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The importance of cathode zinc morphology as an indicator of industrial electrowinning performance

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A number of recent papers have described the use of cyclic voltammetry measurements as a method of controlling the electrowinning step in zinc production. A further advance has been the use of XRD to characterize the crystal orientation of zinc deposits. This paper concerns the use of these techniques by the Electrolytic Zinc Company of Australasia Limited to specify zinc electrowinning conditions during a pilot plant evaluation of a novel zinc plant circuit.

Preliminary small scale electrolysis tests gave unsatisfactory deposits and low current efficiencies ($< 85\%$). The aforementioned techniques were used diagnostically to make step changes to operating conditions and to cell additives. The approach was successful and current efficiencies of 93% were established. The use of XRD, coupled with extensive experience of zinc electrowinning, proved to be more important than cyclic voltammetry. The preferred conditions generated by the small scale tests were successfully implemented in pilot plant trials using a full sized electrolytic cell producing 0.5 t per day of zinc.

Overall, the tests confirmed the expectation that there is a strong correlation between current efficiency and the morphology of zinc deposits.

1. Introduction

Modern electrolytic zinc plant circuits include procedures for leaching ferritic residues and rejecting iron as either jarosite, goethite or haematite residues. The Electrolytic Zinc Company of Australasia Limited (EZ) has recently described an improved form of the jarosite route known as the Low-contaminant Jarosite (LCJ) process [1]. In order to demonstrate the feasibility of the LCJ process and other novel leaching and solution purification methods, an integrated pilot plant was constructed at EZ's Risdon Zinc Plant [2]. The pilot plant contained a complete leaching and solution purification sequence which was operated in closed circuit with one full sized cell, producing approximately 0.5 t per day of electrolytic zinc in the Risdon Zinc Plant cell room. An objective of the pilot plant programme was to demonstrate that zinc could be efficiently deposited from LCJ process pilot plant solutions and readily stripped from plant sized cathodes.

The purified solution generated in the pilot plant was significantly different from that produced in the main Risdon plant. For instance, in the Risdon Plant, cobalt is controlled in the cell feed solution to about 8 $\mathrm{mg\,l^{-1}}$ by precipitation with 1-nitroso-2-naphthol (1N2N). This step introduces aromatic organic compounds into the electrolyte. In the pilot plant circuit cobalt was removed with zinc dust, providing an 'organics-free' electrolyte. Because of this and other differences it was expected that modified conditions would be required to electrowin zinc from pilot plant solution compared with those used for normal Risdon plant solution. Consequently, a programme of small scale (1/1000 of plant cell size) continuous electrolysis tests was carried out to establish suitable electrolysis conditions before the pilot plant was operated as a closed circuit.

This paper describes the small scale electrolytic test programme, the approach used to establish satisfactory zinc deposition conditions, and the adequacy of these conditions when

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applied to scaled-up electrolysis during subsequent pilot plant operation.

Economically important differences in current (faradaic) efficiency of 1–2% over a 48 or 72 h deposition period cannot be reliably quantified in short duration batch tests of 1–6 h. Therefore, when small scale electrolysis tests are used to determine the current efficiency of zinc deposition, continuous operation over a 48 or 72 h deposition period is necessary. The main advantage of small scale tests is the relatively small amount of electrolyte which is required.

There was only time to conduct a limited number of small scale tests before the continuous closed circuit phase of the pilot plant campaign commenced. The results of each electrolysis test and complementary information obtained by the morphological examination of the zinc deposits and cyclic voltammetry measurements on spent electrolytes were used to select and improve deposition conditions in subsequent tests. In interpreting the results consideration was given to recent papers describing the morphology of electrodeposited zinc [3, 4, 5, 6, 7] and relating cyclic voltammetry measurements to current efficiency [8], zinc crystal orientation and morphology [6, 7]. Interpretation also drew heavily on previous experience in zinc electrolysis at Risdon.

For the Risdon plant, conditions producing high current efficiencies and easily stripped zinc are usually characterized by the formation of fine grained, non-porous ductile deposits which have a smooth microsurface on the solution side. The zinc crystal orientation is either random (similar to the ASTM index for zinc powder) or the (101) orientation predominates. In contrast, unsatisfactory conditions are generally associated with at least some of the following features: deposits which are porous, coarse grained, brittle, pinholed, corroded on the back surface (adjacent to the aluminium substrate) or have a rough solution side microsurface. In these deposits the (110), (100), (211) and (112) crystal orientations usually predominate.

Kerby and Krauss [8] of Cominco Limited have shown that the potential at which zinc starts to deposit on a fresh aluminium cathode (defined herein as η_4, the nucleation overpotential) correlates with the current efficiency obtained during zinc electrowinning. For conditions in the cell room of Cominco's Trail Plant, maximum current efficiency is obtained at an optimum η_4 value. Furthermore, the electrolyte can be adjusted to give the optimum η_4 value, and hence the maximum current efficiency, by the addition of glue. This is a polarizing agent that counteracts the effect of depolarizing components such as antimony and germanium which are present as impurities in the electrolyte. In the present investigation, the forward scan of the cyclic voltammetry trace was used to obtain η_4 values in order to determine whether a similar relationship exists between η_4 values and current efficiency for the pilot plant electrolytes. In addition, the effectiveness of η_4 measurements as a diagnostic parameter was also evaluated.

2. Experimental details

2.1. *Small scale electrolysis*

Two PVC cells, each having a volume of 10 litres, and two aluminium cathodes flanked by three lead anodes containing 0.75% silver were used. The submerged area of the two cathodes (590 cm^2) was 1/1000 of that in a Risdon plant cell (59 m^2) but the intercathode spacing (76 mm) was similar in both types of cell. Zinc was deposited over a 48-h cycle at a current density of 500 $A\,m^{-2}$. The continuous addition of feed solution was controlled to give a constant acidity in the cell electrolyte by recirculating spent electrolyte from the cell through an external conductivity probe. An aqueous solution of the additives was injected continuously into the spent electrolyte. Cell additives were prepared as aqueous solutions of animal glue (Davis 4A), 2-naphthol (2N) which was added as the sodium salt, and potassium antimony tartrate.

