cathodic and the anodic half reactions (i.e. Equations 1, 2 and 3).

$$E_{\mathrm{e,Zn}} = -0.763 + (RT/2F)\ln[a_{\mathrm{Zn^{2+}}}/a_{\mathrm{Zn}}] \qquad (18)$$

$$E_{\mathrm{e,H_2}} = 0.0 + (RT/F)\ln[a_{\mathrm{H^+}}/(a_{\mathrm{H_2}})^{0.5}] \qquad (19)$$

$$E_{\mathrm{e,H_2O}} = 1.229 + (RT/2F)\ln[(a_{\mathrm{H^+}})^2(a_{\mathrm{O_2}})^{0.5}/a_{\mathrm{H_2O}}] \qquad (20)$$

The above three equations express the equilibrium potentials in terms of the activities of each species. The oxygen gas, hydrogen gas and zinc metal are each essentially at their standard state and are, thus, assigned a unit activity [10]. The activity of water was assigned a constant value of 0.9. This is equivalent to the activity of water in a 1.0 M $ZnSO_4$, 1.5 M H_2SO_4 electrolyte solution [11]. For the solute species (Zn^{2+} and H^+), the activity is related to the concentration (y_j) by the simple relationship

$$a_j = \gamma_j y_j \qquad (21)$$

where γ_j is known as the activity coefficient and accounts for departures from ideal behaviour. Since the activity equals the product of a concentration and an activity coefficient, the problem becomes one of determining the single ion activity coefficients. Very little work on single ion activity coefficients has been published, with the only reported estimates for the zinc ion being those of Hurlen and Breivik [12]. In this electrowinning cell model, the following (constant) estimates were used for the required single ion activity coefficients:

$$\gamma_{\mathrm{Zn^{2+}}} = 0.1$$

$$\gamma_{\mathrm{H^+}} = 0.5$$

These values were chosen based on calculations carried out using the CSIRO-SGTE Thermodata System [13] for the $ZnSO_4$–H_2SO_4–H_2O system at 25° C. The calculation method used is based on the theory of Whitfield [14] and the interaction data of Pitzer and Kim [15]. The estimated value for the zinc ion agrees well with those calculated by Hurlen and Breivik. The zinc equilibrium potential is, in fact, quite insensitive to the zinc ion activity coefficient with a change from 0.1 to 0.2 only causing a change of about 10 mV (at a 1 M zinc ion concentration).

If the cathodic and anodic processes were perfectly reversible thermodynamically, it would be possible to pass a large current through the reactor without the electrode potentials deviating from their equilibrium values. However, in actual processes an electrode deviates from the equilibrium potential and is said to be polarised. The magnitude of this deviation is known as the overpotential (η), and is defined as the difference between the working electrode potential (E) and the equilibrium potential (E_e). For the zinc electrowinning cell, the overpotentials (in volts) are:

$$\eta_{Zn} = E_c - E_{e,Zn} \qquad (22)$$

$$\eta_{H_2} = E_c - E_{e,H_2} \qquad (23)$$

$$\eta_{H_2O} = E_a - E_{e,H_2O} \qquad (24)$$

where E_c and E_a are the cathodic and anodic working potentials, respectively.

A number of different kinetic equations have been proposed for electrochemical reactions. The most useful of these is the Tafel equation which relates the overpotential (η) to the rate of reaction expressed in terms of the electrode current density (i in A m^{-2});

$$i = i_0 \exp(-\alpha \eta z F/RT) \qquad (25)$$

It can be shown that the Tafel equation is accurate to within 1% (relative to the more complex Butler-Volmer equation) provided that the following condition applies:

$$|\eta| > 0.118/n \qquad (26)$$

In Equation 25, α is a transfer coefficient, z is the number of electrons transferred in the rate determining step and i_0 is the exchange current density. The latter is an important kinetic characteristic of a charge transfer process expressing the fact that a dynamic equilibrium exists at an electrode surface when there is no net current flow or chemical change in the cell. The exchange current, i_0, is most commonly evaluated using [16],

$$i_0 = nFk_0 y_{ob}^{(1-\alpha)} y_{rb}^{\alpha} \qquad (27)$$

where y_{ob} and y_{rb} are the concentrations of the oxidised and reduced species respectively, in the bulk electrolyte, while k_0 is the rate constant at the standard equilibrium potential [9].

For the zinc deposition reaction, the concentration of metallic zinc (the y_{rb} in this case) is constant and thus may be incorporated into the rate constant along with the electron transfer number and the Faraday constant to give,

$$i_{0,Zn} = k'_{0,Zn} [Zn^{2+}]^{(1-\alpha_{Zn})} \qquad (28)$$

noting that the zinc ion is the oxidised species in Reaction 1. The modified standard rate constant ($k'_{0,Zn}$) is strongly dependent on temperature and can be modelled using an Arrhenius type equation,

$$k'_{0,Zn} = A_{0,Zn} \exp(-\Delta G_{Zn}/RT) \qquad (29)$$

where $A_{0,Zn}$ is a pre-exponential (or frequency) factor and ΔG_{Zn} is an activation energy. Similarly, the exchange current density relation for the hydrogen gas reaction can be simplified by taking the concentration of hydrogen gas (the y_{rb} in this case) as constant and incorporating it into the rate constant along with the electron transfer number and Faraday's constant to give,

$$i_{0,H_2} = k'_{0,H_2} [H^+]^{(1-\alpha_{H_2})} \qquad (30)$$

where the temperature dependence of k'_{0,H_2} is analogous to Equation 29.

