

The effects of Dowfroth, antimony and Saponin on zinc electrowinning from Kidd Creek electrolyte

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The effects of Dowfroth alone and in combination with antimony and Saponin on zinc deposition current efficiency and polarization and on the morphology and orientation of 6 h and 24 h zinc deposits electrowon at 500 A m^{-2} and 38°C from Kidd Creek zinc electrolyte were determined. Dowfroth, at concentrations as low as 7 mg dm^{-3} , was strongly polarizing, changed the preferred deposit orientation from basal to intermediate and decreased the current efficiency and zinc deposit quality. Dowfroth had a positive interaction with antimony such that certain combinations of these reagents maximized current efficiency and improved the deposit quality. Saponin combined with various concentrations of Dowfroth resulted in a $<1\%$ change in current efficiency and did not modify the preferred deposit orientation. At optimum Dowfroth + antimony combinations, the addition of Saponin again did not affect significantly the current efficiency. The preferred deposit orientation was either $[101][112]$ or $[101]$ depending on the combination of these reagents employed. Tests run for 24 h for selected combinations of Dowfroth, antimony and Saponin confirmed the results obtained for the 6 h studies.

1. Introduction

In industrial zinc electrowinning it is common practice to add a foaming reagent to the electrolyte to suppress the formation of acid mist over the cells in the tankhouse. The presence of the foaming agent in combination with electrolyte circulation and vigorous oxygen evolution at the anodes results in the formation of a layer of foam on the electrolyte surface that is capable of trapping most of the acid-laden gas bubbles. Dowfroth 250 (containing polypropylene glycol methyl ethers) is added primarily as a foaming agent to suppress acid mist in the Kidd Creek tankhouse.

Recent laboratory evaluations of alternative anodes for zinc electrowinning conducted at the Kidd Creek Metallurgical Site indicated that Dowfroth, in addition to suppressing acid mist, also had a strong influence on zinc deposition current efficiency and zinc deposit morphology. Increasing concentrations of Dowfroth resulted in a lower current efficiency and a highly striated zinc deposit. As a result of this observation, a joint research project was established between Falconbridge, Kidd Creek Division and CANMET to evaluate more thoroughly the effect of reagent additions to the Kidd Creek zinc electrolyte and to determine the optimum combinations which would maximize the current efficiency and improve deposit quality.

As well as adding Dowfroth to the electrolyte, current operating practice in the Kidd Creek zinc tankhouse also includes the addition of antimony and sodium silicate to control zinc deposit growth and strontium carbonate to minimize the level of lead in the zinc deposit. The joint project initiated to evaluate these reagents also included the evaluation of an alternative reagent addition system comprising Saponin as a foaming agent and antimony + animal glue to control deposit growth.

Although animal glue is a common addition agent in most zinc plants, it is not presently added to the Kidd Creek electrolyte. The effects of glue and glue + antimony on the current efficiency (CE) and nucleation overpotential (NOP) for zinc deposition and on the morphology and orientation of zinc deposits from Kidd Creek electrolyte were reported in a previous paper [1]. The results indicated that certain combinations of antimony + glue optimized the CE and consistently produced a $[114][112][103][102][101]$ preferred deposit orientation. A correlation was also observed between the CE values and NOP for zinc deposition such that the CE was a maximum when the NOP of the initial cell electrolyte was 120–130 mV against the mercury/mercurous sulphate electrode (MSE) or when the NOP of the final cell electrolyte was 100–110 mV/MSE. A similar antimony-glue interaction also was observed in Cominco electrolyte and formed the basis

for the development of a continuous analyser for zinc electrolyte [2]

The effects of Saponin alone and in combination with optimum concentrations of antimony and glue on zinc deposition current efficiency and polarization and on the morphology and orientation of zinc deposits electrowon from Kidd Creek electrolyte was the subject of another previous publication [3]. Saponin, at concentrations to 100 mg dm^{-3} , was weakly polarizing, changed the preferred deposit orientation from basal to intermediate and decreased the current efficiency. In combination with optimum glue + antimony levels, Saponin concentrations $\geq 5 \text{ mg dm}^{-3}$ resulted in an increase in the zinc deposition current efficiency and gave either a [1 1 4] [1 1 2] [1 0 3] [1 0 2] [1 0 1] or [1 0 1] [1 1 2] preferred deposit orientation depending on the antimony + glue combination used.

