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Experimental determination of the factors affecting zinc electrowinning efficiency

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A series of experiments were conducted to investigate the factors affecting the efficiency of zinc electrowinning. The experiments were conducted in 10-l cells using a high purity industrial zinc sulphate solution. The lowest specific energy consumption achieved in the cells was 2637 $\mathrm{kW\,h\,t^{-1}}$ Zn under the following conditions:

$70\,\mathrm{g\,l^{-1}}$ Zn in cell solution
$180\,\mathrm{g\,l^{-1}}$ H_2SO_4 in cell solution
45° C cell temperature
$400\,\mathrm{A\,m^{-2}}$ current density

Further energy savings can be achieved by reducing the current density but this would also reduce the cellroom production capacity. Increasing the electrolyte temperature to 50° C also reduced the energy consumption, however additives capable of controlling deposit morphology at these high temperatures were required. The effects of zinc concentration, acid concentration, deposition time and additive levels are also reported.

Nomenclature

CE	current efficiency (%)
$\hat{E}$	specific energy consumption ($\mathrm{kWh\,t^{-1}}$)
F	Faraday constant
I_{total}	total current (amps)
$k1$, $k2$	constants of the Wark equation
M	molecular weight
n	number of electrons transferred per molecule
t	time of deposition (sec)
T	temperature (° C)
V	cell voltage (volts)
W	weight of metal deposited (g)
C^*	concentration of metal ions ($\mathrm{mol\,l^{-1}}$)

1. Introduction

As 80% of the power requirements of a zinc electrolytic refinery originate from the electrowinning process, it is vital to operate the cellroom as close to the optimum operating conditions as possible. In order to obtain this optimum for the refinery of the EZ company at Risdon, it was decided to construct a mathematical model of a zinc electrowinning cell. The model would be used in optimizing the cellroom presently in operation and also assist in the design of a new circuit.

Optimum performance of a cellroom occurs when the energy per tonne of zinc produced is minimized. The mathematical model therefore must be capable of predicting the energy consumption under a range of operating conditions. The two parameters directly controlling the energy consumption are current efficiency and cell voltage. The major variables affecting these two parameters are: zinc and acid concentrations, current density, temperature, impurities and additive levels. The time of deposition can also be important if impurities are present in the electrolyte solution. Hence for the model to be capable of predicting current efficiency, cell voltage and hence energy consumption it must accurately describe the effects of each of these major variables. This required experimental data which could be used to validate and calibrate equations within the mathematical model. It soon became evident however that the experimental data reported in the literature was inadequate for this task. Much of the literature concentrates on the effects of impurities [1–10] and not the effects of the other major variables.

One exception is that of Wark [11] who presented an outline of a series of experiments conducted both in the presence and absence of cobalt. He concluded that the current efficiency could be calculated by the

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following expression

$$\left[\frac{\text{mol ZnSO}_4}{\text{mol H}_2\text{SO}_4}\right] \text{in solution} = \frac{1}{k1}\left[\frac{\text{g Zn}}{\text{g H}_2}\right] = \frac{1}{k2}\left[\frac{CE}{1\text{-}CE}\right] \quad (1)$$

where $k1 = 30$ for pure solution.

Unfortunately, no equations or experimental data describing the energy consumption of the zinc electrolytic cell were supplied by Wark. Bratt [12] gave a qualitative description of most of the major variables including the impurities, but it was not backed up by any experimental data. Fosnacht and O'Keefe [10] investigated the effect of acidity on current efficiency and Honey *et al.* [13] provided limited industrial data on current density effects but in both cases very little information was supplied for the other major variables. The most recent investigation was that by Biegler and Frazer [14] using a small rotating disc electrode. However for the purpose of modelling, experimental data was required for larger cells with similar electrode and cell geometry to that of full-size cells, thus enabling scale-up of the model. It was also considered important that the experiments be conducted over a deposition time similar to those used industrially. This is rarely attempted since it requires a continuous operation cell rather than the simpler batch test.

A series of specially designed experiments was therefore conducted at the EZ laboratories in 10-l cells with a high purity industrial electrolyte. The aim of the experiments was to supply detailed information on each of the following variables: zinc and acid concentration, current density, temperature, deposition time and additive level. Electrolyte conductivity and density were also studied. This paper presents the results of these experiments including the effects that the variables have on current efficiency, energy consumption, cathode potential and deposit morphology. A high purity electrolyte was used so that impurity effects would not interfere with the results. Further experiments to investigate the effects of the more common impurities (cobalt, copper, nickel and iron) were carried out at a later stage and will be reported separately.