The Tafel equation is based on the assumption that the rate determining step is the charge transfer process at the electrode surface and not mass transfer to or from the surface. For both reactions in which gas is evolved, hydrogen at the cathode (see Equation 2) and oxygen at the anode (see Equation 3), the charge transfer kinetics are slow and the assumptions of the Tafel equation are valid [10]. For the zinc deposition reaction (see Equation 1), however, an equation derived by Hurlen [17] which incorporates both Tafel kinetics and mass transfer effects was found to be more suitable:

$$i_{Zn} = i_{0,Zn} [((i_{lc,Zn} - i_{Zn})/i_{lc,Zn}) \exp(-\alpha_{Zn} \eta_{Zn} z_{Zn} F/RT) - \exp((1 - \alpha_{Zn}) \eta_{Zn} z_{Zn} F/RT)] \qquad (31)$$

In this equation, the limiting current density (i_{lc}) is given by,

$$i_{lc} = mnFy_{ob} \qquad (32)$$

where m is the cathodic mass transfer coefficient (in m s^{-1}) and y_{ob} is the concentration of Zn^{2+} in the bulk electrolyte. The cathodic mass transfer coefficient in a zinc electrowinning cell is primarily a function of the micro-convective effects at the cathode surface caused by the evolution of hydrogen bubbles on the zinc deposit [29, 30, 31]. Janssen [18] modelled this effect using the following equation,

$$m = K(V_{H_2})^{0.3} \qquad (33)$$

where K is a constant and V_{H_2} is the volumetric rate of hydrogen evolution (in dm^{3}s^{-1}) which may be calculated from Equation 39 and the ideal gas law, given the pressure p (in atm):

$$V_{H_2} = r_{gen,H_2} RT/p \qquad (34)$$

2.4. *Electrochemical equations*

One of the basic design equations for an electrochemical reactor is the electroneutrality condition [19].

$$\sum_{i=1}^{N} (n_i y_i) = 0 \qquad (35)$$

where n_i and y_i are the number of electrons transferred per molecule and the electrolyte concentration for the ith (of a total N) species, respectively. In most applications of the model, the concentrations of all the cations are specified and Equation 35 is used to calculate the concentration of the anions (i.e. the sulphate ion). Electroneutrality within the cell is maintained by equating the total cathodic current (I_c) to the total anodic current (I_a);

$$I_c = I_a \qquad (36)$$

The total current passing through an electrode is the sum of the currents arising from all reactions occurring on its surface. For the zinc electrowinning model this may be written as,

$$I_c = i_c A_c = (i_{Zn} + i_{H_2}) A_c \qquad (37)$$

$$I_a = i_a A_a = i_{H_2O} A_a \qquad (38)$$

where i_{Zn}, i_{H_2} and i_{H_2O} are the current densities (in $A\,m^{-2}$) associated with Reactions 1 to 3, respectively, and A_c and A_a are the cathode and anode areas (in m^2). As mentioned previously, it is assumed that the manganese reaction on the anode is negligible.

Faraday's Law describes the relationship between the jth reaction rate (r_j in $mol\,s^{-1}$) and the quantity of electricity consumed;

$$r_j = i_j A/nF \qquad (39)$$

In the above equation, i_j is the current density associated with the jth reaction, A is the electrode area and F is Faraday's constant.

The total cell voltage (V_{cell} volts) is calculated by summing the voltage drops for the electrodes and across the solution between the electrodes ($E_{solution}$),

$$V_{cell} = |E_c| + |E_a| + E_{solution} + E_{loss} \qquad (40)$$

where E_c and E_a are the cathode and anode potentials, respectively. E_{loss} is a measured correction term which accounts for the voltage loss across the busbars, contacts and the manganese scale on the anode surface, and in industrial cells is generally of the order 0.1 to 0.2 V. $E_{solution}$ is related to the electrolyte conductivity (σ in $S\,m^{-1}$), the electrode gap width (Δb in m) and the current density;

$$E_{solution} = \Delta b\, i_c/\sigma \qquad (41)$$

The electrolyte conductivity is calculated using Equation 45. In the 10 litre cells being modelled here, the small amount of gas being produced at the electrodes can be shown [6] to have a negligible effect on electrolyte conductivity and hence on the solution voltage drop. The electrode gap also varies slightly as the deposit forming on the cathode grows. However, this is a small effect which could be adequately modelled using a gap width typical of that which occurs halfway through a deposition cycle.

The final electrochemical equations employed in the model are those describing the average current efficiency and the electrical energy used by the process per tonne of zinc produced.

The current efficiency (ε in %) for the deposition of zinc is defined as,

$$\varepsilon = 100(i_{Zn}/i_c) \qquad (42)$$

The energy consumption (P) gives the electric power required per unit weight of zinc produced [10],

$$P = V_{cell} I_c t / W_{Zn} \qquad (43)$$

where t is the deposition time (seconds) and W_{Zn} is the mass of zinc deposited (g). This expression for P can alternatively be expressed as,

$$P = 81960 V_{cell}/\varepsilon \ (\mathrm{kW\,h\,tonne^{-1}}) \qquad (44)$$

Hence the energy consumption can be minimised by selecting the electrolysis conditions so that the current is used solely for zinc deposition and by making the cell voltage as low as possible. Theoretically, the lowest energy consumption occurs when the current efficiency is 100% and the cell voltage equals the equilibrium voltage. The energy consumption for zinc electrowinning under these conditions would be 1630 kW h $tonne^{-1}$. This compares with a value of around 3000 kW h $tonne^{-1}$ obtained by most industrial cellrooms.

2.5. *Electrolyte conductivity correlation*

The conductivity of the solution has a significant effect on the cell voltage. A detailed study of the conductivity of acidic metal sulphate solutions was carried out by Majima *et al.* [20]. Their conductivity prediction procedure, however, is quite complex and was not considered suitable for use in the present cell model. Therefore, a simpler linear correlation was used based on experimental data taken during the 10 litre cell studies [1];

$$\sigma = 32.0 + B(T - 35) + 19.6([H_2SO_4] - 1.12) - 11.1([C^*] - 1.25) \qquad (45)$$

where T = temperature (° C), B = temperature coefficient ($= 0.27[H_2SO_4]$), and C^* = effective Zn^{2+} concentration, given by ($[Zn^{2+}] + [Mn^{2+}] + [Mg^{2+}] + 0.5[NH_4^+]$). All concentrations [. . .] are in M.

