JOURNAL OF APPLIED ELECTROCHEMISTRY 24 (1994) 377–383

Industrial applications of a mathematical model for the zinc electrowinning process

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Received 11 June 1993; revised 16 August 1993

A dynamic mathematical model for a full-size zinc electrowinning cell, operating with high purity feed, has previously been presented. Several possible industrial applications of the model are demonstrated in this paper. The examples considered were (i) the optimization of cell operating conditions, for both maximum zinc production and minimum energy consumption cases, (ii) a preliminary investigation of the benefits of a dual circuit configuration and (iii) the dynamic simulation of a (feedback) controlled cell. In each case, by providing information on energy consumption, current efficiency and zinc production rate, use of the model permitted the economic potential of these options to be readily determined.

1. Introduction

As 80% of the power requirements for an electrolytic zinc refinery originate from the electrowinning process, it is economically vital to operate the cellroom as close to the optimum operating conditions as possible. Optimum performance of a cellroom may be defined in a number of ways, such as requiring that the energy per tonne of zinc produced be minimized. However defined, the optimal cellroom performance can be determined using a validated mathematical model of the steady-state zinc electrowinning process. As a first step to achieving this objective, a series of carefully designed experiments were conducted at the refinery of the Electrolytic Zinc Company (EZ) in Hobart, Australia. These experiments, which were carried out in $10\,dm^3$ cells using a high purity zinc sulphate electrolyte, investigated the major factors affecting the efficiency of zinc electrowinning [1]. A dynamic mathematical model for these pilot-plant scale cells was then developed and calibrated using the experimental results [2]. This model consisted 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 density. The pilot-plant model was then modified to make it applicable to full-size cells [3]. The resulting mathematical model could accurately predict the current efficiency and energy consumption of full-size zinc electrowinning cells under a range of industrial operating conditions.

The final paper in this series demonstrates some of the possible industrial applications of the full-size cell model by presenting a number of case studies. First, the steady-state version of the model was applied to several plant optimization problems where the minimum energy consumption (per tonne of zinc produced) or the maximum zinc production rate were calculated. A second use of the steady-state version of the model is in the design of possible future cellrooms. This aspect was demonstrated by considering two alternative cellroom configurations and using the model to determine which is the more efficient in terms of energy consumption.

The dynamic nature of the model allows process control studies to be undertaken. In the final case study, simulations were performed in which a controller was used to control the conductivity of the cell electrolyte by adjusting the feed flowrate to the cell.

A full description of these (and other) model applications has been presented by Scott [4].

2. Optimization of cell performance

At the time of this study, the EZ refinery was operating with a relatively low concentration feed electrolyte (about $110\,g\,dm^{-3}$ zinc). Studies using both the pilot-plant cells and the steady-state cell model indicated that significant performance improvements could be achieved if a higher concentration feed electrolyte were used [4]. This would allow the use of a higher cell acidity while maintaining a zinc concentration in the cells that would ensure a high current efficiency. Using high acidity cell electrolyte also has added benefits in other parts of the refinery, such as the leaching circuit.

Note that all modelling (both the steady-state and dynamic) and optimization work in this study was carried out using the commercial SpeedUp flowsheeting package [5].

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2.1. *Objective function and constraints*

To carry out a process optimization, SpeedUp requires four things:

(i) An objective function. This is the variable (or function of one or more variables) to be optimized.

(ii) A list of all operational constraints. These are a set of inequalities that restrict certain variables (or functions of variables) to lie within a specified range. When the optimal solution is such that an operational constraint becomes an equality, then that constraint is said to be 'active'.

(iii) A steady-state model. This may be thought of as a set of equality constraints that an optimum must satisfy.

(iv) The specification of a set of free variables. These variables are adjusted by the optimizer until the objective function is minimized (or maximized, as required).

The first cellroom optimization (Section 2.2) used an objective function which maximized the rate of zinc production per cell. The second cellroom optimization (Section 2.3) used an objective function of the minimum energy consumption per tonne of zinc produced. These two objective functions reflect the situations that most commonly occur in a zinc refinery. If the zinc market is strong, the aim is to produce as much zinc as possible. Slightly higher operating costs (due to higher energy consumption per tonne of zinc) are more than offset by the extra profit made from selling more zinc. However, if the market for zinc is weak, the aim is to make the zinc as cheaply and efficiently as possible, and hence the energy consumption must be minimised.