2.2. *Large scale electrolysis*

A single cell in the Risdon cell room was dedicated to the treatment of pilot plant solution and was operated in closed circuit with the pilot plant in a three-month campaign. For comparison purposes an identical cell treating Risdon plant solution was evaluated in parallel. Both cells were equipped with their own automatic temperature, feed addition and additive control systems. During this phase of the investigation, deposition conditions for pilot plant solutions were based on the preferred parameters which had been established by the earlier small scale investigation. Conditions in the comparison cell were identical except for the type of feed solution and the use of normal Risdon plant additives, consisting of an aqueous solution of glue and 2N.

2.3. *Deposit examination*

Morphological examination of zinc deposits involved visual inspection and optical microscopic examination of both solution side and fractured cross-sections using a Wild type 376788 low power (× 50) binocular microscope. Deposits were photographed at × 12 magnification for comparison purposes. A Phillips type PW1010 X-ray diffraction unit was used to determine the preferred crystal orientations which were calculated using the ASTM index for zinc powder as a comparison.

2.4. *Polarization measurements*

Nucleation overpotentials (η_4) were measured by determining the initial zinc deposition potential (compared with -1016 mV with respect to SCE) corresponding to a current density of $4\,\mathrm{A\,m^{-2}}$. This involved decreasing the potential of a fresh aluminium cathode in contact with a zinc electrolyte at a constant rate of $2\,\mathrm{mV\,s^{-1}}$ from a potential corresponding to zero current to a potential corponding to a cathodic current of $10\,\mathrm{A\,m^{-2}}$. For this purpose, a potentiostat built at Risdon was used in conjunction with a Hewlett Packard model 3310B voltage scan generator.

Values for η_4 were measured on spent electrolyte samples collected immediately after the termination of each deposition test in order to eliminate ageing effects. Values for η_4 were also determined on synthetic spent electrolyte samples prepared by adjusting the composition of pilot plant feed solutions with A.R. grade sulphuric acid, distilled water and potassium permanganate. Significant concentrations of permanganate ions were invariably present in Risdon and pilot plant spent electrolytes. Permanganate is an important oxidant which determines the relative concentrations of variable valency inorganic components in zinc electrolytes. It can also oxidize aromatic organic compounds if they are present in feed solution or if they are used as a cell additive (e.g. 2N).

3. Results and discussion

3.1. *Comparison of plant and pilot plant feed solutions*

As mentioned previously, Risdon zinc plant operations involve the control of cobalt by precipitation with 1N2N, which introduces a number of aromatic organic species into the feed solution. These compounds react when mixed with spent electrolyte from the cells and during subsequent zinc electrolysis, forming additional aromatic organic compounds in spent electrolyte. The Risdon plant electrolyte is thus at least unusual, and probably unique, with respect to the presence of $\mathrm{mg\,l^{-1}}$ concentrations of compounds such as 2N, 1N2N and isobenzofuranone (IBF). A further unusual feature of the cobalt control step is the treatment of only sufficient solution to give a cobalt concentration of about $8\,\mathrm{mg\,l^{-1}}$ in solution passing to the electrolytic cells. In contrast, most other zinc producers remove cobalt almost completely ($0.1\,\mathrm{mg\,l^{-1}}$) from their cell feed solution by a zinc dust purification step. The substantial amount of cobalt in the Risdon electrolyte is a factor underlying the use of a combination of animal glue and 2N as cell additives. Addition of 2N to the cell also contributes to the presence of aromatic organic compounds in the Risdon electrolyte. Sometimes antimony is also added to the cells.

In the pilot plant, a two-stage zinc dust purification procedure was used to remove copper, cadmium, nickel and cobalt, together with a pretreatment involving the adsorption of organic, and possibly some inorganic, components from the solution using activated carbon. Consequently, pilot plant solutions were almost completely free of aromatic organic compounds and the problems they sometimes cause during zinc electrolysis were avoided. The compositions of pilot plant and Risdon plant electrolytes are compared in Table 1.

Table 1. Comparison of the composition of LCJ process pilot plant and Risdon zinc plant purified solutions as fed to electrolysis cells

Solution source	*Solution composition*												
	g l^{-1}			*mg l^{-1}*									
	Zn	*SO_4*	*Cl*	*1N2N*	*2N*	*IBF*	*Fe*	*Co*	*As*	*Sb*	*Ge*	*Ni*	*Cu*
LCJ process pilot plant	133	255	240	< 0.1	< 0.1	0.1	0.2	3.8	0.02	0.03	0.003	0.2	0.01
Risdon zinc plant	108	234	210	1.35	0.5	1.6	0.4	7.9	0.10	0.08	0.008	0.1	0.01

Because there are advantages at Risdon in electrowinning zinc from electrolytes containing significant cobalt concentrations, the pilot plant was operated to produce a cell feed solution containing 4–5 mg l^{-1} cobalt, a slightly lower level than exists in the present Risdon circuit. The pilot plant purification procedures also provided more effective removal of arsenic, antimony and germanium than the methods used on the Risdon plant.

Based on Risdon zinc plant experience, it was expected that the high cobalt levels in pilot plant solutions might necessitate the continued use of 2N as a cell additive in combination with animal glue. Consequently, both these additives were used in the initial small scale electrolysis tests. Nevertheless, it was appreciated that if the use of 2N could be avoided the pilot plant circuit would have the desirable feature of being devoid of aromatic organic compounds.