2.6. *Electrolyte density correlations*

Electrolyte density was included in the model primarily so that its value as a measured and/or controlled variable in full-size cells could be examined via dynamic simulation. The results from such studies will be presented in a latter paper.

No equations for solution density could be found in the literature relevant to the $ZnSO_4$–H_2SO_4–H_2O system. Therefore, empirical correlations were used, based once again on experimental data taken during the 10 litre cell studies [1]. The density of neutral feed electrolyte (ρ_n) is given by,

$$\rho_n = 1000 + 2.25[Zn^{2+}] + 2.41[Mn^{2+}] + 4.36[Mg^{2+}] + 3.23[NH_4^+] \qquad (46)$$

while the density of spent electrolyte (ρ_s) is given by,

$$\rho_s = 1000 + 2.18[Zn^{2+}] + 2.41[Mn^{2+}] + 4.36[Mg^{2+}] + 3.23[NH_4^+] + 0.56[H_2SO_4] \qquad (47)$$

where both densities and all concentrations [. . .] are in $g\,dm^{-3}$. The effect of temperature on density was not modelled.

3. Parameter estimation in the pure solution model

Before the pure solution mathematical model could be used, values were required for a number of parameters. Estimation of each of these parameters is discussed below.

3.1. *Transfer coefficients and transfer numbers*

The Tafel equation for the hydrogen reaction (see

Equation 2) is:

$$i_{H_2} = i_{0,H_2} \exp(-\alpha_{H_2}\eta_{H_2} z_{H_2} F/RT) \quad (48)$$

There is general agreement in the literature (for example, [21]) that the value of the transfer coefficient for the hydrogen gas reaction (α_{H_2}) is 0.5, and consequently this value is used in the model. Since the mechanism of this reaction involves only one electron [22], the transfer number (z_{H_2}) is assigned a value of 1.

Current density versus electrode potential experiments carried out by Scott [6] indicated that at high zinc concentrations the value for $\alpha_{Zn} \cdot z_{Zn}$ was approximately 0.8. This agreed well with values reported previously [23, 24, 25]. Since Parsons [27] and Bard [28] both recommended a value of 2 for the transfer number (z_{Zn}), a value of 0.4 was used for the transfer coefficient.

3.2. *Tafel data for the oxygen evolution reaction*

As with most reactions involving gas evolution, the overpotential-current density relationship for the anodic decomposition of water can be described using the Tafel equation [10],

$$i_{H_2O} = i_{0,H_2O} \exp[(1 - \alpha_{H_2O})\eta_{H_2O} z_{H_2O} F/RT] \quad (49)$$

which can be simplified and rearranged into the logarithmic form,

$$\eta_{H_2O} = a + b \log_{10}(i_{H_2O}) \quad (50)$$

The simpler latter equation is used in the zinc electrowinning model as the anodic reaction is not of primary importance to the model calculations. Industrial silver-lead anodes, with the normal thin coating of manganese dioxide, were used in a series of overpotential experiments [6] to determine the Tafel slope and hence values for the two constants in Equation 50. The values obtained at 35° C were $a = 0.306$ and $b = 0.146$. These values did not change significantly over the range of temperatures typically used in industrial cells.

3.3. *Initial estimation of rate constants* (*no mass transfer*)

Initially, values for the rate constants $k'_{0,Zn}$ and k'_{0,H_2} were calculated at 35° C, assuming no mass transfer effects, and using the averaged data from the 12 pure solution pilot-plant cell experiments run at "standard" conditions (zinc concentration in cell = $55\,g\,dm^{-3}$; acidity in cell = $110\,g\,dm^{-3}$; current density = $500\,A\,m^{-2}$; cell temperature = 35° C; deposition time = 42 h; additives = $25\,mg\,dm^{-3}$ glue + $0.04\,mg\,dm^{-3}$ Sb; see [1] for more details). Such a parameter estimation was straightforward as the cell model was solved using the SPEEDUP [26] flowsheeting package. For a specified number of equations in the model, enough independent variables must be specified (i.e. given values) so that the final equation set to be solved is "square" (i.e. there are an equal number of equations and unknown variables). Normally, the rate constants would be set variables and the current efficiency and cathode overpotential would be calculated. Here, however, the current efficiency and the overpotential are set to their experimentally determined values and the rate constants are calculated. The model results (using these calculated rate constants) are compared with experimental results over a range of zinc concentrations in Figure 1.

3.4. *Inclusion of mass transfer effects*

Without the inclusion of cathodic mass transfer effects, the sharp drop in current efficiency at low zinc

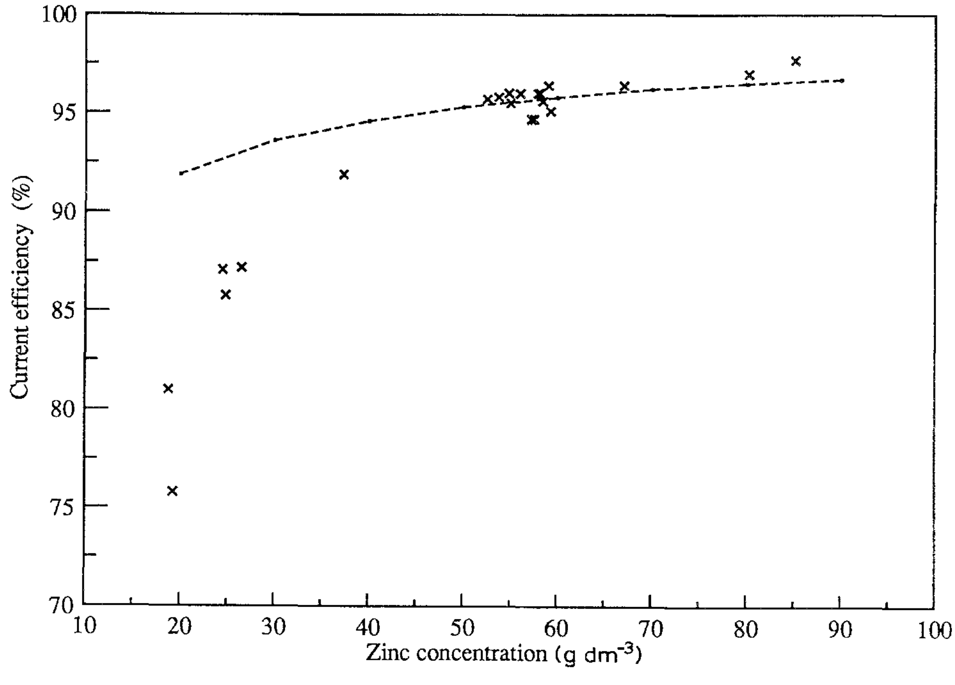

Fig. 1. Current efficiency against zinc concentration in the cell (model contains no mass transfer effects). (x) Experiment, (- - -) model. Conditions: acidity = $110\,g\,dm^{-3}$; temp. = 35° C; deposition time = 42 h; current density = $500\,A\,m^{-2}$.