The operational constraints which were applied for both these optimization cases reflect the practical limitations on the EZ cellroom, at the time this study was conducted, and were as follows:

(i) Current density $\geqslant 300\,\mathrm{A\,m^{-2}}$
(ii) Current density $\leqslant 420\,\mathrm{A\,m^{-2}}$
(iii) Cell temperature $\geqslant 30^\circ\,\mathrm{C}$
(iv) Cell temperature $\leqslant 40^\circ\,\mathrm{C}$
(v) Zinc feed concentration $\leqslant 160\,\mathrm{g\,dm^{-3}}$

The current density could not exceed $420\,\mathrm{A\,m^{-2}}$ due to limitations on the electrical rectifiers. A minimum value of $300\,\mathrm{A\,m^{-2}}$ was also set to prevent the production rate from being decreased to an unrealistic level. The cell temperature must be greater than (about) 30° C since the cooling system was incapable of reducing the temperature below this level. A maximum temperature of 40° C was also set since pilot-plant experiments [1] had indicated that above this temperature the zinc deposited becomes nodular and electrical shorting could become a problem. In addition, at higher temperatures there was concern that lead contamination of the zinc deposit might be difficult to control [6]. The upper limit of $160\,\mathrm{g\,dm^{-3}}$ for the zinc feed concentration was imposed to ensure that there were no operational problems with solubility limitations or high viscosity in other parts of the refinery.

As well as the above constraints, the following variables were given set values:

(a) Cobalt in feed = $0.3\,\mathrm{mg\,dm^{-3}}$
(b) Manganese in feed = $7.0\,\mathrm{g\,dm^{-3}}$
(c) Magnesium in feed = $4.0\,\mathrm{g\,dm^{-3}}$
(d) Ammonium in feed = $3.5\,\mathrm{g\,dm^{-3}}$
(e) Deposition time = 72 h

In zinc electrowinning, additives (animal glue and antimony) are used to help control the morphology of the zinc deposit (i.e. to keep it as smooth as possible, [1, 4]). The mechanism by which these additives work is unknown. The model used in this study assumed that an *adequate* dosing of additives was used.

2.2. *Maximum zinc production*

The aim of the first optimization undertaken was to determine the maximum zinc production (per cell). The free variables used in this case were as follows: zinc concentration in the feed, acid concentration in the cell, cell temperature, and current density.

It should be noted that an extra operational constraint was added for this case. The minimum cell acidity was set at $120\,\mathrm{g\,dm^{-3}}$. Acidities lower than this were undesirable since the performance of the leaching circuit in the refinery would be expected to fall quite significantly. The results of this optimization are presented in Table 1 which shows that the maximum zinc production rate (per cell) of $0.64\,\mathrm{tonne\,day^{-1}}$ is expected to be achieved at the highest allowable cell temperature, current density and feed zinc concentration with the cell acidity at its lowest possible value. The maximum zinc production rate case thus has a fully constrained optimum, with the same number of active constraints (marked in Table 1 with an asterisk) as there are free variables.

2.3. *Minimum energy consumption*

In the second optimization, the aim was to determine the minimum energy consumption per tonne of zinc

Table 1. Maximum zinc production using a high purity electrolyte

Cellroom parameter	*Value*
Zinc in feed (*)	$160\,\mathrm{g\,dm^{-3}}$
Zinc in cell	$77.0\,\mathrm{g\,dm^{-3}}$
Acidity in cell (*)	$120\,\mathrm{g\,dm^{-3}}$
Cell temperature (*)	40° C
Current density (*)	$420\,\mathrm{A\,m^{-2}}$
Current efficiency	96.8%
Energy consumption	$2905\,\mathrm{kW\,h\,tonne^{-1}}$
Maximum zinc production (per cell)	$0.64\,\mathrm{tonne\,day^{-1}}$

* Active constraints.

