

A Mathematical Model of a Zinc Electrowinning Cell

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A detailed fundamental model of a zinc electrowinning cell has been developed and validated for both steady state and dynamic simulations. This model was used to investigate the effects of a range of operating variables and to find their optimum values. As well as providing useful design information for a planned upgrading of the EZ refinery, more generally it demonstrates the potential benefits to the minerals industry of the applications of modern CAD flowsheeting techniques. The SPEEDUP equation oriented CAD package was found most suitable for this task as the user can easily generate models specific to his site with any number of components and mixture properties.

Introduction

Flowsheet simulation models are now widely used in the petrochemicals industry and increasingly so in the minerals industry. Such models can be used for the design of new processes as well as optimization of existing ones. In the field of electrowinning, the equations that describe the electrolytic cells have often been outlined¹⁻¹⁰, but have rarely been applied to specific industrial processes. One exception is that of Bryson¹¹ who developed a simplified equation set for modelling the zinc electrowinning process.

This paper outlines the development of a detailed fundamental model of the zinc electrowinning process. The model contains the most extensive equation set yet published. Numerical solution was achieved using the SPEEDUP flowsheeting package for both steady state and dynamic simulations¹². A wide range of

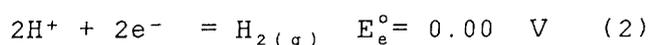
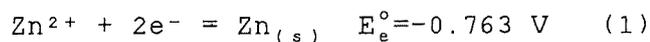
experiments were carried out to validate both the electrowinning and cell hydrodynamic equation sets.

This example demonstrates the existence and suitability of numerical tools capable of solving the complex equation sets found in mineral circuits. Detailed mechanistic models are a prerequisite for proper process design, control and optimisation exercises.

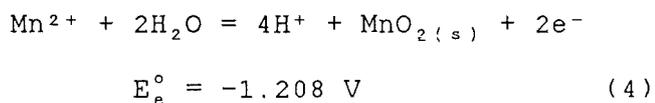
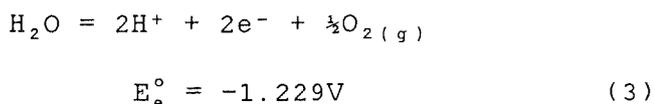
Zinc electrowinning principles

At the EZ Risdon plant in Tasmania, zinc ores are roasted, dissolved in sulphuric acid and then highly purified. Metallic zinc is won from the purified zinc sulphate solution by electrolysis using aluminium cathodes and lead anodes¹³.

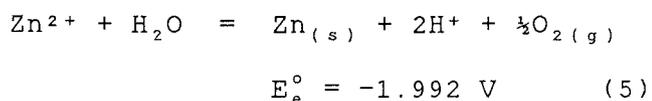
The cathodic half reactions with standard potentials are :



The anodic half reactions are :



Generally, 90% of the cathodic current is used in the production of zinc by reaction (1), and 99% of the anodic current is used by reaction (3). Combining reactions (1) and (3) gives the overall desired reaction :



The major variables that affect these reactions are :

- Zn^{2+} concentration
- H^+ concentration
- current density
- temperature.

These, therefore, are the key variables that must be considered when developing the mathematical model. As each of these is in turn dependent on several other variables, the resulting simulation model has many equations. The effect of each of the major variables has been investigated in a series of experiments undertaken in order to obtain electrochemical data for use in model development¹⁴.

Additives and impurities (apart from magnesium, manganese and ammonium ions) were not modelled. The effects of these could be included at a later stage in the model development consistent with an experimental program to validate necessary equations.

Model development

Equations have been developed to model the effects of the 7 major species present in the electrolyte of the EZ refinery at Risdon. These are Zn^{2+} , H^+ , SO_4^{2-} , H_2O , Mn^{2+} , Mg^{2+} and NH_4^+ . The equation set for these seven species can be divided into four main sections, which will be examined in turn :

- 1) Mass balance equations
- 2) Energy balance equations
- 3) Electrochemical equations
- 4) Conductivity and density correlations.