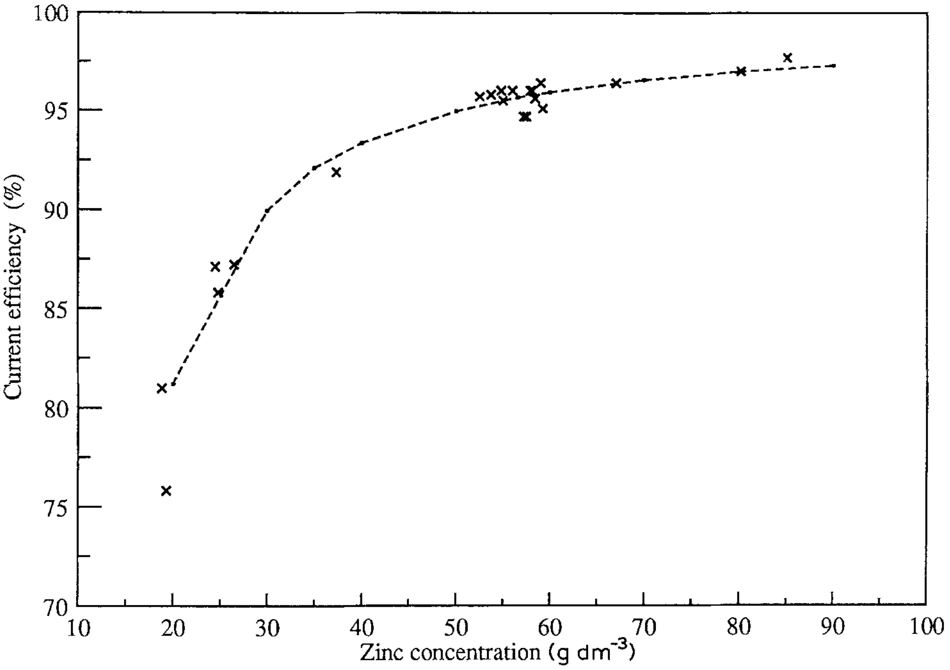

Fig. 2. Current efficiency against zinc concentration in the cell (model contains cathodic mass transfer effects). (x) Experiment, (– – –) model. Conditions: same as Fig. 1.

concentrations is not predicted by the model. The inclusion of mass transfer effects (see Equations 31–33), with the mass transfer constant ($K = 1.66 \times 10^{-3}$) being estimated by a least-squares fit between the model and experimental current efficiencies, meant that the model could now predict the low zinc concentration drop off in current efficiency (see Fig. 2). There is good agreement between the mass transfer coefficients determined above and those measured experimentally. At "standard" cell conditions the model predicts a mass transfer coefficient (m) of $4.9 \times 10^{-5}\,\mathrm{m\,s^{-1}}$ which compares favourably with a value of $5.3 \times 10^{-5}\,\mathrm{m\,s^{-1}}$ obtained experimentally by measuring the trace deposition of copper [6].

3.5. *Temperature dependence of the rate constants*

The rate constants for the zinc and hydrogen reactions are both assumed to have an Arrhenius temperature dependence (see Equation 29). Values for the frequency factors ($A_{0.\mathrm{Zn}}$ and $A_{0.\mathrm{H_2}}$) and activation energies (ΔG_{Zn} and $\Delta G_{\mathrm{H_2}}$) in these temperature dependencies have not been reported in the literature and, therefore, were estimated using the experimental data. The same method used to calculate the rate constants at 35° C was repeated for cell temperatures of 25, 40, 45 and 50° C. The current efficiency and cathode potential were set to their experimental values within the SPEEDUP model and the rate constants calculated.