Table 2. Minimum energy consumption using a high purity electrolyte

Cellroom parameter	*Value*
Zinc in feed (*)	160 g dm^{-3}
Zinc in cell	69.0 g dm^{-3}
Acidity in cell	132.3 g dm^{-3}
Cell temperature (*)	40° C
Current density (*)	300 A m^{-2}
Current efficiency	95.6%
Minimum energy consumption	2706 kW h tonne^{-1}
Zinc production (per cell)	0.45 tonne day^{-1}

* Active constraints.

produced. The constraints and free variables were the same as those used for the maximum zinc production case, except that no lower limit was imposed on the cell acidity. The results of this optimization are presented in Table 2, where once again the active constraints have been marked with an asterisk. It is clear from the results shown in Tables 1 and 2 that the cell operating conditions necessary to achieve maximum zinc production and minimium energy consumption are quite different.

2.4. *The effect of major operating variables*

In the above two optimizations, certain constraints were placed on some cell operating conditions. This was necessary due to practical limitations that exist in industrial cellrooms, such as that at the EZ refinery. If a new cellroom were to be designed, however, some of these constraints might no longer apply. The cell model was, therefore, also used to determine what level of electrochemical performance could be achieved in such a new cellroom.

The first variable to be considered was cell temperature. A series of optimizations (to find the minimum energy consumption per tonne of zinc) was carried out at electrolyte temperatures of 30, 35, 40, 45 and 50° C. The results shown in Fig. 1 indicate that the lowest energy consumption would be achieved using a cell temperature of 45° C. It should be stressed, however, that before such a (relatively) high cell temperature was used, pilot-plant trials

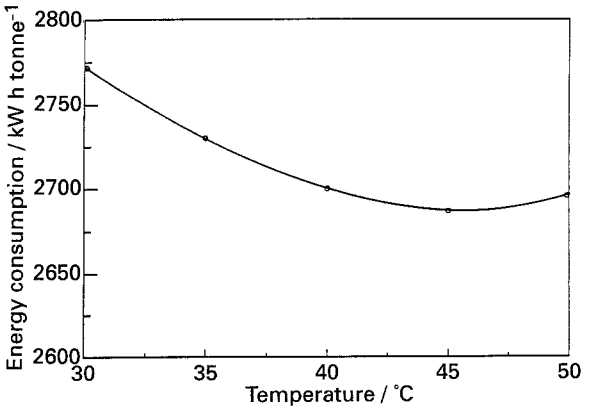

Fig. 1. Minimum energy consumption against cell temperature. (Zinc feed concentration: 160 g dm^{-3}; current density: 300 A m^{-2}; deposition time: 72 h).

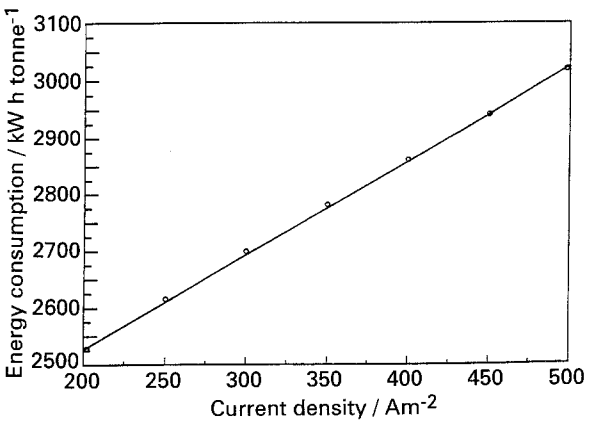

Fig. 2. Minimum energy consumption versus current density. (Zinc feed concentration: 160 g dm^{-3}; temperature = 40° C; deposition time: 72 h)

would probably be necessary to determine what additives were needed under these conditions. The high performance achievable at 45° C is strongly dependent on the feed electrolyte being of a high purity. If feed purity deteriorated, a lower cell temperature would need to be used otherwise severe resolutioning of the zinc deposit might well occur. The fact that there is a minimum in the energy consumption at 45° C is, indeed, due to the fact that even with a high purity electrolyte (only 0.3 mg dm^{-3} cobalt), a slight drop in performance occurs at higher temperatures due to resolutioning.