Mass balance equations

Each of the seven chemical species is defined by a mass balance of the form :

$$[\text{INPUT}] + [\text{GENERATION}] - [\text{CONSUMPTION}] - [\text{OUTPUT}] = [\text{ACCUMULATION}] \quad (6)$$

The INPUT is the product of the volumetric flowrate of feed to the cell and the concentration of the species in the feed. The GENERATION term defines any reactions where one of the chemical species is produced. H^+ is produced at the anode by reaction (2). The consumption term describes any reactions which consume one of the chemical species. Zn^{2+} , H^+ , H_2O and Mn^{2+} are all consumed. Zn^{2+} and H_2O are consumed by reaction (5) while H^+ and Mn^{2+} are consumed by side reactions (2) and (4). The OUTPUT term accounts for the amount of each species leaving the system. There are two outputs, the overflow of the spent solution and loss due to evaporation. It is assumed that water is lost through evaporation, and this is modelled using a modified Antoine equation for acidic solutions. ACCUMULATION is the time derivative

defining the rate of change of mass of each species. At steady state the derivative equals zero.

Energy balance equations

The energy balance of a system can also be determined analogously to equation (6). The INPUT term defines the amount of energy entering the system. Energy enters both in the feed stream and as electrical energy. The OUTPUT defines energy leaving the system with the exit stream. The CONSUMPTION term defines any endothermic processes. This includes the overall heat of reaction and the heat of evaporation. The GENERATION term is not required for the zinc cell since no exothermic reactions occur. Equation (6) can now be written more specifically as :

$$H_f + H_e + H_1 + H_r + H_{evap} - H_d = [\text{ACCUMULATION}] \quad (7)$$

H_1 accounts for the heat lost to the atmosphere through conduction and radiation.

Electrochemical equations

Each cell must maintain electrical neutrality :

$$\sum_{j=1}^x n(j).C(j) = 0 \quad (8)$$

where $n(j)$ = the charge of component j

$C(j)$ = the concentration of component j (mol/l)

It is necessary to consider both the thermodynamics and kinetics of the electrolytic process. The equilibrium potential of each species is given by a thermodynamic equation, the Nernst equation :

$$E_e(j) = E_e^\circ(j) + \frac{R.T}{n(j).F} \cdot \ln \left[\frac{a_o(j)}{a_r(j)} \right] \quad (9)$$

where $E_e(j)$ = equilibrium potential (volts)

$a_o(j), a_r(j)$ = activity of the oxidised and reduced species of component j .

Activities should be employed in this equation as errors can result if concentrations are used. The activity of a species is related to its concentration by equation (10).

$$\begin{aligned} a_o(j) &= \gamma_o(j).C_o(j) \\ a_r(j) &= \gamma_r(j).C_r(j) \end{aligned} \quad (10)$$

where γ = activity coefficient of component j

The driving force or overpotential for each species can then be described as the difference between the working electrode potential E , and the equilibrium potential.

$$\eta(j) = E - E_e(j) \quad (11)$$

where $\eta(j)$ = overpotential (volts)

The kinetics are more complex and a number of equations have been proposed. The most useful is the Tafel equation which in its cathodic form is;

$$i(j) = i_o(j) \cdot \exp \left[\frac{\alpha(j).z(j).F.\eta(j)}{R.T} \right] \quad (12)$$

where $i(j)$ = current produced by the reduction of component j (A/m²).

Equation (12) relates the overpotential for each species to the rate of reaction expressed in terms of current density. It assumes that the rate determining step is the charge transfer at the electrode surface and not the mass transfer of the species to the surface. For both the reactions in which gas is evolved, hydrogen at the cathode (reaction (2)) and oxygen at the anode (reaction (3)), the charge

transfer kinetics are slow and the assumptions of the Tafel equation are valid.