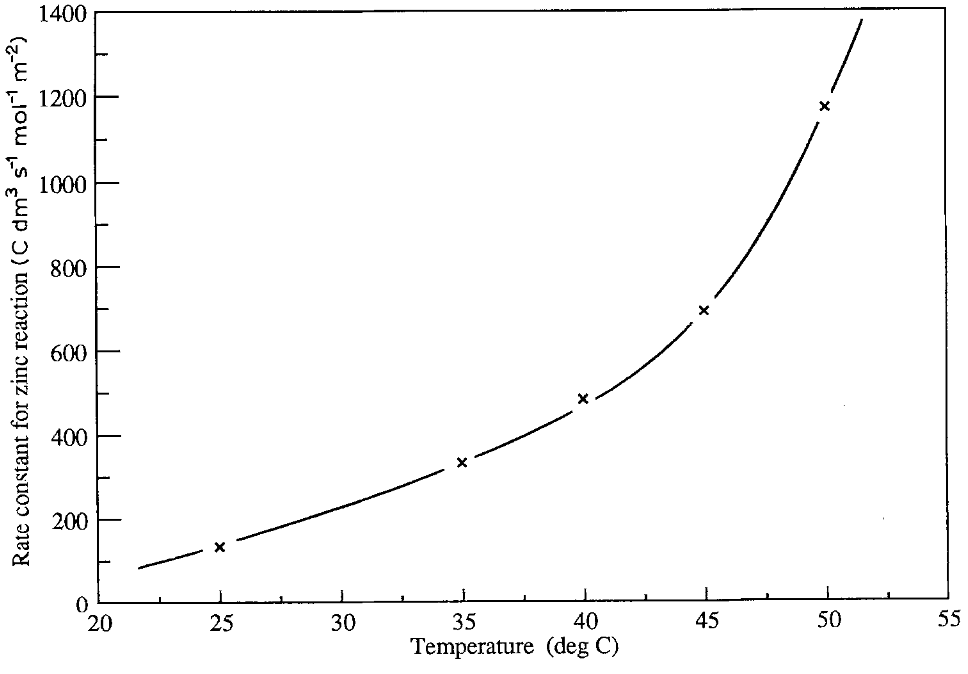

Fig. 3. Effect of cell temperature on the zinc deposition rate constant. Conditions: acidity = $110\,\mathrm{g\,dm^{-3}}$; zinc = $55\,\mathrm{g\,dm^{-3}}$; deposition time = 42 h; current density = $500\,\mathrm{A\,m^{-2}}$.

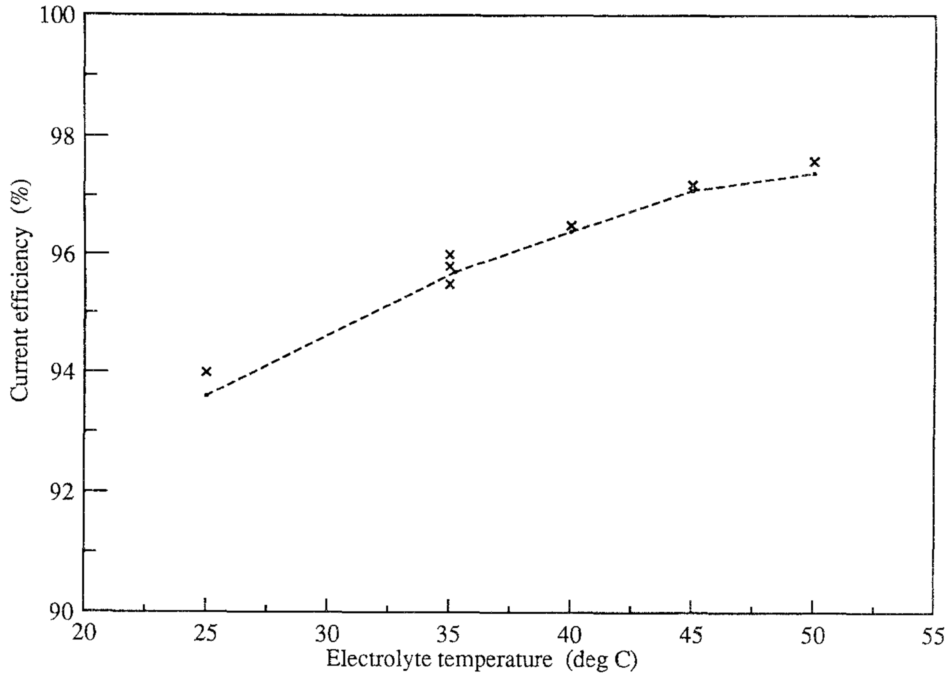

Fig. 4. Current efficiency against cell temperature. (x) Experiment, (– – –) model. Conditions: same as Fig. 3.

Figure 3 shows clearly the exponential relationship between the zinc deposition rate constant ($k'_{0,\mathrm{Zn}}$) and cell temperature. These values for the rate constants were used to calculate the frequency factors and activation energies for both the zinc and hydrogen reactions:

$$A_{0,\mathrm{Zn}} = 1.97 \times 10^{14}\ (\mathrm{C\,dm^3\,s^{-1}\,mol^{-1}\,m^{-2}})$$

$$\Delta G_{\mathrm{Zn}} = 69500\,\mathrm{J\,mol^{-1}}$$

$$A_{0,\mathrm{H_2}} = 353\ (\mathrm{C\,dm^3\,s^{-1}\,mol^{-1}\,m^{-2}})$$

$$\Delta G_{\mathrm{H_2}} = 48700\,\mathrm{J\,mol^{-1}}$$

The model predicted current efficiencies for a range of temperatures from 25 to 50° C are compared with the experimental results in Fig. 4.

3.6. *Evaporation coefficient*

Experimental measurements [6] indicated that, at "standard" conditions, there was an average decrease in volumetric flow between the feed and cell overflow streams of about 3%. The model indicated that about 1% was the result of the decomposition of water at the anode with evaporation from the liquid surface of the cell accounting for the rest. The evaporation constant

Table 1. A comparison of model predictions and experimental results

$[Zn^{2+}]$ ($g\,dm^{-3}$)	$[H_2SO_4]$ ($g\,dm^{-3}$)	*Temperature* (°*C*)	*Current density* ($A\,m^{-2}$)	*Current efficiency* (%)		*Energy* ($kWh\,tonne^{-1}$)	
				Expt.	Model	Expt.	Model
54.5	64.8	34.8	500	97.4	96.9	2912	2967
52.6	88.4	35.1	500	95.9	96.0	2858	2882
53.5	135.0	35.3	500	94.4	94.6	2779	2793
54.5	155.5	34.7	500	93.6	94.1	2773	2776
55.3	154.7	34.7	500	94.2	94.2	2808	2774
57.9	109.8	35.4	350	96.1	95.9	2687	2662
54.8	112.5	35.3	650	95.9	95.1	2940	2985
38.8	181.3	34.9	500	91.1	90.4	2825	2846
39.2	88.8	34.9	500	94.8	94.0	2914	2924
55.6	110.4	34.8	500	95.7	95.5	2870	2832
55.8	109.5	34.9	500	96.5	95.6	2823	2832
56.8	110.4	35.0	500	95.9	95.7	2861	2828
65.8	115.2	35.3	100	95.9	95.2	2453	2362
58.4	158.3	40.4	500	95.3	95.3	2727	2708
49.0	171.6	40.3	500	92.8	93.9	2783	2726
57.0	161.0	40.3	500	93.9	95.1	2776	2709
24.8	112.3	35.3	500	85.8	86.5	3105	3109
66.4	181.5	44.8	400	94.5	96.0	2637	2562
48.5	216.3	44.5	400	91.9	93.7	2658	2598
61.9	109.5	35.4	180	94.6	95.9	2530	2465

(K_{evap} in Equation 10) was, thus, estimated by running the model at "standard" experimental conditions but specifying that the exit flowrate was 2% less than the inlet flow. A value for K_{evap} of 2.5×10^{-4} was thus obtained.