The second variable considered was current density. Figure 2 shows the optimum energy consumption achievable over the current density range 200 to 500 A m^{-2}. The best performance is achieved at the lowest allowable current density. The production rate of a refinery decreases with the current density, a problem which most new cellrooms overcome by increasing the size of the cathodes [7] so as to maintain the same production rate.

Simulations were also carried out for zinc feed concentrations over the range 140 to 180 g dm^{-3}. Figure 3 shows that lower energy consumption can be achieved by increasing the feed concentration. However, the improvement possible is quite small, with only 15 kW h tonne^{-1} being saved by increasing the concentration from 160 to 180 g dm^{-3}.

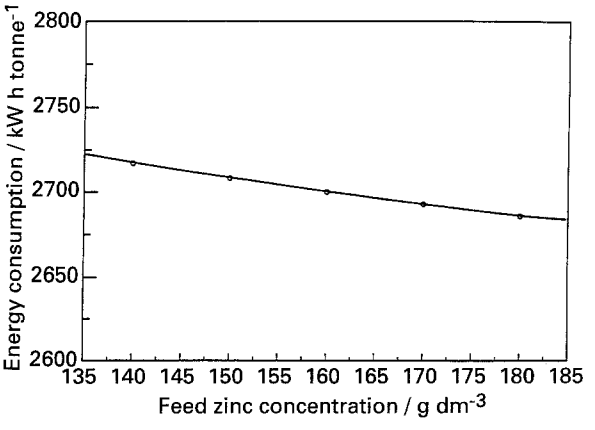

Fig. 3. Minimum energy consumption versus zinc feed concentration. (Temperature: 40° C; current density: 300 A m^{-2}; deposition time: 72 h).

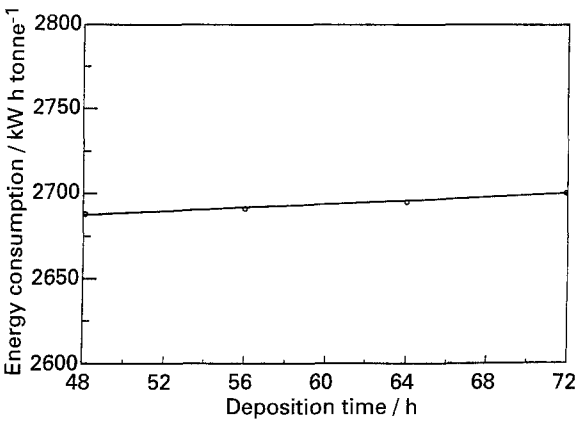

Fig. 4. Minimum energy consumption versus deposition time. (Zinc feed concentration: 160 g dm^{-3}; temperature: 40° C; current density: 300 A m^{-2}).

Consequently, whether a zinc feed concentration of 180 g dm^{-3} (or higher) were to be used would probably depend more on its effect in other parts of the refinery.

Figure 4 shows that there is a very slight increase in energy consumption with deposition time, from 2688 kW h tonne^{-1} at 48 h to 2700 kW h tonne^{-1} at 72 h. This is due to a resolutioning reaction on the zinc surface caused by the presence of low level impurities in the cell electrolyte. At even lower impurity concentrations, this effect would become less pronounced and a slight drop in energy consumption with deposition time would occur due to the thicker zinc deposit reducing the ohmic drop between the electrodes. Despite the slight rise in energy consumption with time shown in Fig. 4, long deposition times should be used so that cathode stripping costs can be reduced. The limit would depend on how thick the zinc deposit could become before short-circuiting between deposit and the anode became a problem.

The final variable considered in this assessment of likely new cellroom operating conditions was cell acidity. Figure 5 shows that although the best performance occurs at 133 g dm^{-3}, there would only be an 11 kW h tonne^{-1} increase in energy consumption if an acidity of 150 g dm^{-3} were used. However, a major advantage of using a higher