3.2. *Small scale electrolysis*

3.2.1. Normal Risdon conditions. Initial tests compared the deposition of zinc from pilot plant and normal Risdon plant feed solutions at a spent electrolyte acidity of 108 g l^{-1} using normal Risdon additives at rates of 400 g glue + 178 g 2N per tonne of deposited zinc. These rates correspond to concentrations of 33 and 14.7 mg l^{-1} of feed, respectively.

The results of these tests are contained in Table 2 and the zinc deposits are compared in Fig. 1. While the results for Risdon plant solution were satisfactory, both the current efficiency and deposit quality were unacceptable for the pilot plant solution. This was surprising because the pilot plant solution appeared to have superior purity, at least with respect to inorganic impurities (see Table 1).

Long term experience of zinc deposition at

Table 2. Results of small scale electrolysis tests comparing LCJ process pilot plant and Risdon zinc plant feed solutions using the additives and conditions used on the Risdon zinc plant

Solution source	*Current efficiency (%)*	*Preferred zinc crystal orientation*	*Deposit appearance*
LCJ process pilot plant	84.1	(100), (110), (211)	Rough, coarse grained, brittle, very pinholed and porous. Corrosion on the face adjacent to the aluminium substrate (Fig. 1b).
Risdon zinc plant	91.4	(101)	Smooth, fine grained, ductile and free of pinholes and pores (Fig. 1a).

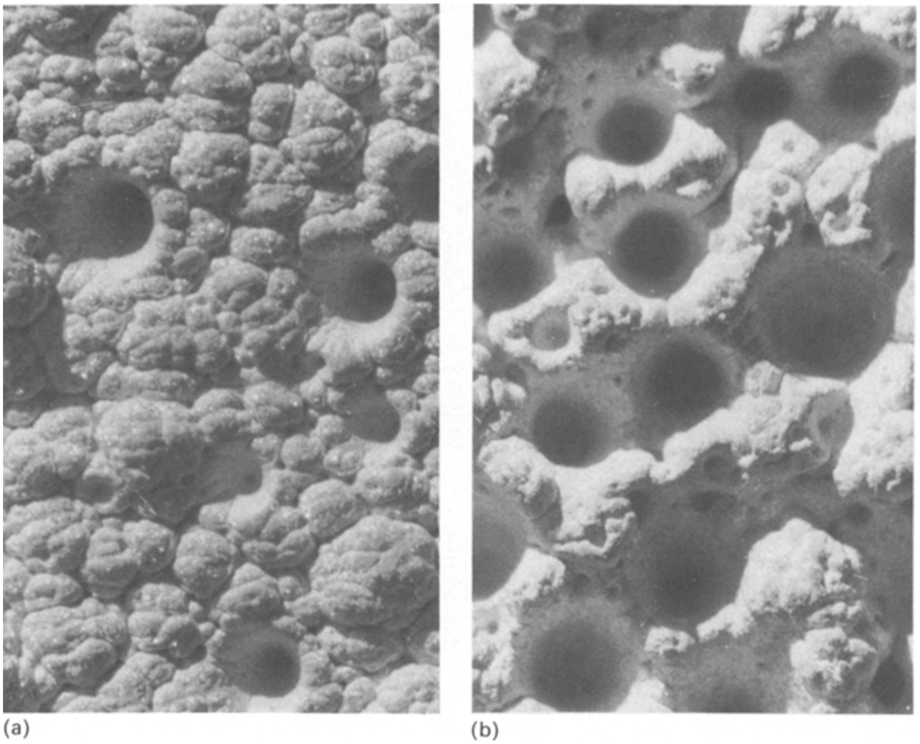

Fig. 1. Zinc deposits formed under Risdon zinc plant electrolysis conditions using glue and 2N as additives: (a) from Risdon zinc plant feed solution; (b) from LCJ process pilot plant feed solution. (Figure width = 5 mm).

Risdon suggested the following reasons for the unsatisfactory deposits formed from pilot plant solution:

(a) Excessive concentrations of 2N and other aromatic organic compounds can cause pinholing and porous zinc deposits. These effects are attributed to an increase in the size and adherence of hydrogen bubbles forming at the solution surface of the zinc deposit, thus preventing zinc growth in localized areas. A decrease in the concentration of 2N or its elimination as an additive would be expected to rectify this condition.

(b) When the (100) and (110) crystal orientations are dominant, as in the deposit formed from pilot plant solution, the zinc crystal platelets tend to stack perpendicularly to the aluminium substrate and the deposit is brittle and difficult to strip. This phenomenon is often associated with low antimony concentrations in an electrolyte. In the absence of organic additives the presence of antimony in a zinc electrolyte results in a preference for the (002) orientation and platelets tend to stack parallel to the aluminium substrate [5, 6, 7]. When the antimony concentration of an electrolyte is adjusted to suitable levels, usually in the range 0.06–0.08 mg l^{-1}, and glue is simultaneously used as an additive, the platelets are decreased in size and stacked at a variety of angles resulting in a compact, non-porous ductile deposit which is easily stripped. From the results in Table 1 it was apparent that the antimony concentration of pilot plant solution was less than the preferred range, indicating that antimony additions of the order of 0.04 mg l^{-1} should be beneficial.

(c) Both the current efficiency and the smoothness of the zinc deposit are adversely affected when the composition of spent electrolyte has a zinc to sulphuric acid concentration ratio substantially greater than 0.5 and/or a zinc concentration $\geqslant 60$ g l^{-1}. For the tests reported in Table 2, the pilot plant solution and the resultant spent electrolyte contained 133 and 61 g l^{-1} of zinc respectively and the zinc to acid ratio in spent electrolyte was 0.56 by weight. Consequently, either diluting the feed solution or increasing the acidity of the spent electrolyte should be beneficial for the electrolysis of pilot plant solution.