4. Validation of the pure solution model

Using the model with the parameter values as estimated in the previous section, a comparison was next made between the experimental data from the pilot-plant cells and the model predictions. Only data that had not been used for parameter estimation were used in this comparison. The comparison range for most of the major variables was quite large. For example, the current density varied from 100 to 650 A m^{-2}, while the acidity varied from 65 to 210 g dm^{-3}. Table 1 lists the results.

The average percent absolute error between the model predictions and the experimental data is 0.6% for the current efficiency and 1.4% (equivalent to 40 kWh tonne^{-1}) for energy consumption. These errors are comparable to the accuracy of the experimental data itself, which under "standard" conditions have been estimated to be 0.5% for current efficiency and 1.0% for the energy consumption.

To test the sensitivity of the model to variations in the estimated parameters, a series of simulations were performed with each parameter in turn being set at 10% above and 10% below its estimated value. The effects on current efficiency and energy consumption are given in Table 2.

As expected because of their position in the exponential part of the Arrhenius temperature dependence, changes in the zinc and hydrogen activation energies (ΔG_{Zn} and ΔG_{H_2}) have a significant effect on the model predictions. It should be remembered, however, that in estimating such values from experimental data any error made in calculating an activation energy should, to some extent, be compensated for by a corresponding "error" in the frequency factor. In Table 2, only the activation energies have been changed.

The exchange coefficient for the hydrogen reaction (α_{H_2}) also has a large effect on the model predictions. However, the value of 0.5 used in the model is consistent with values given in the literature. The least sensitive parameter is the evaporation coefficient (K_{evap}). Even a 50% change to the estimated value has a negligible effect on either the current efficiency or the energy consumption.

5. Model results

As an example of what can be done once a validated model is available, Figs 5–7 are plots of current efficiency and power consumption for a high purity feed (Zn^{2+} in feed = 160 g dm^{-3}) against zinc concentration in the cell (or acidity, as the two are related), cell temperature and current density when each in turn is varied about a nominal base set of conditions (cell acidity = 160 g dm^{-3}; cell temperature = 35° C; current density = 500 A m^{-2}).

This model only applies to the operation of a (10 litre) pilot-plant cell using a high purity electrolyte. Based on experimental data, this model has been extended to include both the effects of major feed impurities (copper, cobalt and nickel), as well as full-size cell effects such as non-perfect mixing and manganese dioxide scale on the electrodes [6]. Such a model provides a means for plant engineers to quantitatively predict and assess the likely effects of proposed changes in circuit design and/or operation. For exam-

Table 2. Sensitivity of model to estimated parameters

Parameter	Δ (*Parameter*)	Δ (*Current efficiency*)	Δ (*Energy*)
α_{Zn} (= 0.4)	+ 10%	+ 0.2%	+ 0.1%
	− 10%	− 0.3%	− 0.5%
α_{H_2} (= 0.5)	+ 10%	− 9.7%	+ 10.6%
	− 10%	+ 2.8%	− 1.9%
$A_{0,Zn}$ (= 1.97×10^{14})	+ 10%	+ 0.2%	− 0.2%
	− 10%	− 0.2%	+ 0.3%
A_{0,H_2} (= 353)	+ 10%	− 0.3%	+ 0.3%
	− 10%	+ 0.3%	+ 0.3%
ΔG_{Zn} (= 69500)	+ 10%	− 12.0%	+ 17.0%
	− 10%	+ 2.8%	− 4.5%
ΔG_{H_2} (= 48700)	+ 10%	+ 2.0%	− 2.0%
	− 10%	− 15.0%	+ 17.0%
K (= 1.66×10^{-3})	+ 10%	+ 0.2%	− 0.4%
	− 10%	− 0.3%	+ 0.5%
$\eta_{H_2O} = 0.306 + 0.146 \log_{10} (i_{H_2O})$	+ 10%	0.0%	+ 2.0%
	− 10%	0.0%	− 2.0%
K_{evap} (= 2.5×10^{-4})	+ 10%	0.0%	0.0%
	− 10%	0.0%	0.0%

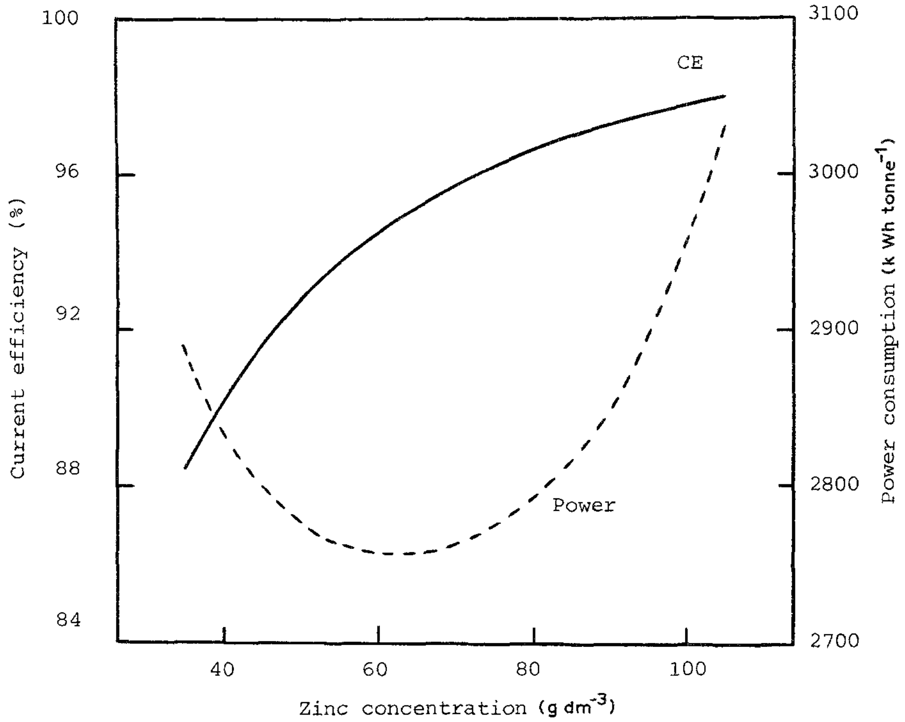

Fig. 5. Final model predictions — effect of zinc concentration in cell on electrowinning performance. Current density = 500 A m^{-2}; temp. = 35°C.