The development of the mathematical model, using the experimental data, is also discussed elsewhere [15, 16].

2. Experimental details

There were two main considerations in the design of the experimental equipment. Firstly, since deposition times of up to 72 h were to be investigated, continuous rather than batch operation electrolytic cells had to be used in order to maintain steady state conditions. A batch process would not be appropriate since cell concentrations would change. Secondly, all efforts were made to simulate the conditions of a full-size cell wherever practical.

Two 10-l cells each containing 2 aluminium cathodes (at a spacing of 76 mm) and 3 silver-lead anodes (0.75% Ag) were used. These electrodes were cut from full size cathodes and anodes obtained from the EZ cellroom. Each cathode had an immersed surface area of 590 cm^2. Peristaltic pumps provided the feed and additive to the cell. Solution left the cell via an overflow weir which could be raised or lowered to obtain the correct solution level. Much of the spent leaving the cell was recirculated in order to promote a high degree of mixing. Two controllers were required in order to maintain the cell conditions at steady state. These were (1) feed rate controller to maintain constant cell acidity, (2) cell temperature controller.

Cell conductivity in the range 10–70 S m^{-1} was measured by a conductivity probe. The signal from the probe was compensated for temperature variations and then used to control the feed and additive rates. The cell acidity was derived from the conductivity measurement and could be calibrated by carrying out an acid titration. By use of the conductivity controller, experiments could be carried out at a constant acidity to an accuracy of ±2%. A temperature sensor in the cell controlled a 300 W heater element inserted in the cell. This limited temperature variations to within ±1%.

All other instrumentation was for acquiring accurate experimental data. Total current to both cells, and individual current to each of the 4 cathodes was measured as millivolt drops across calibrated current shunts. This gave an accuracy of 0.1% confirmed by summing the individual cathode currents and comparing it with the measurement for total cell current. Cell voltage was continuously monitored to an accuracy of 10 mV. A record of how current efficiency was changing during the deposition cycle was obtained using a 2 kg load cell. The load cell measured the changing weight of the front cathode in each cell due to the deposition of zinc. Cathode potentials were measured periodically using a Luggin capillary connected to a standard calomel electrode (SCE). All measurements were recorded on both a 30-point chart recorder and logged using a PDP 11/23 computer.

The overall current efficiency for each experiment was calculated using equation (2).

$$CE = \frac{WnF}{tI_{\text{total}}M} \times 100\% \quad (2)$$

Equation (3) gives the specific energy consumption:

$$\hat{E} = \frac{VI_{\text{total}}t}{W} = \left[\frac{V}{CE}\right]\left[\frac{100nF}{M}\right] \quad (3)$$

By substituting the relevant values for zinc this gives:

$$\hat{E}(\text{kWh t}^{-1}) = 81970\left[\frac{V}{CE}\right] \quad (4)$$

Table 1. Standard conditions used in the experimental programme

Zinc concentration in cell	$55\,\mathrm{g\,l^{-1}}$
Acidity in cell	$110\,\mathrm{g\,l^{-1}}$
Current density	$500\,\mathrm{A\,m^{-2}}$
Temperature	35.0° C
Deposition time	42 h
Additives	$25\,\mathrm{mg\,l^{-1}}$ glue + $0.04\,\mathrm{mg\,l^{-1}}$ Sb

3. Experimental programme

The experiments were based on the set of standard conditions presented in Table 1, using a high purity industrial zinc sulphate electrolyte.

Each variable in turn was investigated (Table 2) while all others remained at the standard conditions. This allowed the effect that each parameter had on current efficiency and energy per tonne of zinc to be investigated.

In all experiments magnesium, manganese, ammonium and chloride ions were kept constant at $4.6\,\mathrm{g\,l^{-1}}$, $12.2\,\mathrm{g\,l^{-1}}$, $2.5\,\mathrm{g\,l^{-1}}$, $0.115\,\mathrm{g\,l^{-1}}$, respectively. All harmful impurities were kept at low concentrations so that they would not interfere with the results. Cobalt levels were below $0.3\,\mathrm{mg\,l^{-1}}$. A large range of zinc sulphate–sulphuric acid solutions were also analysed in the laboratory to obtain data on conductivity and density.