For the zinc reaction, an equation derived by Bard and Faulkner¹⁵ which incorporates both Tafel kinetics and mass transfer effects was found to be more suitable :

$$i(j) = \left(\frac{i_1(j) - i(j)}{i_1(j)} \right) \cdot i_0(j) \cdot \exp(-\alpha(j) \cdot z(j) \cdot F \cdot \eta(j) / (R.T)) \quad (13)$$

where $i_1(j)$ = limiting current density.

The limiting current density is given by :

$$i_1(j) = m \cdot n \cdot F \cdot C_o(j) \quad (14)$$

where m = mass transfer coefficient.

The exchange current density $i_0(j)$, is an important kinetic characteristic of an electron transfer process. A dynamic equilibrium exists at the surface when there is no net current or net chemical change in the cell. The rate of reduction of each species equals the rate of oxidation. This rate expressed in terms of current density is $i_0(j)$. Pletcher¹⁶ defines the exchange current density as :

$$i_0(j) = n \cdot F \cdot k_o^\ominus(j) \cdot [a_o(j)]^{(1-\alpha(j))} \quad (15)$$

The rate constant, k_o^\ominus , is strongly dependent on temperature. An Arrhenius equation is appropriate.

$$k_o^\ominus(j) = A_o(j) \cdot \exp(-e(j) / (R.T)) \quad (16)$$

where $A_o(j)$ = frequency factor (m/sec)

$e(j)$ = activation energy (J/mole)

The relationship between the rate of reaction expressed in terms of charge transfer (or current) and moles per second is given by the Faraday equation;

$$A \cdot i(j) = r(j) \cdot F \cdot \Delta(n(j)) \quad (17)$$

The total current passing through

an electrode is the sum of the currents of all the reactions occurring on its surface.

$$i(\text{total}) = \sum_{j=1}^X i(j) \quad (18)$$

The overall cell voltage is calculated by summing the voltage drops of the electrodes and across the solution between the electrodes.

$$V = E_c + E_a + E_1 + \frac{b \cdot i_{\text{total}}}{\text{cond}} \quad (19)$$

E_1 is a measured correction term to allow for voltage losses across the busbars and contacts, and generally equals 0.1 to 0.2 volts.

The final electrochemical equations employed are those describing the current efficiency and the total energy used by the process :

$$CE = \frac{i_{zn} \cdot 100\%}{i_{\text{total}}} \quad (20)$$

$$P = \frac{81974 \cdot V}{CE} \quad (21)$$

Conductivity and density correlations

Conductivity

The conductivity of the solution has a significant effect on the cell voltage and therefore on power consumption. A fundamental mechanistic model was viewed as unnecessary and a simpler correlation approach was adopted in which conductivity is determined by calculating the deviation from a standard solution.

$$\text{Cond} = 32.0 + B(T-308) + 0.20(H_2SO_4 - 110) - 0.17(C^* - 82) \quad (22)$$

where; H_2SO_4 and C^* are in g/l and B = acid/temperature coefficient = 0.0028(H_2SO_4)

Contributions of the cations are equated to zinc based on their ionic

charge. Experimental work has shown this assumption to be correct for the range of concentrations encountered in a zinc electrolytic cell.

$$C^* = 65.4(Zn+Mn+Mg+0.5(NH_4)) \quad (23)$$

where concentrations are in mol/l

Density correlation

Density was included in the model primarily to study its value as a variable that can be used for cell control. Correlations were obtained for both acidic and neutral solutions.

$$\rho_o(f) = 1000 + 2.25(Zn) + 4.36(Mg) + 2.41(Mn) + 3.22(NH_4) \quad (24)$$

$$\rho_o(s) = 1000 + 2.18(Zn) + 0.56(H_2SO_4) + 4.36(Mg) + 2.41(Mn) + 3.22(NH_4) \quad (25)$$

Both correlations have been tested over a wide range of conditions as might be found at EZ, Risdon.

Cell mixing characteristics

Accurate full-scale modelling of a zinc electro-winning cell required a description of the cell hydrodynamics. Rawling and Costello¹⁷ conducted a detailed study of a copper refinery cell and proposed a model consisting of four volume elements. Bryson¹¹ used a simpler model which consisted of a well mixed region with a bypass fraction of 0.1.