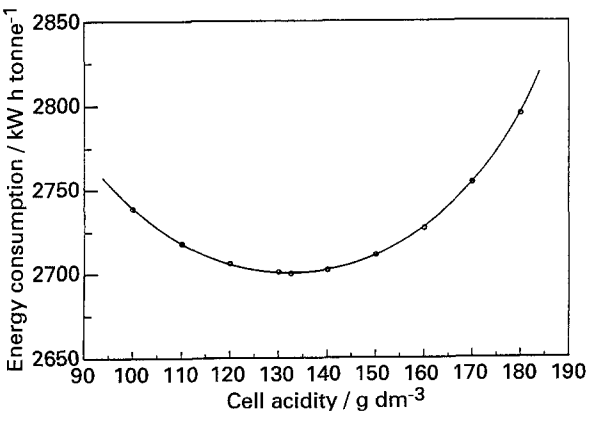

Fig. 5. Minimum energy consumption versus cell acidity. (Zinc feed concentration: 160 g dm^{-3}; temperature: 40° C; current density: 300 A m^{-2}; deposition time: 72 h).

cell acidity would be that the performance of the leaching section of the refinery would be greatly improved. These observations formed the basis for a consideration of a dual circuit refinery.

3. Feasibility of a dual circuit arrangement

As noted above, the minimum energy consumption for a high purity feed containing 160 g dm^{-3} zinc occurs at a cell acidity of 133 g dm^{-3}. However, the leaching circuit of a refinery generally performs better if higher acidities are used. The ideal situation would thus be if both these conditions could be satisfied. This can be achieved by using a 'dual circuit' arrangement in which the majority of cells are operated at the lower acidity level (that gives minimum energy consumption), while the remaining cells are operated so as to provide high acidity liquor for the leach circuit. Figure 6 shows the dual circuit arrangement that is most commonly used. At the EZ refinery, a dual circuit type arrangement has been proposed by simply reducing the feed flowrate (and, therefore, increasing cell acidity) to the sixth cell in each set of cascade cells (see Fig. 7; note that at EZ, heat is removed from cascade cells via cooling coils located within each cell). Since all electrolyte passes through the sixth cell, if it is operated at high acidity then only high acidity solution would leave the cellroom. In this proposed arrangement, cells 1 to 5 in each cascade would be operated at low acidities so as to achieve minimum energy consumption.

In this case, SpeedUp was used to optimize a cascade of cells, so as to obtain the minimum energy consumption (averaged over all six cells). To achieve this, a flowsheet was constructed where the output of cell i became the input to cell $i+1$. This flowsheet simulation consisted of some 600 equations. The constraints used were similar to those for a single cell (Section 2.1), except that an extra constraint was imposed on the sixth cell:

$$[\text{Acidity}]_{\text{cell}\,6} \geqslant 165\ \text{g dm}^{-3}$$

The objective function used was the average energy consumption (P_{av}),

$$P_{\text{av}} = (P_{\text{cell}\,1} + P_{\text{cell}\,2} + P_{\text{cell}\,3} + P_{\text{cell}\,4} + P_{\text{cell}\,5} + P_{\text{cell}\,6})/6$$

where $P_{\text{cell}\,i}$ is the energy consumption of cell 'i'.

The results of this optimization are given in Table 3.

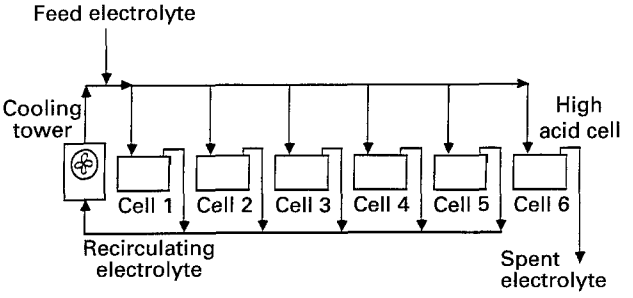

Fig. 6. Conventional dual circuit cellroom.

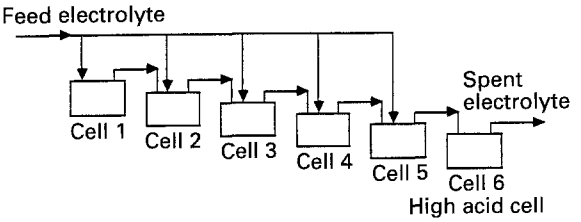

Fig. 7. Proposed dual circuit configuration for the EZ cascade cells.