4. Results and discussion

4.1. *Density and conductivity*

A number of different empirical and semi-empirical correlations were examined for the prediction of density and conductivity, based on experimental results for a large range of solutions. For both density and conductivity linear equations based on the deviation of the solution from a standard condition were found to be most appropriate. In the density equation the standard condition is that of pure water.

$$\text{Density}\ (\mathrm{g\,l^{-1}}) = 1000 + 0.88\,[\mathrm{ZnSO_4} + \mathrm{MgSO_4} + \mathrm{MnSO_4} + (\mathrm{NH_4})_2\mathrm{SO_4}] + 0.56[\mathrm{H_2SO_4}] \quad (5)$$

where concentrations and density are in $\mathrm{g\,l^{-1}}$.

$$\text{Conductivity}\ (\mathrm{S\,m^{-1}}) = 32.0 + B(T - 35) + 19.6(\mathrm{H_2SO_4} - 1.12) - 11.1(C^* - 1.25) \quad (6)$$

where

$$B = \text{temp coefficient} = 0.27(\mathrm{H_2SO_4})$$

and

$$C^* = ([\mathrm{Zn^{2+}}] + [\mathrm{Mn^{2+}}] + [\mathrm{Mg^{2+}}] + 0.5[\mathrm{NH_4^+}])$$

and all concentrations are in $\mathrm{mol\,l^{-1}}$.

For the prediction of conductivity, the molar effect of manganese and magnesium was found to be similar to that for zinc. The effect of $\mathrm{NH_4^+}$ is only half that of zinc due to its lower ionic charge. $\mathrm{H^+}$ ions have extremely high mobilities due to a unique transport mechanism whereby they jump between neighbouring water molecules [17]. This explains the increase in conductivity with increasing acidity. The addition of metal ions however, lowers the activity of water through solvation effects. Water tied up in solvating ions does not participate in the jump mechanism of the $\mathrm{H^+}$ ions [18], and results in a decrease in the solution conductivity. The effect of temperature on conductivity (i.e. B in Equation 6) was found to be dependent on the acidity of the solution.

Table 2. Deviations from standard conditions

Zinc concentration in cell	20, 25, 37, (55), 67, $80\,\mathrm{g\,l^{-1}}$
Acidity in cell	65, 87, (110), 132, $155\,\mathrm{g\,l^{-1}}$
Cell temperature	25, (35), 40, 45, 50° C
Current density	100, 350, (500), $650\,\mathrm{A\,m^{-2}}$ (all at $21\,000\,\mathrm{A\,h\,m^{-2}}$)
Additives	0, 0.25, (1) times the standard level

Standard conditions are in brackets.

4.2. *Zinc concentration*

The effect of increasing the concentration of zinc in the cell from $20\,\mathrm{g\,l^{-1}}$ to $85\,\mathrm{g\,l^{-1}}$ is illustrated in Fig. 1. The current efficiency increases rapidly at concentrations between 20–$50\,\mathrm{g\,l^{-1}}$. This is due to the increasing reaction rate for the zinc deposition reaction as the number of zinc ions in solution rises. The specific energy consumption (Fig. 1) decreased sharply from 3320 to $2820\,\mathrm{kWh\,t^{-1}}$ between $20\,\mathrm{g\,l^{-1}}$ Zn and $50\,\mathrm{g\,l^{-1}}$ Zn. This is a direct result of the sharp increase in current efficiency over this range. The specific energy consumption starts to level off above $50\,\mathrm{g\,l^{-1}}$ as

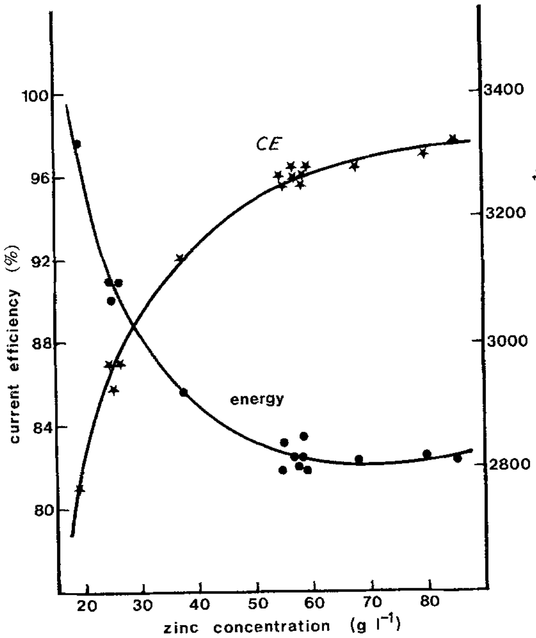

Fig. 1. Effect of zinc concentration on electrowinning performance. (Acidity = $110\,\mathrm{g\,l^{-1}}$; temperature = 35° C; current density = $500\,\mathrm{A\,m^{-2}}$.)