ple, the steady-state model can be readily optimised to determine what conditions result in the minimum power requirement per tonne of zinc possible within a plant's operational constraints. Similarly, the dynamic version of the model can be used to compare alternative cellroom control schemes. Details of the extended model and various applications (both steady-state and dynamic) will be presented in a latter paper.

6. Conclusions

A (dynamic) mathematical model has been developed for a (10 litre) pilot-plant size zinc electrowinning cell operating with a high purity feed. The model consists of a set of 95 equations comprising mass balances, an overall energy balance, thermodynamic and kinetic equations, electrochemical and mass transfer equations and correlations for electrolyte conductivity and den-

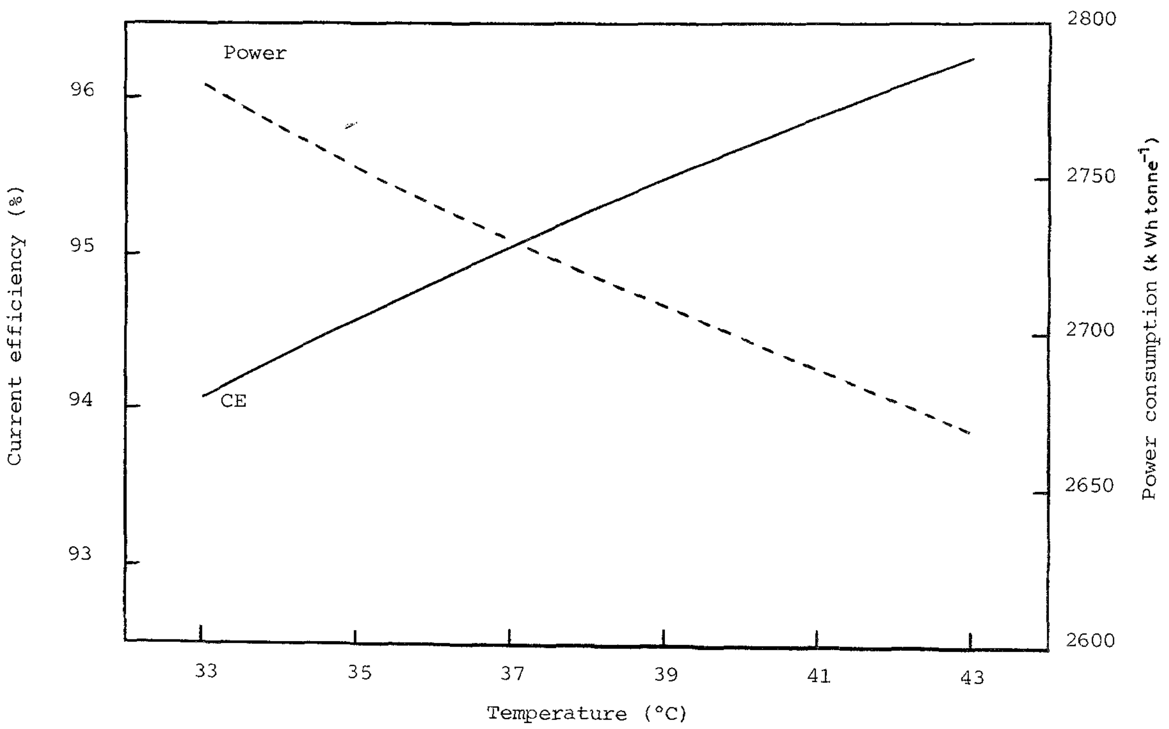

Fig. 6. Final model predictions — effect of cell temperature on electrowinning performance. Current density = 500 A m^{-2}; cell acidity = 160 g dm^{-3}.