Tracer tests carried out on three industrial cells at Risdon indicated that a model consisting of two well mixed tanks was appropriate (figure 1). In line with physical considerations the volume of the top tank, V_t , was taken as the volume of the electrolyte in the electrode region. The volume of the bottom tank, V_b , was that between the bottom of the electrodes and the top of the manganese dioxide mud (which settles

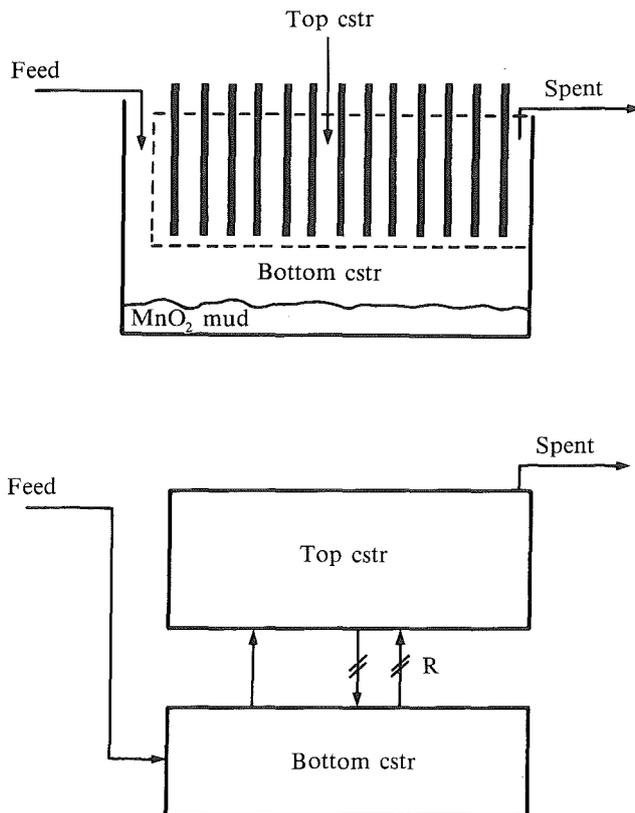


FIGURE 1. (Top) Diagram of a zinc electro-winning cell
(Bottom) Model representation

at the bottom of the tank).

- The best fit was obtained when
- 1) All the feed went to the bottom tank.
 - 2) No electrolyte from the bottom tank by-passed the top tank. This indicated that the feed entering the region under the electrodes was drawn up into the electrode region and did not pass straight through the cell.
 - 3) A moderate value of R , the recirculation between top and bottom tanks was used. The values that gave best fit are given in table (1).

The internal recirculation pattern of a cell was not only driven by feed flow rate but also by the large amount of rising bubbles between the electrodes. (If the current density was reduced, the amount of bubbling

TABLE 1

Recirculation Rate, R, within an Electrowinning Cell

The 3 cells studied were at the EZ Refinery, Risdon.

	Cell feed rate (L/min)	R(L/min)
1st cell in Cascade unit	6.0	54
3rd cell in Cascade unit	18.0	40
Recirculating cell	118	145

would decrease, and therefore R, the recirculation parameter would be expected to decrease.) Further details of this work are presented by Shewring¹⁸.

SPEEDUP modelling

Barton and Pitblado¹⁹ showed there are only a few general purpose computer aided design (CAD) tools for the minerals processing industry. This is in significant contrast to the chemicals and petrochemicals industries which have several (PROCESS, FLOWPACK, FLOWTRAN, ASPEN, SPEEDUP). Part of the reason is the more predictable performance of chemical plant equipment since chemical properties and process unit operations, although complicated, can be well simulated. Minerals flowsheets are much more influenced by the feed ore properties and many unit operations are site specific, thus generalised packages are less useful.