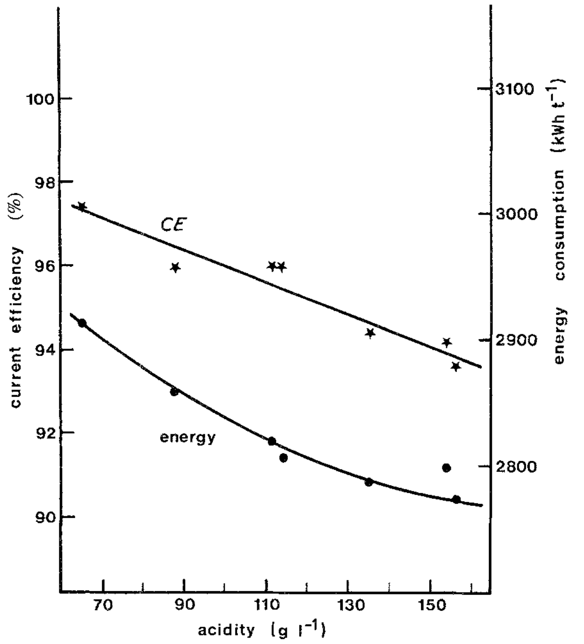

Fig. 2. Effect of acid concentration on electrowinning performance. (Zinc concentration = 55 g l^{-1}; temperature = 35° C; current density = 500 A m^{-2}.)

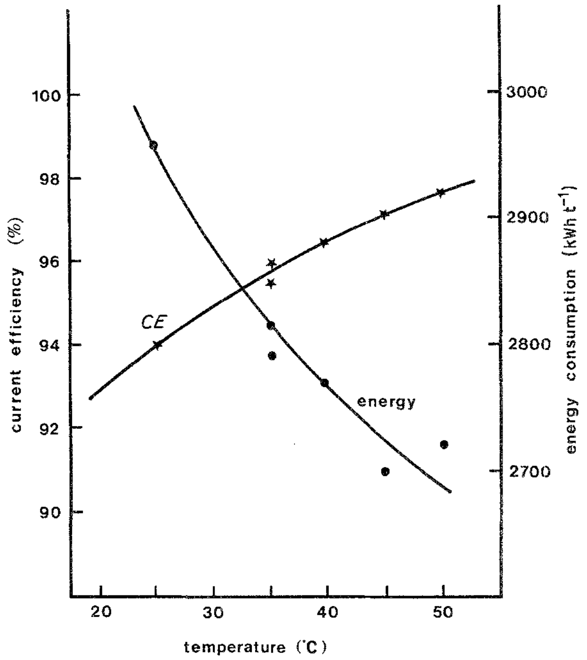

Fig. 3. Effect of temperature on electrowinning performance. (Zinc concentration = 55 g l^{-1}; acidity = 110 g l^{-1}; current density = 500 A m^{-2}.)

current efficiency gains are offset by increasing cell voltage. Cell voltage increased from 3.26 V at 20 g l^{-1} to 3.35 V at 85 g l^{-1} due to the lower solution conductivity as zinc concentrations increase (see equation 6).

The cathode potential dropped from 1.120 V (against SCE) at 20 g l^{-1} Zn to 1.070 V at 85 g l^{-1}. As the availability of zinc ions for deposition increases, a lower driving force is required, hence the lower cathode potential.

4.3. *Acidity*

The current efficiency decreased linearly from 97.4% at 65 g l^{-1} sulphuric acid to 94.0% at 155 g l^{-1} acid (Fig. 2). Mackinnon [4] obtained a very similar current efficiency of 93.6% under comparable operating conditions for 150 g l^{-1} acidity. As the concentration of hydrogen ions increases, the rate of hydrogen evolution becomes greater. Since hydrogen evolution and zinc deposition are reactions both competing for each unit of available current at the cathode, any increase in the rate of one, must be associated with a decrease in the rate of the other. Therefore the rate of zinc deposition must decrease with increasing acidity, which results in a lower cell current efficiency. The cell voltage dropped with increasing acidity from 3.46 V to 3.20 V due to the effect acid has on conductivity (see equation 6).