The various remedial measures suggested above were evaluated in a series of small scale electrolysis tests in which deposition conditions were systematically varied between tests to determine which of the above factors were critical. The sequence in which deposition conditions were changed in the subsequent programme is outlined below.

(i) Eliminate 2N as an additive.

(ii) Evaluate two rates of glue addition (360 and 720 $g\,t^{-1}$ of zinc deposited).

(iii) Increase the sulphuric acid concentration of spent electrolyte from 108 to 124 $g\,l^{-1}$.

(iv) Decrease the zinc concentration of pilot plant feed solution from 133 to 115 $g\,l^{-1}$ by dilution with water.

(v) Add, with the other additive(s), the equivalent of 0.04 $mg\,l^{-1}$ of antimony to the feed solution.

3.2.2. Modified conditions. The results of the small scale electrolysis tests, aimed at defining satisfactory conditions for the deposition of zinc from pilot plant solution, are shown in Table 3.

Although the exclusion of 2N as an additive eliminated the pinholing and porosity of the zinc deposit (compare Fig. 1b with Figs 2a and 2b), the crystal orientation was unaltered and it was necessary to increase the rate of glue addition to obtain both a substantial increase in current efficiency and a smooth deposit. At both glue rates the zinc deposit remained brittle and coarse grained. Addition of 0.04 $mg\,l^{-1}$ of antimony to the feed eliminated these remaining deficiencies yielding a deposit of ideal quality and a further substantial increase in current efficiency. Indeed the 95.0% current efficiency achieved at the higher glue addition rate is an exceptionally good result and can be considered to be a near maximum value for 48 h deposition from an industrial electrolyte at a current density of 500 $A\,m^{-2}$.

Comparison of Figs 2 and 3 illustrates the grain refining and surface smoothing effect which was achieved by the addition of antimony. This addition also modified the crystal structure, resulting in either a random structure or a preference for the 101 plane. When antimony was added the deposits were dense, non-porous, ductile and readily stripped from the aluminium substrate.

In the absence of antimony, increasing the acidity of the spent electrolyte decreased the roughness of the deposit. However, the deposit morphology was unsatisfactory and the current efficiency remained substantially lower than the levels achieved when antimony was added. Dilution of the feed solution was a more effective measure than increasing the spent acidity, resulting in smoother deposits and a moderate improvement in current efficiency. However, the deposits remained relatively coarse grained and brittle and current efficiencies were substantially less than those obtained by the addition of antimony.

For the entire range of conditions evaluated, the addition of 0.04 $mg\,l^{-1}$ of antimony resulted in an average improvement in current efficiency of 5.4% when 2N was not used as an additive (Table 4). Antimony additions also increased the current efficiency when glue and 2N were used as a combined additive. However, the current efficiency (91.5%) was slightly less than the average achieved in the absence of 2N (92.9%) and the deposit was porous, slightly pinholed and corroded (Fig. 4). For all the tests involving the addition of antimony in the absence of 2N, there was an advantage in increasing the rate of glue addition from 360 to 720 $g\,t^{-1}$ of zinc deposited. The average improvement in current efficiency was 1.0% (Table 4). In the absence of antimony additions an increase in the rate of glue addition only provided a substantial improvement in current efficiency under the low acid conditions using undiluted feed solution.

3.3. *Large scale electrolysis*

The objective of the small scale tests was to define reliable zinc deposition conditions for use when the pilot plant was operated in closed circuit. The results in Section 3.2 show that when glue and antimony are used as additives, pilot plant solution can be satisfactorily electrolysed for a range of zinc concentrations in feed solution and sulphuric acid concentrations in spent

Table 3. The effect of variations in glue, antimony and 2N as additives, the sulphuric acid concentration of spent electrolyte and the zinc concentration of feed solution on the electrolysis of zinc from LCJ process pilot plant solution

Additives (g t^{-1} of zinc deposited)		*H_2SO_4 in spent electrolyte (g l^{-1})*	*Zn in feed solution (g l^{-1})*	*Antimony added to feed solution (mg l^{-1})*					
				0			*0.04*		
Glue	*2N*			*Deposit* morphology*	*Preferred crystal orientation*	*Current efficiency (%)*	*Deposit morphology*	*Preferred crystal orientation*	*Current efficiency (%)*
360	0	108	133	Rough at low glue rates, brittle and coarse grained. Neither pinholed nor porous	(211) (110) (100)	84.5 (Fig. 2a)	Smooth, ductile and fine grained Neither pinholed nor porous	101 or random	94.6 (Fig. 3a)
720	0	108	133			89.2 (Fig. 2b)			95.0 (Fig. 3b)
360	0	124	133	Smoother than for low acidity, brittle and coarse grained. Neither pinholed nor porous	(211) (110) (100)	85.9 (Fig. 2c)	Nodular, ductile and fine grained. Small pinholes. No corrosion	(211) (101) (110)	90.4 (Fig. 3c)
720	0	124	133			85.8			91.9
360	0	108	115	Smooth, brittle and coarse grained. Neither pinholed nor corroded. Smoother at high glue rates	(211) (110) (100)	90.6 (Fig. 2d)	Dark coloured, slightly brittle and porous	(211) (101) (110)	91.8 (Fig. 3d)
720	0	108	115			88.6	Smooth, fine grained and non-porous		93.3
360	160	108	133	Rough and coarse grained. Pinholed, porous and corroded	(211) (110) (100)	84.1 (Fig. 1b)	Smooth and fine grained but porous. Moderate pinholing and corrosion	(211) (101)	91.5 (Fig. 4)

* In most tests without antimony additions the zinc was visibly smoother at the high glue rate than at the low glue rate (see Figs 2a,b).