There are a number of flowsheet CAD architectures in use. Rosen²⁰ reviews the important features of the various types, including the two most

important - sequential modular and equation oriented. The sequential modular structure is the most common and in many respects is similar to an automated manual calculation procedure. Because of its fixed, calculation structure, a sequential modular package is inefficient for many flowsheet problems. The equation oriented architecture as described by Shacham et al²¹ is more efficient. Perkins¹² discusses the SPEEDUP CAD flowsheet program, one of the first equation oriented packages. SPEEDUP (Simulation Package for the Evaluation and Evolutionary Design of Unsteady Processes) was developed at Imperial College, London, over a number of years. It is a powerful tool for the solution of minerals flowsheet problems, both steady state and dynamic.

The key features of SPEEDUP that make it attractive for minerals flowsheet simulation are :

- it can simulate dynamic response as well as steady state;
- operation is interactive and flowsheet changes are easy;
- flowsheet optimisations should be particularly efficient;
- site specific models can easily be generated by users, either as equations or as subroutines;
- any combination of arbitrary specifications may be made, so long as they are feasible;
- equations may be expressed in any form and order;
- it provides a suite of state-of-the-art numerical methods to solve the flowsheet.

SPEEDUP collects together the full set of defining equations for all

unit operations, which need not be in any calculation sequence. The collected equations form a set in which the total number of equations is M and variables N. For any real flowsheet, N always exceeds M, and provides for N-M specifications. Once the N-M specifications are made, the flowsheet problem reduces to a numerical one of M simultaneous equations in M unknowns, and in principle a solution may be obtained by standard means. With this approach, the types of specifications (feed streams, parameters etc) are unimportant, so long as they are all independent. Thus design class problems are solved with equal ease to performance problems.

Model calibration

Pilot plant scale experiments were carried out in two 10 litre cells each containing two aluminium cathodes and three silver-lead anodes (0.75% Ag). Each cathode had an immersed surface area of 590 cm². The addition of fresh feed electrolyte to the cells was controlled in order to maintain a constant cell acidity. Cell temperature was also controlled. The cells were well instrumented in order to obtain the data required for model calibration. Experimental measurements were continuously recorded by a 30 point chart recorder and a PDP 11/23 computer. The effects of each of the major variables - zinc concentration, acid concentration, temperature, current density and deposition time - were investigated one at a time, while all other variables were held constant, in a high purity industrial electrolyte¹⁴.

Calibration of a number of the model parameters was carried out by comparing model results with the experimental results. The sum of the squares of the errors for both current efficiency and cathode overpotential were calculated for each set of parameters tested. The set of parameters that gave the best fit were :

$$\alpha(\text{zn}) = 0.4$$

$$\alpha(\text{H}^+) = 0.5$$

$$k_o^{\circ}(\text{zn}) = 2.69 \times 10^{-4} \text{ cm/sec at } 35 \text{ C}$$

$$k_o^{\circ}(\text{H}^+) = 3.08 \times 10^{-12} \text{ cm/sec at } 35 \text{ C}$$

These are within the range of values reported by Bard²². The value used for the charge transfer number, z, for zinc deposition was 2. This was recommended by Parsons²³, and confirmed by Tafel slope experiments conducted in the experimental cells.

The mass transfer coefficient was obtained using the same method as that reported by Ettel et al²⁴ where a trace impurity was deposited on the electrode surface. Copper, the trace impurity selected, was tested at five different levels between 0.05 mg/l and 2.6 mg/l. A value of 9×10^{-4} cm/sec was obtained.

The electrowinning model

A fully calibrated zinc electrowinning cell model capable of both steady state and dynamic simulations has been developed for use in optimisation and industrial case studies. The model, consisting of 200 variables and 121 equations, represents a substantial numerical problem as many of the equations are highly non-linear.

Only an equation oriented

flowsheeting package (such as SPEEDUP) represents a feasible solution method to such a problem.

Model results

Steady state simulation

A series of runs were carried out to determine an approximate optimum operating condition for a high purity feed electrolyte of 160 g/l Zn. The effects of 1) zinc and acid concentration; 2) temperature; 3) current density were assessed with respect to current efficiency and power consumption.