The present study was undertaken to confirm the polarizing effect of Dowfroth and to determine its interaction with antimony in Kidd Creek zinc electrolyte. Also, the fact that a previous study [3] showed that Saponin was only a weak polarizing agent suggested that Dowfroth could be at least partially replaced by Saponin in the electrolyte reducing polarization whilst maintaining the performance of the foam layer. Thus, the effect of Dowfroth + Saponin + antimony additions were evaluated in the present study.

2. Experimental details

The electrowinning cells and experimental procedure were described in detail in previous papers [1, 3]. Both feed and cell electrolytes were prepared from purified neutral and cold spent solutions received from Kidd Creek. The electrolyte composition was maintained at 55 g dm^{-3} Zn and 200 g dm^{-3} H_2SO_4 throughout the electrolysis period. The various addition agents including Dowfroth 250, potassium antimony tartrate and Saponin were supplied by Kidd Creek and were added to both the feed and cell electrolytes at the desired concentrations as aliquots from stock solutions which contained 600 mg dm^{-3} Dowfroth 250, 30 mg dm^{-3} Sb and 500 mg dm^{-3} Saponin.

The 6 h electrowinning tests were done at 38°C and 500 A m^{-2} current density using aluminium cathodes ($12.9 \times 10^{-4} \text{ m}^2$) and platinum anodes to avoid lead contamination of the zinc deposits [4]. A few tests were run for 24 h for specific additive combinations to confirm the trends identified in the shorter experiments. For these tests, Pb-Ag anodes (supplied by Kidd Creek) were used, and SrCO_3 was added to the electrolyte to minimize lead contamination. The current efficiency was calculated from the weight of zinc deposited and the number of coulombs passed. Sections of the deposits were examined by X-ray diffractometry (XRD) to determine their preferred orientation relative to the ASTM standard for zinc powder and by scanning electron microscopy (SEM) with a secondary electron detector to determine the

Table 1. The effect of Dowfroth on the CE, orientation and NOP for 6 h zinc deposits electrowon at 500 A m^{-2} and 38°C

Dowfroth (mg dm^{-3})	CE (%)	Orientation*	NOP (mV)	
			Initial	Final
0	91.0	002, 103	140	125
3	87.6	112, 103, 102, 114, 101	150	150
7	88.0	101	140	155
10	87.5	101	155	145
15	86.2	101	140	140
20	85.4	101	170	160
25	84.9	101	190	155
30	83.6	101	175	150
40	83.3	101	190	145
50	82.0	101	210	145
75	81.2	101	230	150

* Relative to ASTM standard for zinc powder

deposit morphology. A portion of each 24 h zinc deposit was analysed for lead. Cyclic voltammetry (CV) experiments [1, 3] were conducted to determine the nucleation overpotential (NOP) for zinc deposition. The CV tests were done in duplicate using 150 ml of both the initial and final cell electrolytes at room temperature. The NOP values were consistent within $\pm 3 \text{ mV}$ on duplicate measurements.

3. Results and discussion

3.1. Dowfroth effects

The effect of Dowfroth additions from 0 to 75 mg dm^{-3} on the current efficiency (CE) for 6 h zinc deposits electrowon at 500 A m^{-2} and 38°C is summarized in Table 1 and a plot of CE against Dowfroth concentration is shown in Fig. 1. The CE decreases by about 3% with the addition of 3 mg dm^{-3} Dowfroth to the electrolyte: the CE then remains fairly constant to 10 mg dm^{-3} Dowfroth. For $> 10 \text{ mg dm}^{-3}$ Dowfroth there is a gradual decrease in the CE to 81.2% at 75 mg dm^{-3} Dowfroth (Table 1).

The morphologies of the 6 h zinc deposits electrowon from electrolyte containing various Dowfroth concentrations are shown in a series of SE micrographs, Fig. 2, and the deposit orientation results are

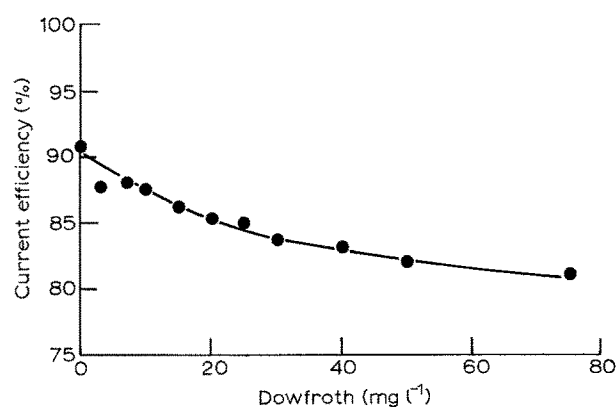


Fig. 1. Plot of current efficiency against Dowfroth concentration for 6 h zinc deposits electrowon at 500 A m^{-2} and 38°C .