The combined effect of current efficiency and cell voltage resulted in a gradual decrease in specific energy consumption from 2910 kWh t^{-1} at 65 g l^{-1} acid to 2780 kWh t^{-1} at 155 g l^{-1}. This indicates that the benefits of lower cell voltage at higher acidities more than offsets the slightly lower current efficiencies, thus providing overall energy savings.

The cathode potential was not noticeably affected by changes in acidity, remaining at approximately 1.086 V (against SCE). A slight decrease would be expected, however it was below the limit of detection. Although the cathode potential is a mixed potential consisting of contributions from both the zinc and hydrogen reactions, the contribution from the zinc deposition reaction in most instances far outweighs that from the hydrogen reaction. Therefore the acidity has little effect on cathode potential under normal operating conditions.

4.4. *Cell temperature*

The current efficiency increased with temperature from 94.0% at 25° C to 97.7% at 50° C (Fig. 3).

The specific energy consumption declined rapidly with increasing temperature (Fig. 3) from 2960 kWh t^{-1} at 25° C to 2700 kWh t^{-1} at 50°C. The reason for this decrease is due both to the increasing current efficiency and the decreasing cell voltage as the temperature rises. Cell voltage decreased from 3.39 V at 25° C to 3.21 V at 45° C.

The increase in current efficiency is the reverse to that experienced in the cellroom at Risdon and hence was unexpected. At Risdon, resolutioning of zinc caused by the high cobalt level is activated by increasing temperature and results in low current efficiencies. In pure electrolyte no significant resolutioning occurs.

Cathode potential decreased from 1.108 V to 1.044 V between 25° C and 50° C. At high temperatures the rate constants of both cathodic reactions increase and hence a lower driving force is required.

The deposit surface became progressively rougher as the temperature increased. It was considered that operation up to 45° C would be practical in the cellroom but that at higher temperatures electrode shortening would become a problem due to nodule formation. If an alternative additive which prevents the nodule

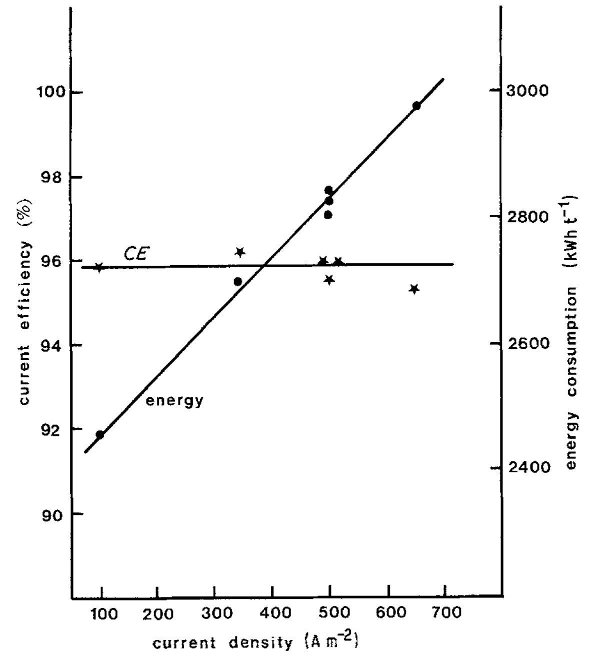

Fig. 4. Effect of current density on electrowinning performance. (Zinc concentration = 55 g l^{-1}; acidity = 110 g l^{-1}; temperature = 35° C.)

formation becomes available, operation at temperatures as high as 50° C could be viable.

4.5. *Current density*

These experiments were carried out at constant coulombs passed in order to separate coulombic and current density effects. As the standard experimental conditions were 500 A m^{-2} for 42 h (21 000 A h m^{-2}) all other tests were also conducted at 21 000 A h m^{-2}.