As expected, the minimum average energy consumption occurs when most of the early cells in a cascade are run at an acidity (132 g dm^{-3}) close to that corresponding to minimum energy consumption conditions for a single cell. The fifth cell, however, must run at a slightly higher acidity (139 g dm^{-3}) so that the minimum acceptable acidity in the last cell (165 g dm^{-3}) can be achieved. The average energy consumption over all six cells in the cascade is 2715 kW h tonne^{-1}. If a single circuit arrangement were used with all cells operating at 165 g dm^{-3}, the average energy consumption would be 2753 kW h tonne^{-1}. This dual circuit arrangement, therefore, has the potential to achieve a saving of 38 kW h tonne^{-1}. The attraction of this dual circuit arrangement for the cascade cells at EZ is that it would not require any additional capital or operating costs. The economic benefits can be achieved by simply adjusting the feed flowrates to the six cells in a cascade.

4. Process control studies

In Sections 2 and 3 all simulation and optimization results were obtained using the steady-state version of the zinc electrowinning cell model. In this Section, the dynamic capabilities of the model will be demonstrated by considering closed-loop control for the first cell in a cascade at the EZ refinery. The measured (and controlled) variable is the cell electrolyte conductivity while the manipulated variable is the feed flowrate to the cell. At constant temperature, the conductivity reflects the zinc to acid ratio of the cell electrolyte, and can thus be used to maintain this ratio at a set value. To prevent any fluctuations in cell temperature from adversely affecting the control, a modified conductivity σ' (which is independent of temperature) was used;

$$\sigma' = 32.0 + 19.6([H_2SO_4] - 1.12) - 11.1([C^*] - 1.25)$$

where C^* is an 'equivalent zinc concentration' [2].

The proportional-integral (PI) controller employed was described using the following equation;

$$Q_f = K_c e + \frac{1}{\tau_I}\int e \, dt$$

where Q_f is the feed flowrate (dm^3 s^{-1}), e is the (measured–required) modified conductivity (S m^{-1}), K_c is the controller gain (= 0.01 in consistent units) and τ_I is the integral time constant (= 5000 s^{-1}).

The PI controller was tuned (i.e. values found for K_c and τ_I) using a conventional quarter-decay ratio method [8] with the values obtained given above.

Two case studies were considered, both of which typify common operating changes that occur in an industrial cellroom:

(i) A step change in current density from 300 to 400 A m^{-2}. The zinc feed concentration in this case was 160 g dm^{-3}.

(ii) A ramp decrease (occurring over a ten hour period; starting at a time of 15 min on Figs 11 and 12) in the zinc concentration of the feed electrolyte from 160 to 140 g dm^{-3}. The current density in this case was 400 A m^{-2}.

4.1. *Step change in current density*

The resulting open-loop (i.e. no controller in place) and closed-loop responses are shown in Figs 8 and 9. In the open-loop case, the conductivity increased from 40 S m^{-1} to over 50 S m^{-1}, a change of more than 25%. In the closed-loop case, the controller maintained the conductivity within 2% of the set-point value. The use of a controller also

Table 3. Minimum energy consumption for a cascade of cells

Parameter	*Cell 1*	*Cell 2*	*Cell 3*	*Cell 4*	*Cell 5*	*Cell 6*
Energy consumption /kW h tonne^{-1}	2706	2707	2707	2707	2709	2753
Current efficiency /(%)	95.6	95.6	95.6	95.6	95.2	92.8
Zinc production /tonne day^{-1}	0.45	0.45	0.45	0.45	0.45	0.44
Cell acidity /g dm^{-3}	132	132	132	132	139	165
Cell feedrate /dm^3 min^{-1}	3.42	3.42	3.41	3.41	2.45	0.0
Cell temperature /°C	40	40	40	40	40	40
Current density /A m^{-2}	300	300	300	300	300	300

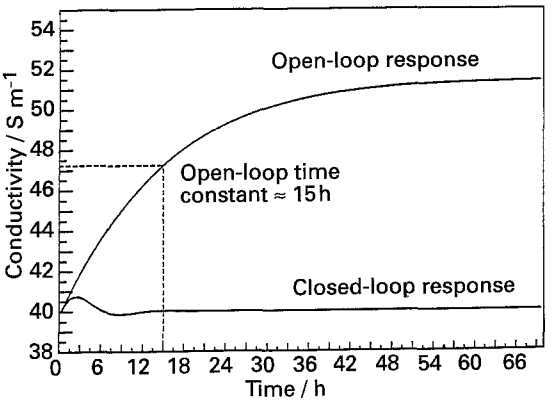

Fig. 8. Open and closed-loop responses of conductivity to a step increase in current density.