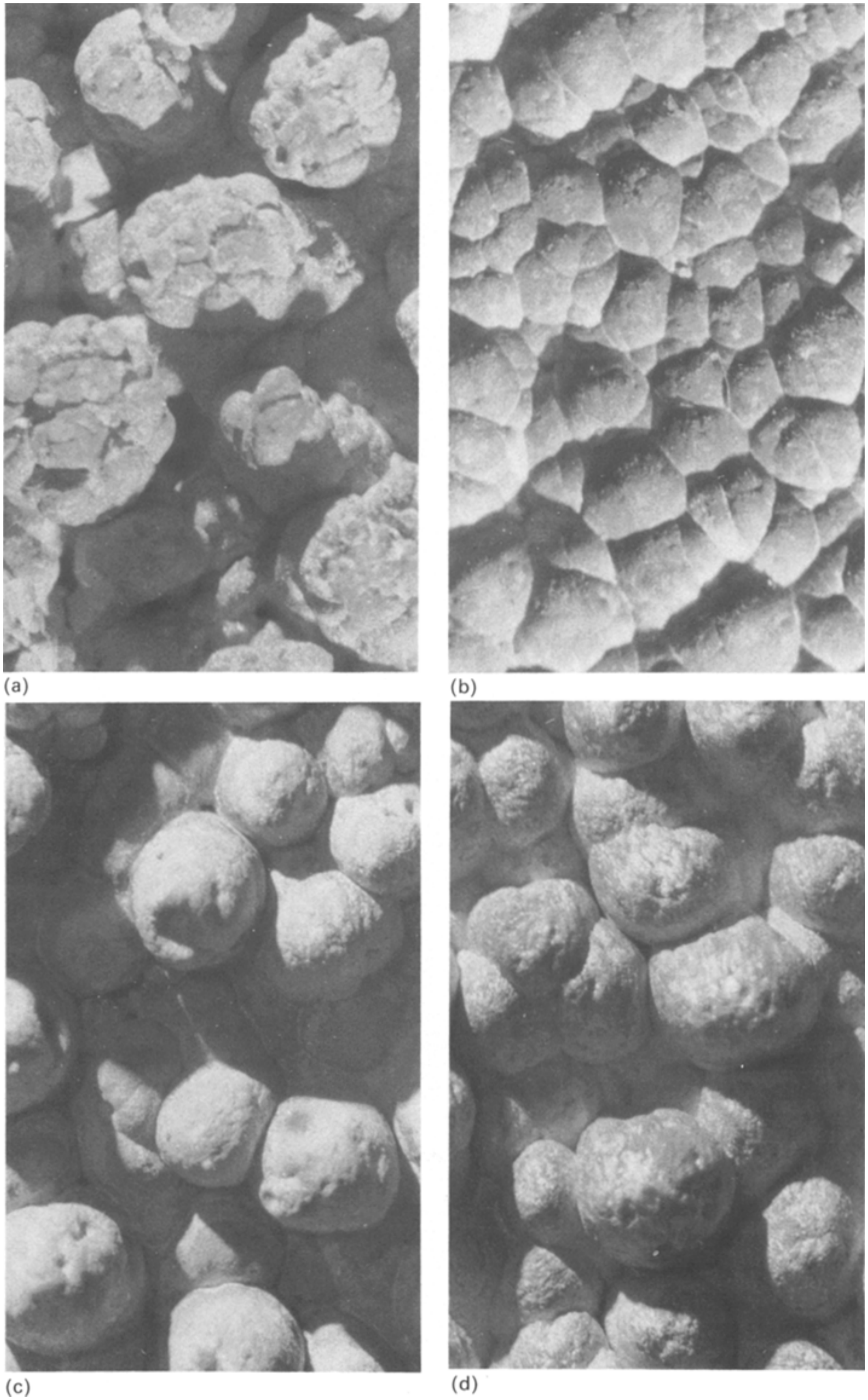

Fig. 2. Deposits from LCJ process pilot plant feed solution in the absence of added antimony: (a) low glue addition; (b) high glue addition; (c) low glue addition, high acidity; (d) low glue addition, diluted feed. (Figure width = 5 mm.)