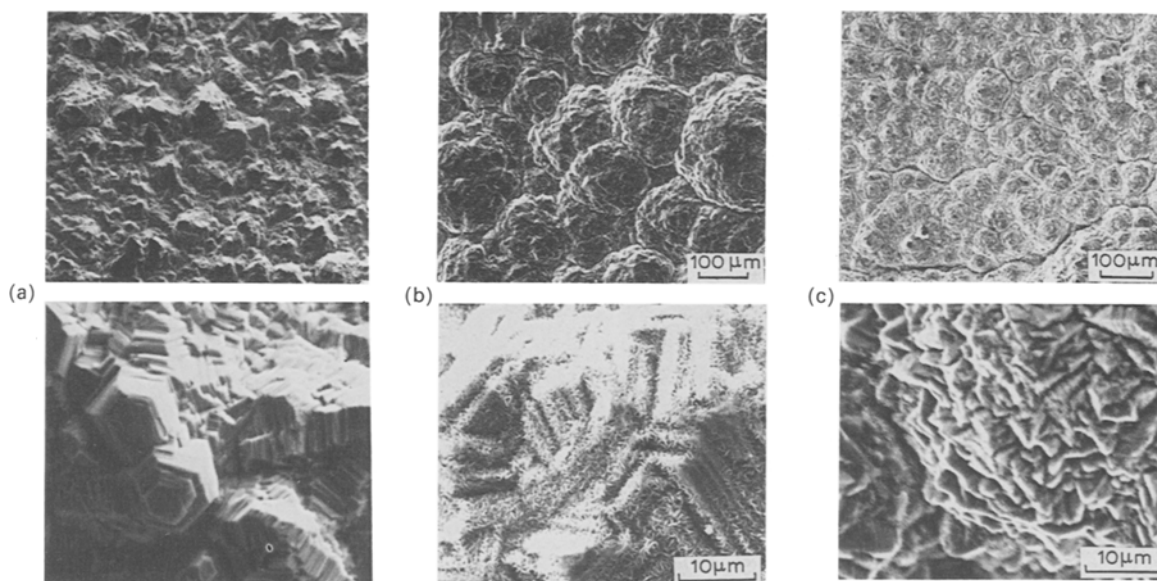


Fig. 2. SE micrographs showing the morphology of 6 h zinc deposits electrowon at 500 A m^{-2} and 38°C from electrolytes containing (a) 0, (b) 3 and (c) 30 mg dm^{-3} Dowfroth.

summarized in Table 1. In the absence of Dowfroth, the zinc deposit consists of closely packed nodules of varying grain size, Fig. 2a. Higher magnification indicates that these nodules consist of hexagonal zinc platelets aligned at low angles ($< 30^\circ$) to the aluminium cathode. This results in a $[002] [103]$ preferred deposit orientation, Table 1.

The addition of 3 mg dm^{-3} Dowfroth changes the preferred deposit orientation to $[112] [103] [102] [114] [101]$, Table 1. This is reflected in the deposit morphology shown in Fig. 2b; the nodules consist of hexagonal zinc platelets aligned at intermediate ($30^\circ\text{--}70^\circ$) angles to the aluminium cathode. Dowfroth concentrations $> 3 \text{ mg dm}^{-3}$ resulted in the preferred deposit orientation becoming exclusively $[101]$, Table 1. This indicates a strong polarizing effect which is confirmed by the deposit morphology shown in Fig. 2c. The deposit obtained for 30 mg dm^{-3} Dowfroth consists of grain refined nodules smaller than those in the deposit obtained for 3 mg dm^{-3} Dowfroth, *cf.* Fig. 2b.

The above results indicate that Dowfroth additions to zinc electrolyte have an effect on zinc deposition polarization. Zinc deposition polarization was measured using cyclic voltammetry as described in previous publications [1, 3]. These measurements indicated that the addition of Dowfroth to the electrolyte resulted in a significant increase in the NOP for zinc deposition. The NOP values for the initial and final electrolytes were obtained for Dowfroth additions from 0 to 75 mg dm^{-3} and are listed in Table 1. There is a significant increase in the initial NOP with increasing Dowfroth concentrations $> 15 \text{ mg dm}^{-3}$ although the final NOP values remain fairly constant, Table 1.