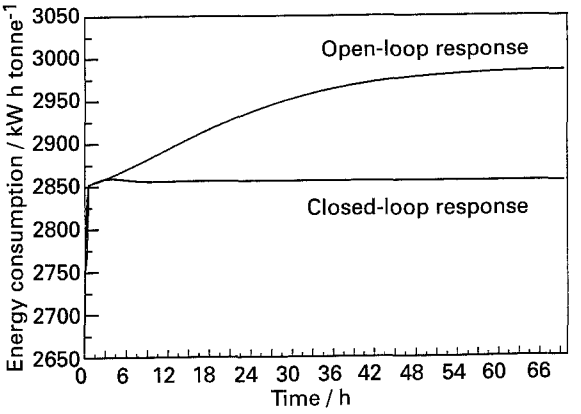

Fig. 10. Open and closed-loop responses of energy consumption to a step increase in current density.

saved considerable energy as shown in Fig. 10. When no controller was used, the step change in current density caused an increase (between initial and final steady-state values) in energy consumption of about 240 kW h tonne^{-1}. However, with the controller in operation the energy consumption only increased by 110 kW h tonne^{-1}.

4.2. *Ramp decrease in zinc concentration of feed electrolyte*

The open and closed-loop responses for this case are shown in Figs 11 and 12. Without a controller, the energy consumption slowly increased by 70 kW h tonne^{-1} as the zinc concentration fell. With a PI controller used, however, the drop in performance was again considerably less. The conductivity deviated less than 0.2% from its set-point value while the energy consumption only increased by 40 kW h tonne^{-1}.

These two case studies illustrate the point that process control holds out the potential for savings in electrical power equally as large as those achievable by steady-state optimization.

5. Other applications (and limitations) of the cell model

In the previous sections, a number of applications of the mathematical model of a zinc electrowinning cell have been demonstrated. Many other uses exist, although only two more will be mentioned here.

(a) An investigation of other cell arrangements and operating conditions. For instance, there are a number of advantages [4] to operating a small number of cells at very high acidities (of the order 180–200 g dm^{-3}). The model could be used to predict the energy consumption, current efficiency and zinc production for such proposed options.

(b) The investigation of poor cellroom performance. If the cellroom's current efficiency began to drop significantly below that predicted by the model, this could serve as an early warning that operational problems might well exist. Such a comparison would be quite possible, as the model has been scaled up to describe full-size cells [3].

As with any mathematical model, it must be realised that certain limitations exist and care should be taken in its use. Some of the more important limitations of the model should be clearly pointed out. Firstly, the model contains both estimated parameters and (mathematical) descriptions of physical mechanisms that will only apply within a certain range of cell operating conditions. This should be remembered if any attempt is made to predict cell performance under operating conditions which are quite different to those that are generally found in zinc refineries. Secondly, as

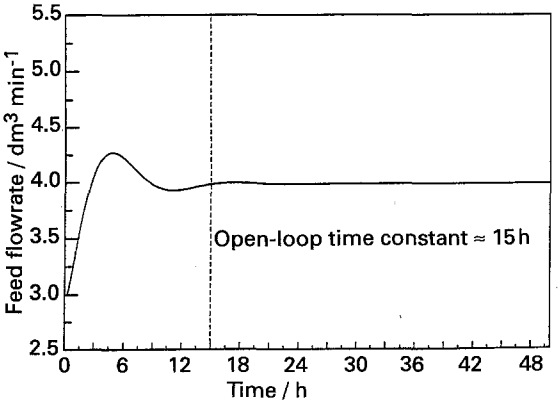

Fig. 9. Closed-loop variation of feed flowrate for a step increase in current density.