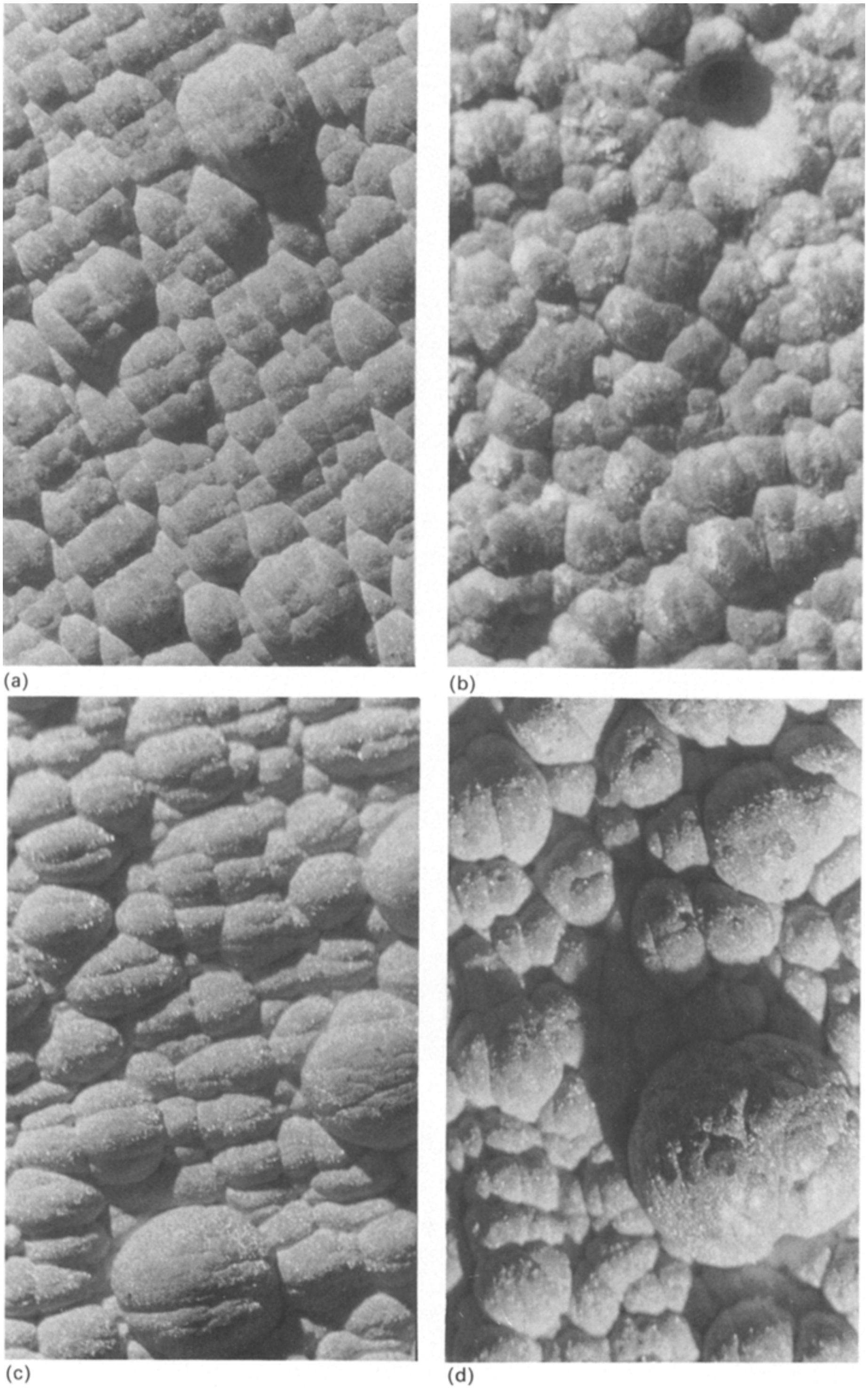

Fig. 3. Deposits from LCJ process pilot plant feed solution with 0.04 mg l^{-1} antimony added: (a) low glue addition; (b) high glue additon; (c) low glue addition, high acid; (d) low glue addition, diluted feed. (Figure width = 5 mm).

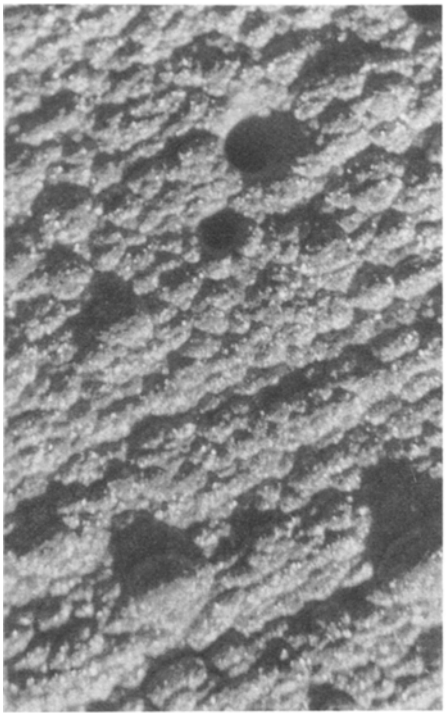

Fig. 4. Deposit from LCJ process pilot plant feed solution with 0.04 mg l^{-1} antimony added and using both glue and 2N as cell additives. (Figure with = 5 mm.)

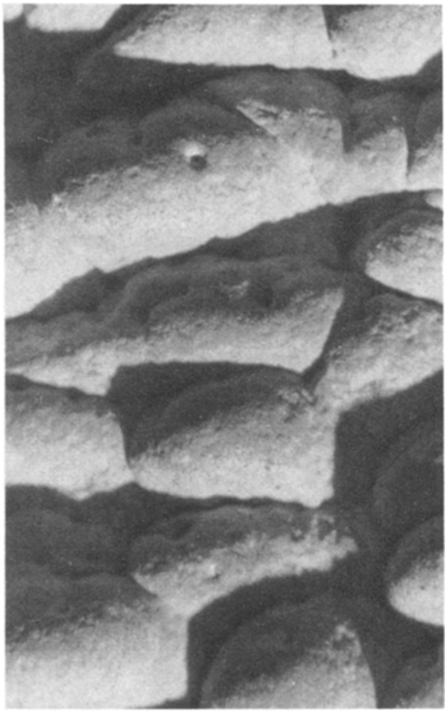

Fig. 5. Deposit from LCJ process pilot plant feed solution in a zinc plant cell under conditions recommended from small scale tests. (Figure width = 5 mm.)

electrolyte. Furthermore, the current efficiency was relatively insensitive to the glue concentration when 0.04 mg l^{-1} of antimony was added. Although antimony additions at least partially compensated for the adverse pinholing and corrosion caused by the use of 2N, the use of 2N as an additive was rejected because it had not been proved that it was effective over a range of electrolyte compositions. Also, the elimination of 2N achieved the aforementioned advantage of removing aromatic organic compounds from the pilot plant circuit. Based on the above results, the following conditions were used for the large scale electrolysis tests:

Glue addition, 440–540 g t^{-1} of zinc deposited
Antimony addition, 0.04 mg l^{-1} of feed solution
Feed zinc concentration, 133 g l^{-1}
Spent electrolyte sulphuric acid concentration, 105 g l^{-1}
Deposition time, 72 h
Current density, 400 A m^{-2}
Temperature, 35° C
Lead anodes, 0.012% silver

These conditions were satisfactory and current efficiencies of up to 94% were achieved. Under steady-state conditions the average current efficiency was 92.5% over six deposition cycles. The zinc stripped well, both manually and when removed by an automatic stripping machine. Although the zinc deposits were slightly nodular their microsurfaces were smooth and fine grained with a non-porous, ductile structure free of pinholes and corrosion (Fig. 5).