The SPEEDUP package is particularly well suited to this type of analysis, since the set of specified variables can easily be changed without altering the problem structure. Other simulation packages would be structured for a particular set of specifications and any other set could only be achieved, if at all, by a costly and inefficient set of iterative calculations.

Zinc and acid concentration

The model was run at a number of cell acidities in the range 80-200 g/l H_2SO_4 , for a constant cell temperature of 35° C. Figure (2) demonstrates that the lowest power usage will be achieved at 150 g/l H_2SO_4 . This corresponds to a spent zinc concentration of 65 g/l. At acidities above 180 g/l the power consumption rises sharply due to the rapid decline in current efficiency.

Temperature

The next set of simulations were run at a constant cell acidity of 160 g/l H_2SO_4 and current density of 500 A/m^2 . Cell temperatures in the range 35-45 C were investigated. Figure (3)

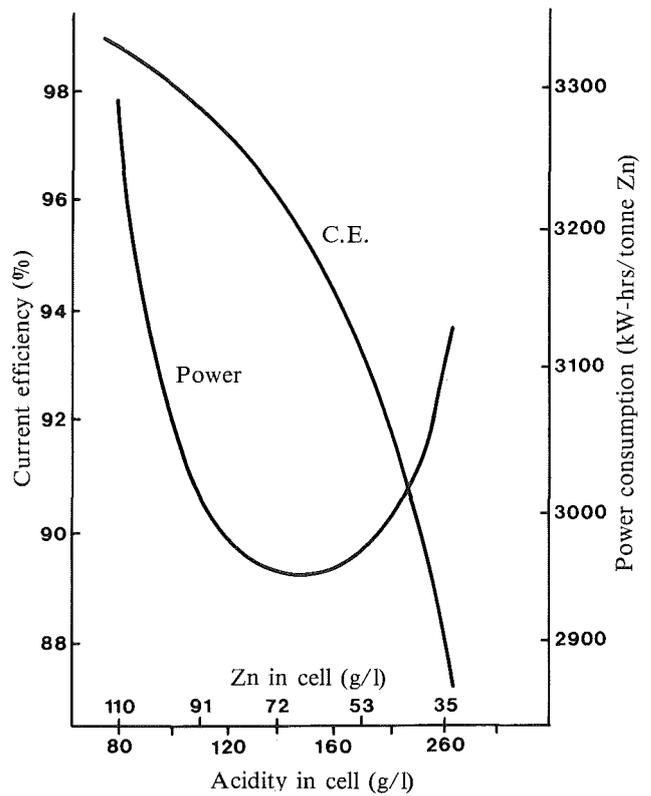


FIGURE 2. Effect of acidity and zinc concentration
Zn in feed 160 g/l, temp. 35°C, current density 500 A/m^2

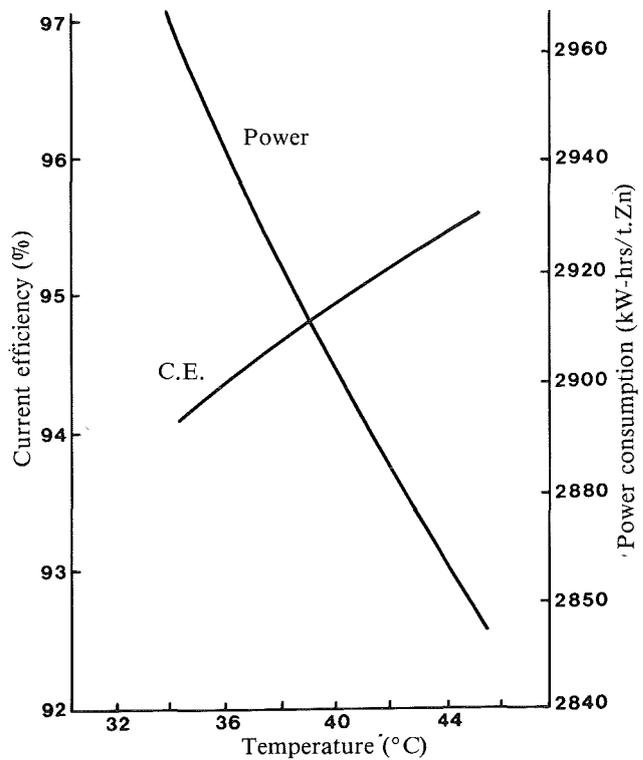


FIGURE 3. Effect of temperature
Zn in feed 160 g/l, cell acidity 160 g/l H_2SO_4 , current density 500 A/m^2