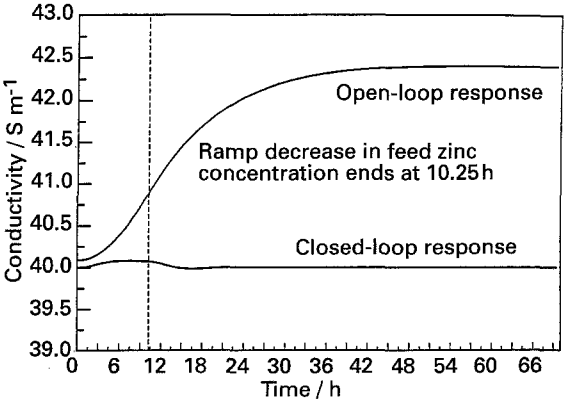

Fig. 11. Open and closed-loop responses of conductivity to a ramp decrease in feed zinc concentration.

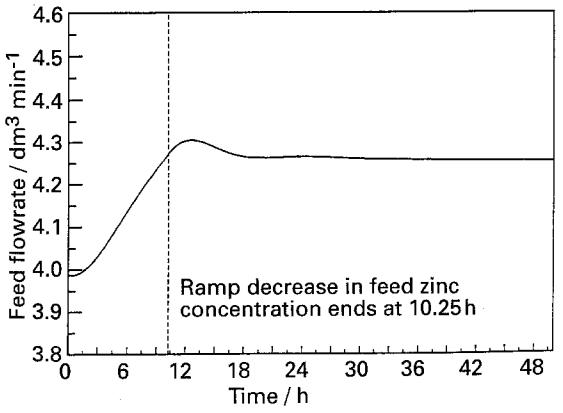

Fig. 12. Closed-loop variation of feed flowrate for a ramp decrease in feed zinc concentration.

with any model, certain simplifications have been made. For example, in this model it is assumed that the correct levels of additives are always used and, consequently, that the morphology of the zinc deposit is fairly smooth. Another key assumption is that a 'pure' feed electrolyte is used and that the residual impurities present do not greatly affect current efficiency. Although empirical equations (based on experimental data) have been developed for two of the major impurities at the EZ refinery (copper and cobalt [4]), other impurities such as cadmium and iron have not been investigated. Finally, it should be remembered that this model can only predict the performance of the cellroom. The impact on other parts of the refinery must also be considered before any changes are made to the design and/or the operation of the cellroom.

Within the limitations given above, however, this mathematical model has been found to be a very cost-effective tool in both the design of possible new cellrooms and in the prediction of electrochemical performance in existing cellrooms under changed operating conditions.

6. Conclusions

Undoubtedly the major advantage of any model such as this is that once it has been developed, it allows a large number of possible options to be evaluated quickly and at relatively little cost. The mathematical model of a zinc electrowinning cell has proved to be an extremely useful tool for evaluating the electrochemical performance of individual cells and complete cellrooms, both existing and proposed.

Finally, although all the results given in this paper were calculated using the commercial SpeedUp package, it would be a relatively simple matter to develop a personal computer based version of the model. For example, a (Fortran) model of a steady-state circuit employing external (i.e. cooling tower) electrolyte cooling has also been developed by the authors. This circuit model typically takes of the order of a minute to run on a 386 personal computer.

Acknowledgements

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

References

[1] A. C. Scott, R. M. Pitblado and G. W. Barton, *J. Appl. Electrochem.* **18** (1988) 120–7.
[2] G. W. Barton and A. C. Scott, *ibid.* **22** (1992) 104–15.
[3] G. W. Barton and A. C. Scott, *ibid.* **22** (1992) 687–92.
[4] A. C. Scott, 'The Development and Application of a Mathematical Model for the Zinc Electrowinning Process', PhD thesis, University of Sydney, Australia (1988).
[5] C. C. Pantelides, *Comp. Chem. Eng.* **12** (1988) 745–55.
[6] A. R. Ault, O. M. G. Newman, A. C. Scott and J.R. Siemon, *Proc. RACI, 7th Aust. Electrochem. Conf.*, Sydney (1988) 114–7.
[7] Y. Bellefroid, 'Zinc 85', *Proc. Int. Symp. Extractive Metallurgy of Zinc*, Tokyo (1985), 383–98.
[8] G. Stephanopoulos, 'Chemical Process Control', Prentice-Hall, Englewood Cliffs, NJ (1984).