Table 4. Effect of variations in glue and antimony addition rate on the current efficiency of zinc deposition in the absence of 2N

Glue addition rate ($g\,t^{-1}$ Zn deposited)	*Current efficiency* (%)		
	Antimony addition rate ($mg\,l^{-1}$)		*Average*
	0	0.04	
360	87.0	92.3	89.7
720	87.9	93.4	90.7
Average	87.5	92.9	90.2

Table 5. (a) Composition of two synthetic spent electrolytes prepared from pilot plant feed solution and containing permanganate. (b) Effect of change in electrolyte additive concentration on determination of η_4

(a)

Electrolyte	*Composition* ($g\,l^{-1}$)			*Nucleation overpotential* η_4(mV) *with no additive*
	Zn	H_2SO_4	MnO_4	
1	44.3	100	0.04	157
2	66.4	100	0.04	135

(b)

Incremental change in additive concentration*	$\Delta\eta_4$ (mV)*		
	Electrolyte 1		*Electrolyte 2*
	Glue only	*Glue + 2N in ratio 1:0.447*	*Glue only*
+ 15 mg glue l^{-1}	+21	+23.5	+15
+ 15 mg glue l^{-1}	+ 9.5	+ 0.5	+ 6
+ 20 mg glue l^{-1}	+ 3.5	–	+12.5
+ 0.032 mg Sb(III)$^{-1}$	− 9	−24	− 9.5

* $\Delta\eta_4$ is expressed as the incremental response to each sequential addition of additive(s); for the first sequential addition η_4 is compared with η_4 for the additive free solution.

The comparison cell was operated on Risdon plant electrolyte using the traditional additives, glue and 2N. The cell treating pilot plant solution operated at an average current efficiency which was 1.0% higher than the comparison cell.

3.4. *Polarization measurements*

3.4.1. Synthetic spent electrolytes. The results of η_4 measurements on synthetic spent electrolytes prepared by adjusting the composition of pilot plant feed solution are shown in Table 5. Interpretation of the results is complicated and it was not possible to draw any conclusions concerning preferred conditions for zinc deposition prior to completion of the small scale electrolysis tests. As discussed below, η_4 is a function of electrolyte composition, additive types and concentrations.

(i) Animal glue (a polarizing agent) increased η_4.

(ii) At low glue concentration 2N did not change η_4, but at higher glue concentrations ($> 15\,\mathrm{mg\,l^{-1}}$) 2N decreased the polarizing ability of glue.

(iii) The effect of antimony, (a depolarizing agent) was greater in the presence of glue and 2N than when used in conjunction with glue alone.

(iv) Variation of η_4 with the zinc concentration of the spent electrolyte, decreased by approximately 1 mV for each $1\,\mathrm{g\,l^{-1}}$ increase in the zinc concentration.

Permanganate, which is formed anodically when zinc plant electrolytes containing manganese sulphate are electrolysed, is considered to play an important role in determining the effect on η_4 of some solution components and additives. Consequently, it was added to the synthetic solutions evaluated above. For instance, permanganate reacts with 2N and its concentration is depleted when 2N is used as an additive. Thus, in the presence of 2N there is less permanganate available to oxidize antimony which is added as Sb(III). Conversely, in the absence of 2N it appears that a greater proportion of the antimony is oxidized to Sb(V) which is considerably less depolarizing than Sb(III).

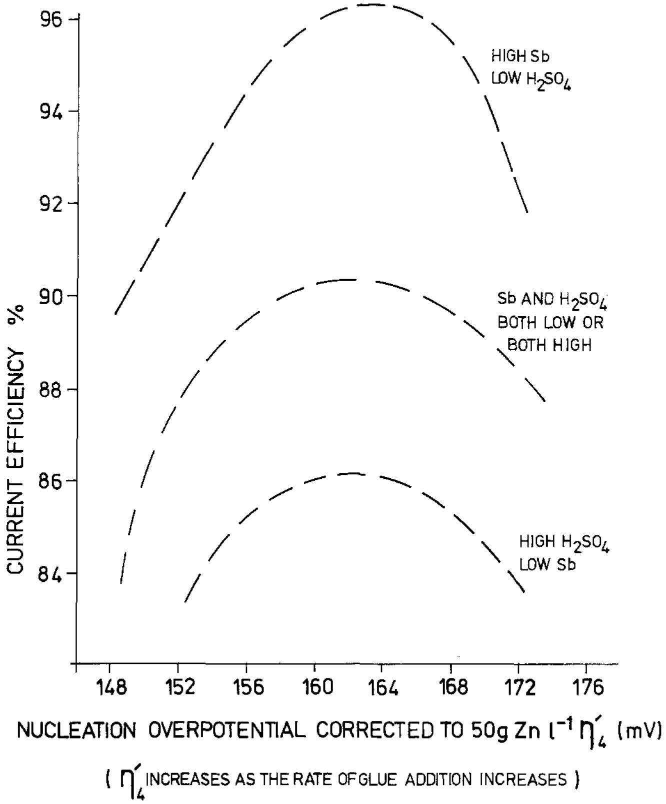

Fig. 6. Trends in the variation of current efficiency with the corrected nucleation overpotential of spent electrolyte for the small scale electrolysis of LCJ process pilot plant solution using animal glue as an additive.