demonstrates that the power consumption dropped from 2950 kW-hrs/t Zn to 2860 kW-hrs/t Zn, due to the small rise in current efficiency and a drop in cell voltage caused by increased solution conductivity. At present most industrial plants do not operate above 40 C due to problems with the addition reagents. However, once this problem is overcome, power savings will be possible by increasing the cell temperature.

Current density

Figure (4) demonstrates that current density has a large effect on power consumption due to the increase in IR voltage across the solution as the current is increased. The power consumption increased linearly at a rate of 80 kW-hrs/t Zn per 100 A/m². Unfortunately however by reducing current density, the production rate

is also reduced. New cellrooms overcome this problem by having cathodes of larger surface area. The same production rate can be obtained at lower current densities and therefore lower power consumption. The new Cominco cellhouse took advantage of this concept by reducing current density from 600-700 A/m² to 400 A/m² and increasing cathode size from 1 m² to 3m² ²⁵.

Dynamic simulation

A dynamic simulation for a cell in a cascade unit of the Risdon cellroom was performed to demonstrate the uncontrolled response to a step change. The feed flowrate was decreased from 0.09 l/s to 0.07 l/s. Figure (5) illustrates the response of zinc concentration in the cell and current efficiency with respect to time. The current efficiency took 40

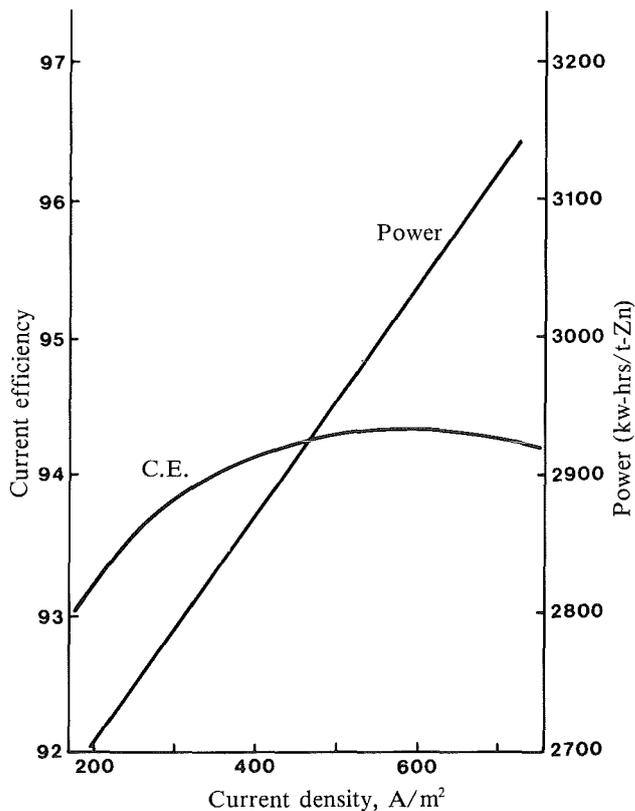


FIGURE 4. Effect of current density
Zn in feed 160 g/l, cell acidity 160 g/l, temp. 35°C