Current efficiency was found to be independent of current density over the range 100–650 A m^{-2} as shown in Fig. 4. Wark [11] obtained similar results over the range 95–920 A m^{-2} using an electrolyte of similar purity. This indicates that there is negligible mass transfer resistance (or concentration overpotential) over the range of current densities and zinc concentrations used industrially. The cell voltage increased linearly from 2.86 V at 100 A m^{-2} to 3.47 V at 650 A m^{-2}. This is primarily due to the increase in the IR voltage drop across the solution. Subsequently there was an increase in specific energy consumption from 2440 kWh t^{-1} at 100 A m^{-2} to 2990 kWh t^{-1} at 650 A m^{-2}. The cathode potential rose from 1.050 V (against SCE) to 1.087 V. At higher current densities a larger driving force is required, and both cathode and anode potentials rise with increasing current density.

Table 3. Effect of deposition time

Time (h)	*Current efficiency* (%)	*Energy consumption* (kWh t^{-1})
8	95.9	2861
24	96.2	2835
42	96.0	2820
56	96.2	2855
72	96.2	2855

(Zn = 55 g l^{-1}, Acidity = 110 g l^{-1}, Temperature = 35° C, Current density = 500 A m^{-2}.)

4.6. *Deposition time*

Experiments over the range 3–72 h indicated that deposition time has no effect on current efficiency (Table 3).

In the Risdon cellroom quite large drops in current efficiency can occur if long deposition times are used. This is attributed to resolutioning reactions, activated by solution impurities, which progressively increase in rate as the deposit grows older. In contrast, when a high purity solution is being electrolysed, deposition time is not a variable which needs to be considered as far as electrochemical performance is concerned. Although deposits became progressively rougher as deposition time increased, it was not sufficient to cause any electrical problems with shorting.

Over the duration of the 72 h deposit, there was a gradual drop in cell voltage of 80 mV. All other runs experienced a similar rate of decrease in voltage. Approximately 20 mV of this decrease is due to a slight drop in effective current density caused by the increasing surface area of the deposit with time. The remainder of the 80 mV drop is due to the narrowing of the electrode gap as the zinc deposit grows, with a consequent effect on solution resistance.

Specific energy consumption remained constant over the range 3–72 h. A very slight drop of approximately 0.3% every 10 h could however be expected due to the gradual decrease in cell voltage.

4.7. *Additive rate*

The additives, animal glue and antimony are added to help control the deposit morphology. However the mechanism by which they work is unknown.

Under standard conditions (55 g l^{-1} Zn, 110 g l^{-1} acid), the additive mixture was added at 0, 0.25 and 1.0 times the rate used in the Risdon cellroom (25 mg l^{-1} animal glue, 0.04 mg l^{-1} Sb). Extra tests with no additive were also carried out at 100, 350 and 650 A m^{-2}. Apart from the test at 100 A m^{-2}, the tests without additive gave almost identical current efficiencies to those with additive. This was also true for power consumption. However, the additives level had a large effect on deposit morphology. When the additives were used, a fairly smooth uniform deposit was obtained at all current densities. When no additive was used, the morphology depended on the current density as shown by Figs 5, 6 and 7. At 100 A m^{-2} and 350 A m^{-2} very shiny smooth deposits were obtained. Close examination of the 350 A m^{-2} deposit revealed a series of vertical furrows across the surface, possibly due to the rising hydrogen bubbles. At 500 A m^{-2} and 650 A m^{-2} the deposit was very rough, with a number of large nodules on the edges. This indicates that if no additives were used at high current densities, shorting would become a serious problem. When one quarter the normal additive level (6.25 mg l^{-1} glue, 0.01 mg l^{-1} Sb) was used under the