3.2. Dowfroth + antimony effects

Antimony, at concentrations $\leq 0.02 \text{ mg dm}^{-3}$, is

usually added to purified zinc electrolyte because it is thought to reduce zinc deposit adherence to the aluminium cathode and because of its beneficial interaction with glue [5, 6]. Antimony is one of the reagents currently added to the Kidd Creek electrolyte, and thus it is desirable to determine its interaction with Dowfroth. The effect of increasing antimony concentrations to 0.02 mg dm^{-3} with $3\text{--}15 \text{ mg dm}^{-3}$ Dowfroth on 6 h zinc electrodeposits was investigated at 500 A m^{-2} and 38°C . The CE, orientation and NOP results are presented in Table 2 and the CE data are plotted as a series of CE against antimony curves in Fig. 3. These results indicate that certain Dowfroth + antimony combinations produce a maximum CE value. As the Dowfroth concentration is increased, more antimony is needed to maximize the CE. At the optimum Dowfroth + antimony combination, the maximum CE value decreased with increasing Dowfroth concentration.

For Dowfroth concentrations of 3 mg dm^{-3} with various antimony concentrations and for 7 mg dm^{-3} Dowfroth with either 0.015 or 0.02 mg dm^{-3} anti-

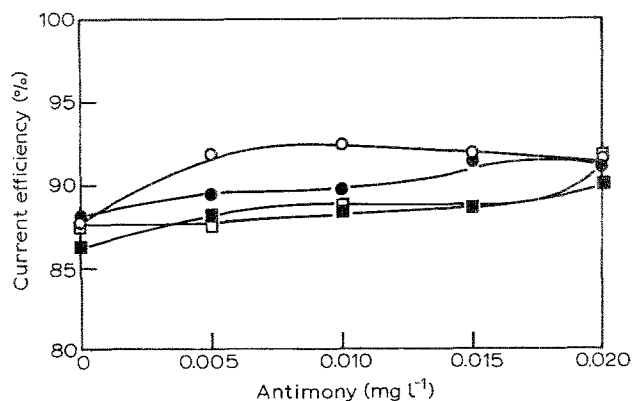


Fig. 3. Plots of current efficiency against antimony concentration for 6 h zinc deposits electrowon at 500 A m^{-2} and 38°C from electrolytes containing (○) 3, (●) 7, (□) 10 and (■) 15 mg dm^{-3} Dowfroth.

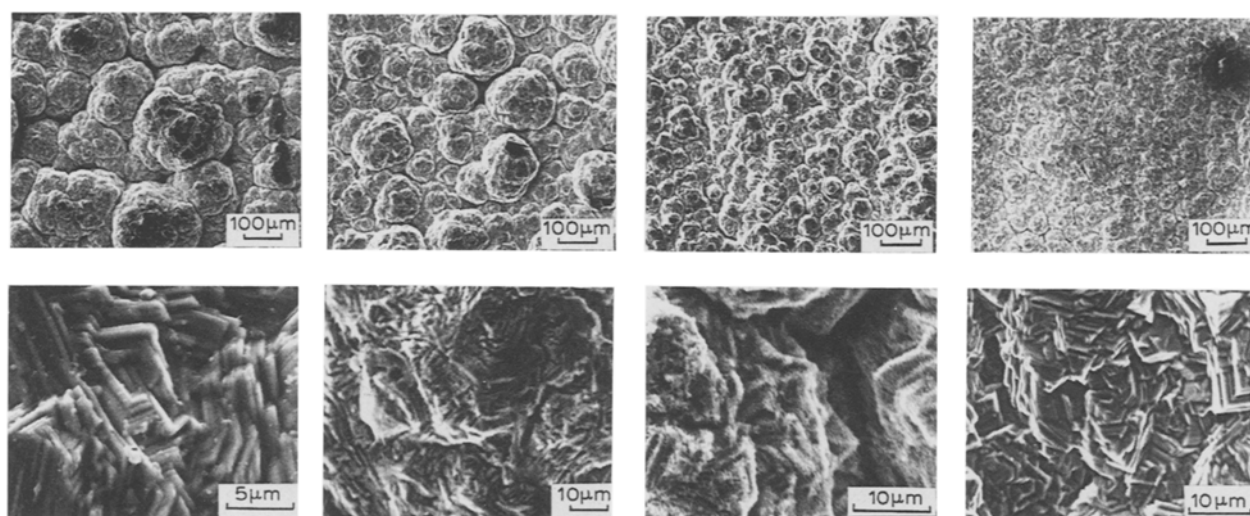


Fig. 4. SE micrographs showing the morphology of 6 h zinc deposits electrowon at 500 A m^{-2} and 38°C from electrolytes containing optimum Dowfroth + antimony concentrations i.e., (a) $3 + 0.01$, (b) $7 + 0.015$, (c) $10 + 0.02$ and (d) 15 mg dm^{-3} Dowfroth + 0.02 mg dm^{-3} Sb.

mony, the preferred deposit orientation was $[101]$ $[112]$, Table 2. For all other Dowfroth + antimony combinations the preferred orientation was $[101]$. The deposit morphology for the Dowfroth + antimony combinations that resulted in maximum CE values is shown in the series of SE micrographs, Fig. 4. As indicated, the deposits consist of rounded nodules that decrease in size with increasing Dowfroth concentration.