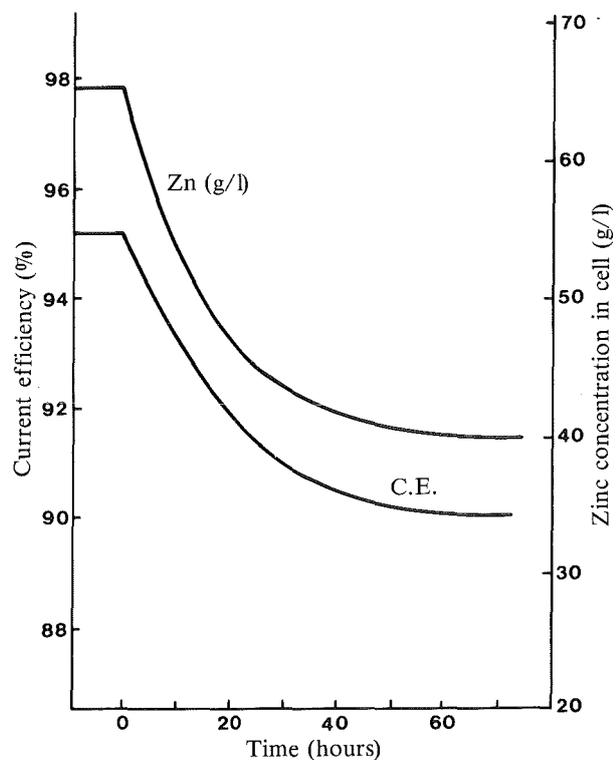


FIGURE 5. Zinc concentration and current efficiency vs time

hours to fall within 0.5% of the new steady-state value. Not only can the model simulate step changes such as the above example, but also pulses, sine wave disturbances and ramp inputs.

Conclusion

To date the use of flowsheeting models in the minerals industry has been limited. A new generation of equation oriented CAD packages (such as SPEEDUP) now provides tools suitable for the steady state and dynamic simulation of complex mineral processes.

A steady state and dynamic model of a zinc electrowinning cell has been developed based on a fundamental mechanistic model using the SPEEDUP package. This is the most detailed model yet published. An extensive set of experiments has been carried out to calibrate the model which contains only four fixed parameters out of 121 equations and 200 variables. The model has been used for steady state optimisation of zinc cell operations and for dynamic analysis of feed variations for control system justification.

Acknowledgements

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Symbols

A Electrode Surface area (m²)
 $A_o(j)$ Frequency factor (Arrhenius eqn.) (m/sec)
 $a_o(j)$ Activity of the oxidised species (moles/l)

$a_r(j)$ Activity of the reduced species (moles/l)
 b Inter-electrode gap (m)
 $C(j)$ Concentration in bulk solution (moles/l)
 CE Current Efficiency (%)
 cond Conductivity (s/m)
 E Working electrode potential (volts)
 $E_e(j)$ Equilibrium potential (volts)
 $E_o^\ominus(j)$ Standard equilibrium potential (volts)
 $e(j)$ Activation energy (Arrhenius eqn.) (J/mole)
 E_a Anode Potential (volts)
 E_c Cathode Potential (volts)
 E_1 Voltage losses in busbar and contacts (volts)
 F Faraday constant (c/mole)
 H_f Heat flow of feed stream (J/s)
 H_e Electrical energy (J/s)
 H_1 Energy losses (J/s)
 H_r Total heat of reactions (J/s)
 H_{evap} Heat of evaporation (J/s)
 H_d Heat flow of discharge stream (J/s)
 $i(j)$ Current density (A/m²)
 i_{total} Total current density (A/m²)
 $i_1(j)$ Mass transfer limiting current density (A/m²)
 i_{zn} Current density for zinc deposition reaction (A/m²)
 $k_o^\ominus(j)$ Standard rate constant (m/sec)
 $n(j)$ Ionic charge
 P Power consumption (kW-hrs/t Zn)
 R Gas constant (J/mole.K)

T	Temperature	(K)
V	Cell voltage	(volts)
$z(j)$	Charge transfer number	
$\alpha(j)$	Transfer coefficient	
$\gamma_o(j)$	Activity coefficient of oxidised species	
$\gamma_r(j)$	Activity coefficient of reduced species	
η	Overpotential	(volts)
ρ_f	Density of feed (neutral) electrolyte	(g/l)
ρ_s	Density of spent (acidic) electrolyte	(g/l)

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