3.4.2. Spent electrolytes. Measurements of η_4 were made on spent electrolyte samples collected at the end of each small scale electrolysis test in order to determine whether correlations similar to those reported by Kerby and Krauss [8] exist between current efficiency and η_4. However, it was necessary to correct the η_4 values for variations in the zinc concentration of spent electrolyte in order to obtain similar relationships. Fig. 6 shows trends in the variation of current efficiency with the nucleation overpotential adjusted to a zinc concentration of $50\,\mathrm{g\,l^{-1}}$ (η'_4) using the correction factor $+1\,\mathrm{g\,l^{-1}}$ of Zn $= -1\,\mathrm{mV}$. From Fig. 6 it is apparent that variations in antimony and sulphuric acid concentration modify the correlation, with the curve moving up and down with increases in the antimony and sulphuric acid concentration, respectively. However, each curve has a similar shape, with the maximum current efficiency corresponding to an optimum η'_4 value of 163 mV. Adding $0.04\,\mathrm{mg\,l^{-1}}$ of antimony near the optimum η'_4 value increases the current efficiency by 5.4%, while an increase in the sulphuric acid concentration of $16\,\mathrm{g\,l^{-1}}$, from $108\,\mathrm{g\,l^{-1}}$, decreases the current efficiency by a similar amount. The results also confirm the Section 3.4.1 conclusion that animal glue can be used to adjust the overpotential to the optimum value and suggest that the optimum η'_4 value is obtained by a glue addition rate of about $500\,\mathrm{g\,t^{-1}}$ of zinc deposited. Based on the limited data available η'_4 is relatively insensitive to the use of 2N as an additive in conjunction with glue and the correlations are not appreciably modified by its presence. The above interpretation confirms the expectation that maximum current efficiency is achieved under the low acid electrolyte conditions adopted in the large scale electrolysis tests.

No attempt was made to adjust the glue or antimony additions either during or between deposition cycles in the large scale tests for which a similar correlation between current efficiency and η'_4 was obtained. However, in the large scale tests the optimum η'_4 value was shifted to 183 mV compared with 163 mV in the small scale tests. Scale-up involved a change from the use of silver–lead to lead anodes. The latter, which were used in the large scale tests, corroded more rapidly and the lead concentration in the spent electrolyte increased by about $2\,\mathrm{mg\,l^{-1}}$. In previous work at Risdon it was found that $1.5\,\mathrm{mg\,l^{-1}}$ of lead increased η_4 by approximately 30 mV when added to a lead-free zinc sulphate electrolyte. Consequently, when η_4 values are compared between spent electrolytes it appears necessary to establish a correction factor to adjust for variations in both zinc and lead concentration. Other minor differences in cell configuration, electrolyte compositon and conditions of electrolysis may also have contributed to the variation in optimum η_4' values. This suggests that the optimum η_4' value will have to be determined for each cell–electrolyte system before it can be used for additive control purposes.

4. Conclusions

Satisfactory zinc electrolysis is characterized by the simultaneous occurrence of a high current efficiency and a good quality zinc deposit which exhibits the following features: a smooth microsurface, non-porous, ductile and with zinc crystals either randomly orientated or with the (101) orientation preferred. Deposits formed under unsatisfactory conditions invariably exhibit deviations from the above ideal morphology.

In this investigation it was possible to use zinc morphological information provided by visual, optical and XRD examination to predict improved conditions for electrolysis of a new electrolyte produced in the LCJ process pilot plant. Electrolytic conditions were modified in a limited campaign of small scale electrolysis tests until satisfactory deposition conditions were defined.

Although a scale-up factor of 1000 was involved these conditions were successfully applied, without further modification, to large scale electrolysis tests in industrial cells. For the preferred conditions the average current efficiencies were 94.8% over 48 h at $500\,\mathrm{A\,m^{-2}}$ and 92.5% over 72 h at $400\,\mathrm{A\,m^{-2}}$ in the small and large scale cells, respectively. While these efficiencies are excellent by industrial standards and, in fact, exceed the present performance of the Risdon Zinc Plant, the trends in Fig. 6 suggest that improvements of the order of 1% might be achieved under optimum conditions. Consequently, confidence is held in the ability of the new technology associated with the LCJ process to produce an electrolyte which can be successfully electrolysed in a full-sized zinc plant.

Overpotential measurements involving the determination of η_4 values did not assist in predicting remedial measures such as a change of additive type following unsatisfactory electrolysis of a new electrolyte. This technique is, therefore, seen as being primarily useful as a control procedure for achieving optimization once optimum deposition conditions have been defined. This mode of control, involving varying the rates of additives, as described by Kerby and Krauss [8], was not evaluated. However, the present results show that η_4 values vary with electrolyte composition, suggesting that a fairly complex control scenario would be required to compensate for the short term variations in electrolyte composition (e.g. zinc concentration) which occur in most zinc plants.

A substantial cobalt concentration was a feature common to the otherwise significantly different pilot plant and Risdon plant electrolytes. Traditionally, the presence of cobalt has been a justification for the use of 2N in conjunction with glue as a cell additive at Risdon. It is perhaps surprising, therefore, that the pilot plant solution was successfully electrolysed without the use of 2N as an additive.

It is possible that a more exhaustive investigation would have defined conditions under which 2N could be successfully used during the electrolysis of pilot plant solution, but it is unlikely that its use would have resulted in a significant improvement in electrolytic performance. Furthermore, there is an advantage in completely eliminating aromatic organic compounds from a zinc plant circuit. The present results do, however, emphasize the need for a reappraisal of the role of 2N as an additive in the existing Risdon Zinc Plant.

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