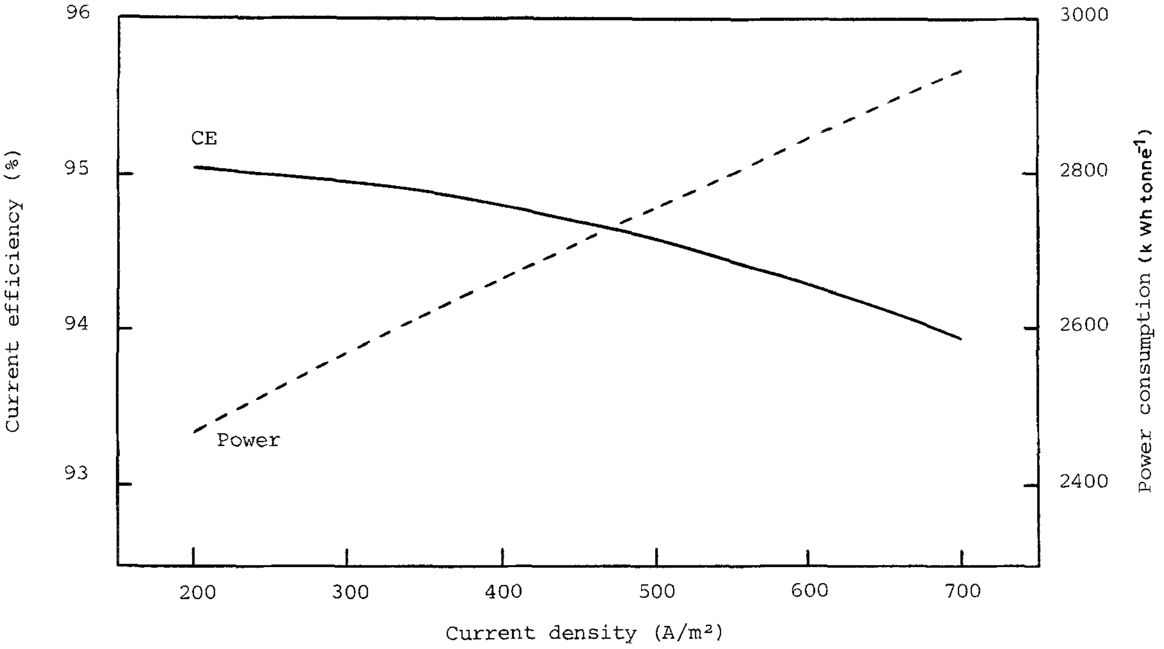

Fig. 7. Final model predictions – effect of current density on electrowinning performance. Cell acidity = 160 g dm^{-3}; temp. = 35°C.

sity. The model assumes that the cell behaves like a well-mixed system.

Values for the model parameters were obtained from the literature or estimated using experimental data. A comparison of model predictions and experimental results gave an average (absolute) error of 0.6% and 1.4%, respectively, for the cell current efficiency and specific power consumption. These values are very close to the estimated errors in the actual experimental data themselves.

The model equations were solved using the SPEEDUP flowsheeting package. Parameter estimation was merely a form of model solution with experimental data being specified and parameters being calculated. Being an integrated package, SPEEDUP also has the facilities to perform both steady-state optimisation and dynamic simulation runs. Although these facilities were not used to generate results presented in this paper, they were both employed in studies carried out using a version of the model that had been extended to include full-size cell effects.

In conclusion, this model (and its extended version) accurately predicts the influence of the major variables on the zinc electrowinning process. As a consequence, it has been successfully used by EZ personnel in various plant design/operation studies. Given the availability of suitable data, this model could be readily "tuned" so as to describe similar electrowinning processes.

Acknowledgements

The authors of this paper would like to thank the Electrolytic Zinc Company and the CSIRO, Division of Mineral Engineering, for their financial and technical support of the work reported in this paper.

References

[1] A. C. Scott, R. M. Pitblado, G. W. Barton and A. R. Ault, *J. Appl. Electrochem.* **18** (1988) 120–7.
[2] F. Laplicque and A. Storck, *ibid.* **15** (1985) 925–35.
[3] W. W. Harvey, *Hydrometallurgy* **2** (1976) 35–50.
[4] T. W. Chapman, 'Hydrometallurgical Process Fundamentals', Plenum Press, New York (1984) pp. 599–616.
[5] A. W. Bryson, 'Modelling the Performance of Electrowinning Cells', Hydrometallurgy 81, Society of Chemical Industry Symposium, UMIST, Manchester (1981).
[6] A. C. Scott, 'The Development and Application of a Mathematical Model for the Zinc Electrowinning Process', Ph.D. Thesis, University of Sydney, Australia (1988).
[7] J. M. Coulson and J. F. Richardson, 'Chemical Engineering', Vol. 1, 3rd ed., Pergamon Press, Oxford (1977).
[8] R. H. Perry and C. H. Chilton, 'Chemical Engineers Handbook', 5th ed., McGraw Hill, New York (1973).
[9] A. J. Bard and L. R. Faulkner, 'Electrochemical Methods', J. Wiley & Sons, New York (1980).
[10] D. J. Pickett, 'Electrochemical Reactor Design', Elsevier Scientific, Amsterdam (1979).
[11] H. V. Tartar, W. W. Newschwander and A. T. Ness, *J. Am. Chem. Soc.* **63** (1941) 28–36.
[12] T. Hurlen and T. R. Breivik, *Acta Chem. Scand.* **A 32** (1978) 447–53.
[13] A. G. Turnbull and M. W. Wadsley, Extractive Metallurgy Symposium, Australian Institute of Mining Metallurgy, Melbourne (1984) p. 79.
[14] M. Whitfield, *Geochimica et Cosmochimica Acta* **39** (1975) 1545–57.
[15] K. S. Pitzer and J. J. Kim, *J. Am. Chem. Soc.* **96** (1974) 5701–7.
[16] D. Pletcher, 'Industrial Electrochemistry', Chapman & Hall, London (1982).
[17] T. Hurlen, *Electrochim. Acta* **7** (1962) 653–68.
[18] L. J. Janssen, *ibid.* **23** (1978) 81–6.
[19] D. N. Bennion, 'Modeling and Reactor Simulation', AIChE Symposium Series No. 229, **79** (1983) pp. 25–36.
[20] H. Majima, E. Peters, Y. Awakura and S. K. Park, *Met. Trans. B.* **18B** (1987) 41–7.
[21] A. L. Rotenyan, N. P. Fedotov and L. U. Sok, *Zh. Fiz. Khim.* **31** (1957) 1295.
[22] S. Trasatti, *J. Electroanal. Chem.* **39** (1972) 163–84.
[23] D. A. Payne and A. J. Bard, *J. Electrochem. Soc.* **119** (1972) 1665–74.
[24] H. Matsuda and Y. Ayabe, *Elektrochem.* **63** (1959) 1164.
[25] A. G. Stromberg and L. N. Popova, *Elektrokhimiya* **4** (1968) 1147.

[26] C. C. Pantelides, *Comp. Chem. Eng.* **12** (1988) 745-755.
[27] R. Parsons, Personal communication (1986).
[28] A. J. Bard, Personal communication (1986).
[29] L. J. Janssen and J. G. Hoogland, *Electrochim. Acta* **15** (1970) 1013-23.
[30] H. Vogt, *ibid.* **23** (1978) 203-5.
[31] F. Ajersch, D. Mathieu and D. L. Piron, *Can. Met. Quarterly* **24** (1985) 53-63.