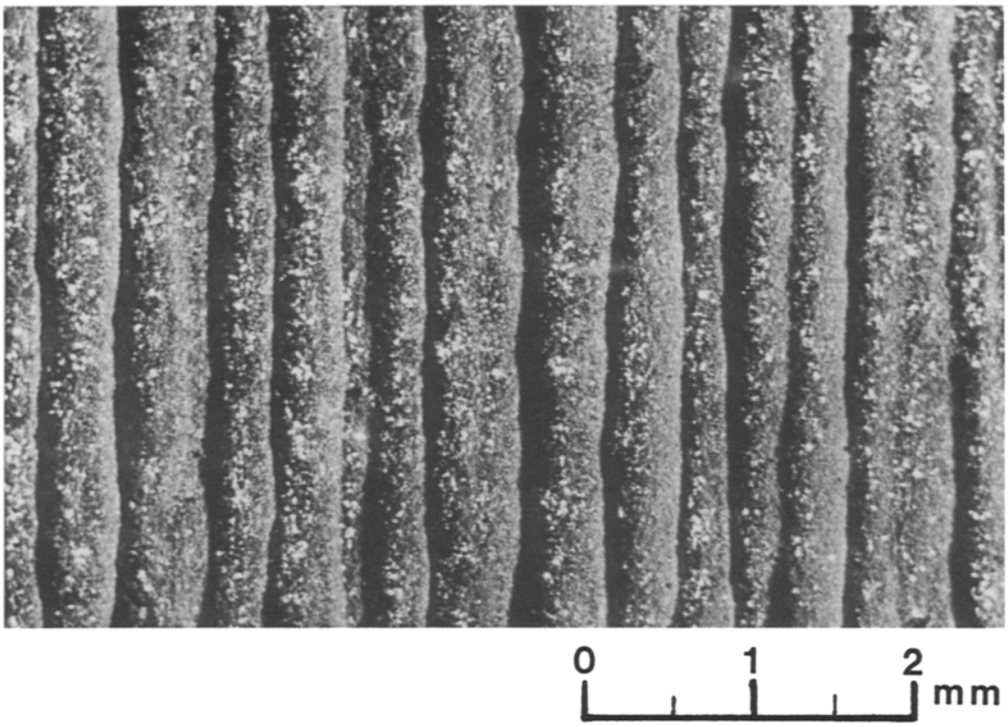

Fig. 5. Appearance of zinc deposit at 350 A m^{-2} (no additives used).

standard conditions, the surface roughness was no longer evident.

5. Conclusions

Based on the systematic variation of experimental parameters it has been possible to determine the optimum operating conditions in terms of specific energy consumption. By also considering the implications of operating in a commercial cellroom, the following conditions were considered to be close to the optimum in terms of both practicality and energy consumption:

60–70 g l^{-1} Zn in cell solution
160 g l^{-1} acid (or higher if possible)
40–45° C cell temperature
350–450 A m^{-2} current density

Two supplementary experiments were carried out in order to test these values. The experimental conditions

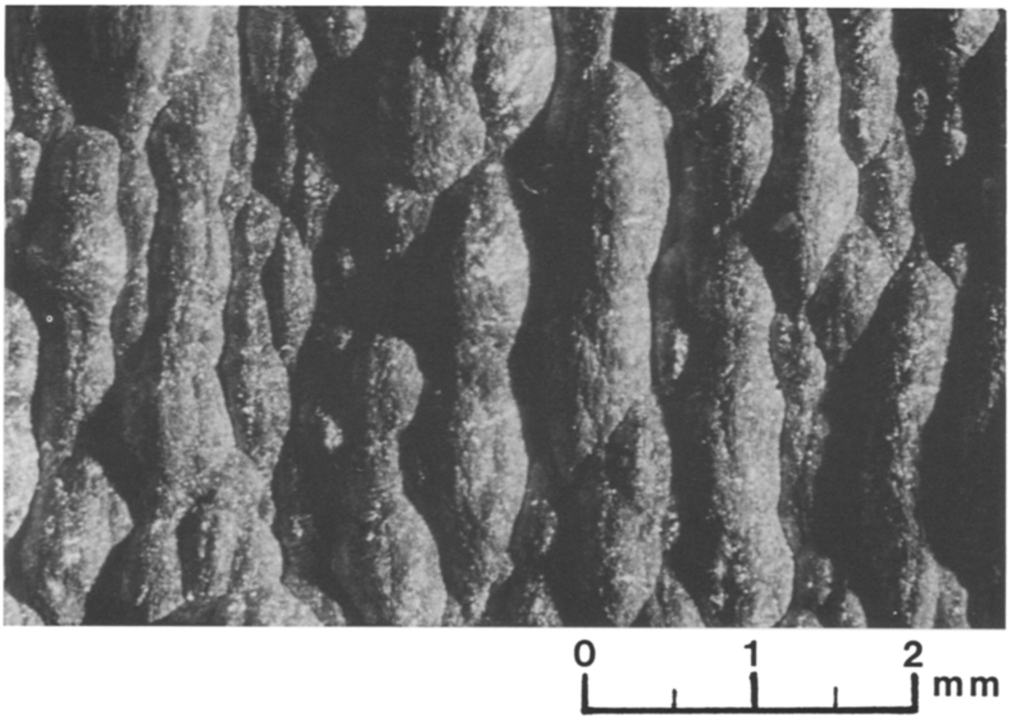

Fig. 6. Appearance of zinc deposit at 500 A m^{-2} (no additives used).