For a given Dowfroth concentration, both the initial and final NOP values decrease with increasing antimony concentration, Table 2. The addition of antimony had the greatest impact on the initial NOP for electrolytes containing 3 mg dm^{-3} Dowfroth. The initial NOP values decreased with increasing antimony reaching a minimum value at 0.01 mg dm^{-3}

antimony. This minimum initial NOP value also corresponded to a maximum CE value. For the higher Dowfroth concentrations, the minimum initial NOP values occurred at higher Sb concentrations and also corresponded to maximum CE values. The final NOP values also decreased with increasing antimony concentration although the actual values were much closer to one another for a given combination of these reagents, Table 2.

3.3. Dowfroth + Saponin + antimony effects

The CE, orientation and NOP data obtained for various combinations of Dowfroth + Saponin + antimony are presented in Table 3. The Saponin concentrations were 1, 3, 5 and 10 mg dm^{-3} at fixed levels

Table 2. The effect of Dowfroth and antimony on the CE, orientation and NOP for 6 h zinc deposits electrowon at 500 A m^{-2} and 38°C

Dowfroth (mg dm^{-3})	Sb (mg dm^{-3})	CE (%)	Orientation*	NOP (mV)	
				Initial	Final
3	0	87.6	112, 103, 102, 114, 101	150	150
3	0.005	91.8	101, 112	120	140
3	0.010	92.3	101, 112	100	130
3	0.015	91.8	101, 112	105	130
3	0.020	91.4	101, 112	110	135
7	0	88.0	101	140	155
7	0.005	89.4	101	130	140
7	0.010	89.7	101	140	155
7	0.015	91.5	101, 112	115	125
7	0.020	91.1	101, 112	130	150
10	0	87.5	101	155	145
10	0.005	87.5	101	160	135
10	0.010	88.7	101	155	145
10	0.015	88.4	101	145	145
10	0.020	91.7	101	130	140
15	0	86.2	101	155	130
15	0.005	88.2	101	150	150
15	0.010	88.5	101	145	145
15	0.015	88.6	101	140	140
15	0.020	90.0	101	140	140

* Relative to ASTM standard for zinc powder

Table 3. The effect of Dowfroth, Saponin and antimony on the CE, orientation and NOP values for 6 h zinc deposits electrowon at 500 A m^{-2} and 38°C

Dowfroth (mg dm^{-3})	Saponin (mg dm^{-3})	Sb (mg dm^{-3})	CE (%)	Orientation*	NOP (mV)	
					Initial	Final
3	0	0.005	91.8	101, 112	120	140
3	1	0.005	90.6	101, 112	140	105
3	3	0.005	91.0	101, 112	140	120
3	5	0.005	90.1	101, 112	130	130
3	10	0.005	90.8	101, 112	145	145
3	3	0.01	92.3	101, 112	130	150
7	0	0.01	89.7	101	140	155
7	1	0.01	92.0	101	115	115
7	3	0.01	92.7	101	110	120
7	5	0.01	91.3	101	130	125
7	10	0.01	92.1	101	130	135
7	3	0.015	92.3	101	140	145
10	0	0.02	91.7	101	130	140
10	1	0.02	90.8	101, 112	125	120
10	3	0.02	92.3	101, 112	135	145
10	5	0.02	90.9	101, 112	135	145
10	10	0.02	92.1	101, 112	140	155

* Relative to ASTM standard for zinc powder

of Dowfroth + antimony; i.e., 3 mg dm^{-3} Dowfroth + 0.005 mg dm^{-3} antimony, 7 mg dm^{-3} Dowfroth + 0.01 mg dm^{-3} antimony and 10 mg dm^{-3} Dowfroth + 0.02 mg dm^{-3} antimony. In general, Saponin additions had no effect on the CE although there appears to be an increase in the CE at all Dowfroth + antimony combinations when Saponin was 3 mg dm^{-3} . At 3 mg dm^{-3} Dowfroth + 3 mg dm^{-3} Saponin increasing antimony to 0.01 mg dm^{-3} resulted in an increase in CE; at 7 mg dm^{-3} Dowfroth + 3 mg dm^{-3} Saponin increasing antimony to 0.015 mg dm^{-3} did not significantly change the CE. The preferred deposit orientation was [101] [112] for 3 and 10 mg dm^{-3}

Dowfroth with various antimony + Saponin concentrations, but was [101] for 7 mg dm^{-3} Dowfroth with antimony + Saponin, Table 3. No consistent trends were noted for the initial and final NOP values. For Dowfroth $> 3 \text{ mg dm}^{-3}$, the addition of 1 mg dm^{-3} Saponin lowers both the initial and final NOP's; the NOP's then begin to increase with increasing Saponin concentration, Table 3.

The deposit morphologies obtained for 3 mg dm^{-3} Dowfroth + 3 mg dm^{-3} Saponin + 0.005 mg dm^{-3} antimony and for 7 mg dm^{-3} Dowfroth + 3 mg dm^{-3} Saponin + 0.01 mg dm^{-3} antimony are shown in Figs 5a and 5b, respectively. These deposit mor-

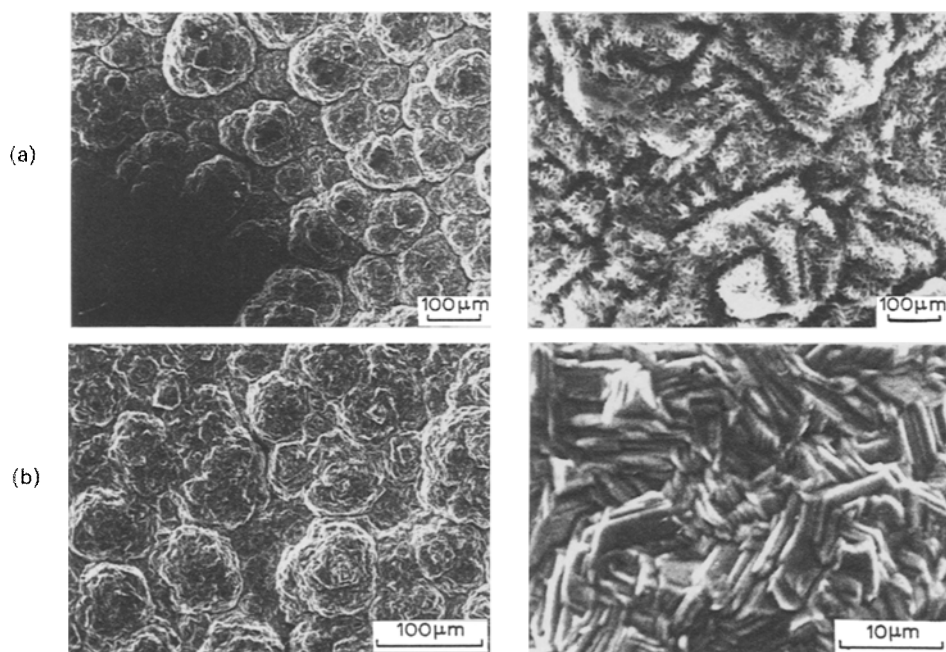


Fig. 5. SE micrographs showing the morphology of 6 h zinc deposits electrowon at 500 A m^{-2} and 38°C from electrolytes containing (a) 3 mg dm^{-3} Dowfroth + 3 mg dm^{-3} Saponin + 0.005 mg dm^{-3} antimony and (b) 7 mg dm^{-3} Dowfroth + 3 mg dm^{-3} Saponin + 0.01 mg dm^{-3} antimony.

Table 4. The effect of Dowfroth, Saponin and antimony on the CE, orientation, NOP and lead content of 24 h zinc deposits electrowon at 500 A m^{-2} and 38°C

Dowfroth (mg dm^{-3})	Sb (mg dm^{-3})	Saponin (mg dm^{-3})	CE (%)	Orientation*	NOP (mV)		Pb (ppm)
					Initial	Final	
3	0.010	–	92.0	101, 112	145	130	33
3	0.015	–	92.6	101, 112	110	130	22
3	0.010	1	91.4	112, 101, 201	150	125	16
3	0.010	3	91.5	101, 112	155	130	12
7	0.015	–	90.0	101	140	115	<6
7	0.015	1	89.8	101	125	135	11
7	0.015	3	90.4	101	135	140	8

* Relative to ASTM standard for zinc powder

phologies are similar to those obtained in the absence of Saponin; cf. Fig. 4.