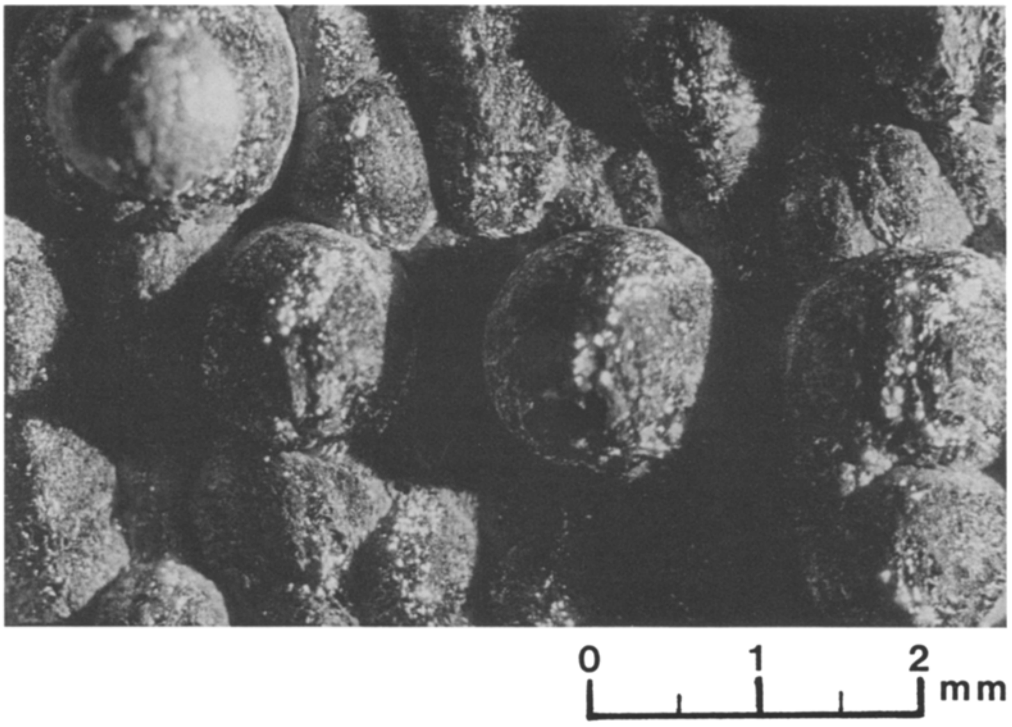

Fig. 7. Appearance of zinc deposit at 650 A m^{-2} (no additives used).

and the resulting current efficiencies are listed in Table 4.

In both the supplementary experiments a similar feed concentration of zinc sulphate was used, however in the second experiment a very high acidity was maintained at the expense of having to use a lower zinc concentration in the cell solution. Although the current efficiency was 2.6% lower in the second experiment, the cell voltage was also reduced due to increased solution conductivity. The final outcome was an energy consumption only slightly greater than that for the first supplementary experiment. These are the lowest energy consumptions that have been obtained from the experimental cells, indicating that both the conditions tested above should prove economically attractive. Further energy savings could be achieved by reducing the current density below 400 A m^{-2}, however since the production rate of a cellroom is proportional to the current density it is not generally considered economic.

Further increases in cell temperature also reduce the energy consumption but only if additives capable of controlling deposit morphology at high temperatures are available. Since deposition times in the range 3–72 h had a negligible effect on electrochemical performance, a reduction in operating costs of a commercial cellroom can be achieved by increasing deposition time and thus reducing the frequency of cathode stripping.

A more precise study of optimum operating conditions can be obtained using the mathematical model which was validiated against the experimental results [16].

Table 4. Supplementary experiments near optimum conditions

1. 70 g l^{-1} Zn in spent	2. 50 g l^{-1} Zn in spent
180 g l^{-1} acid	210 g l^{-1} acid
45° C cell temp.	45° C cell temp.
400 A m^{-2} c.d.	400 A m^{-2} c.d.
42 h deposition	42 h deposition
CE = 94.5%	CE = 91.9%
Power = 2640 kWh t^{-1}	Power = 2660 kWh t^{-1}

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