3.4. 24 h confirmation tests

The results obtained from the addition of various combinations of Dowfroth, Saponin and antimony to diluted neutral leach solutions are presented in Table 4. Increasing antimony from 0.01 to 0.015 mg dm^{-3} in an electrolyte containing 3 mg dm^{-3} Dowfroth results in a small increase in CE, but does not change the preferred orientation or the final NOP, Table 4. The addition of 1 or 3 mg dm^{-3} Saponin to an electrolyte containing 3 mg dm^{-3} Dowfroth + 0.01 mg dm^{-3} antimony results in a small decrease in the CE, but does not significantly alter the preferred orientation or the final NOP.

At 7 mg dm^{-3} Dowfroth + 0.015 mg dm^{-3} antimony the addition of 1 or 3 mg dm^{-3} Saponin did not affect significantly the CE; the preferred orientation remained [101], Table 4.

The deposit morphologies for the 3 and 7 mg dm^{-3}

Dowfroth series are shown in the SE micrographs, Figs 6 and 7, respectively. The deposits shown in Fig. 6 are compact and nodular; the addition of Saponin results in smaller, more distinct nodules, Figs 6b and c. At 7 mg dm^{-3} Dowfroth, the deposit grain size is refined and the nodules have disappeared, replaced by long tubular-like ridges, Fig. 7. The deposits are all very similar.

A comparison of the data for the 6 h tests (Tables 2 and 3) and for the 24 h tests (Table 4) shows that very good agreement was obtained between the corresponding CE, orientation and final NOP results.

Photographs of some of the 24 h zinc deposits electrowon from electrolytes containing either 3 or 7 mg dm^{-3} Dowfroth with various concentrations of antimony and Saponin are presented in Fig. 8. The vertical striations that occur in the presence of 7 mg dm^{-3} Dowfroth are clearly visible.

Portions of the 24 h zinc deposits were analysed for lead, and these results also are presented in Table 4. In most cases, the lead content of the zinc deposits was $< 20 \text{ ppm}$, indicating that these deposits are

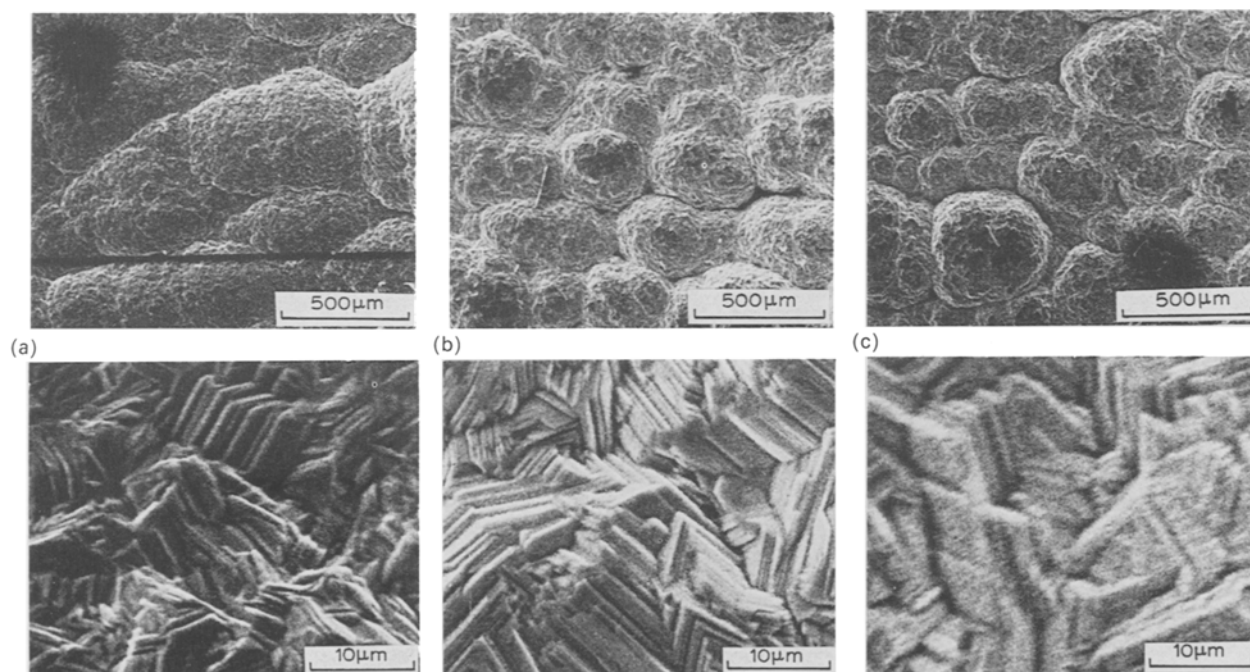


Fig. 6. SE micrographs showing the morphology of 24 h zinc deposits electrowon at 500 A m^{-2} and 38°C from electrolytes containing 3 mg dm^{-3} Dowfroth and various combinations of antimony and Saponin; i.e., (a) 0.01 mg dm^{-3} Sb, (b) 0.01 mg dm^{-3} Sb + 1 mg dm^{-3} Saponin and (c) 0.01 mg dm^{-3} Sb + 3 mg dm^{-3} Saponin.

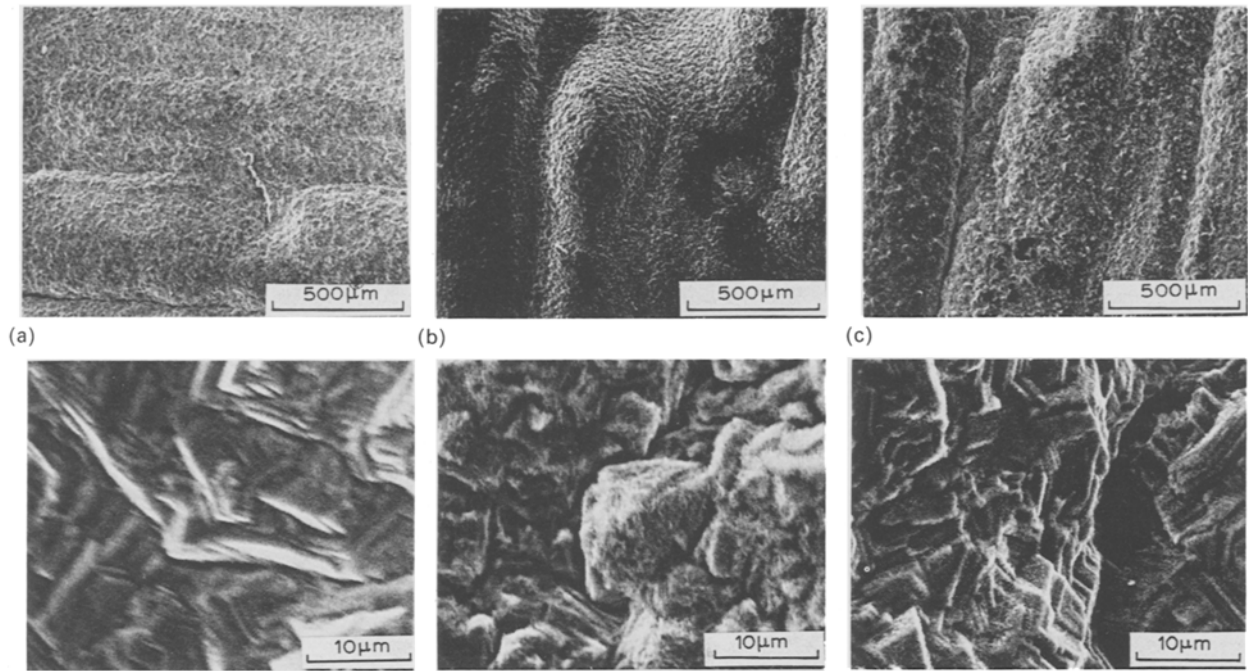


Fig. 7. SE micrographs showing the morphology of 24 h zinc deposits electrowon at 500 A m^{-2} and 38°C from electrolytes containing 7 mg dm^{-3} Dowfroth and various combinations of antimony and Saponin; i.e., (a) 0.015 mg dm^{-3} Sb, (b) 0.015 mg dm^{-3} Sb + 1 mg dm^{-3} Saponin and (c) 0.015 mg dm^{-3} Sb + 3 mg dm^{-3} Saponin.

well within the special high grade zinc specification for lead.

4. Conclusions

The effects of Dowfroth alone and in combination with antimony and Saponin on zinc deposition current efficiency and polarization and on the

morphology and orientation of 6 h and 24 h deposits electrowon at 500 A m^{-2} and 38°C from Kidd Creek electrolyte were determined. Dowfroth alone was a strong polarizer, changed the preferred deposit orientation from $[002][103]$ (basal) to $[101]$ (intermediate) and decreased the current efficiency.

Certain Dowfroth + antimony combinations lowered the nucleation overpotential and maximized

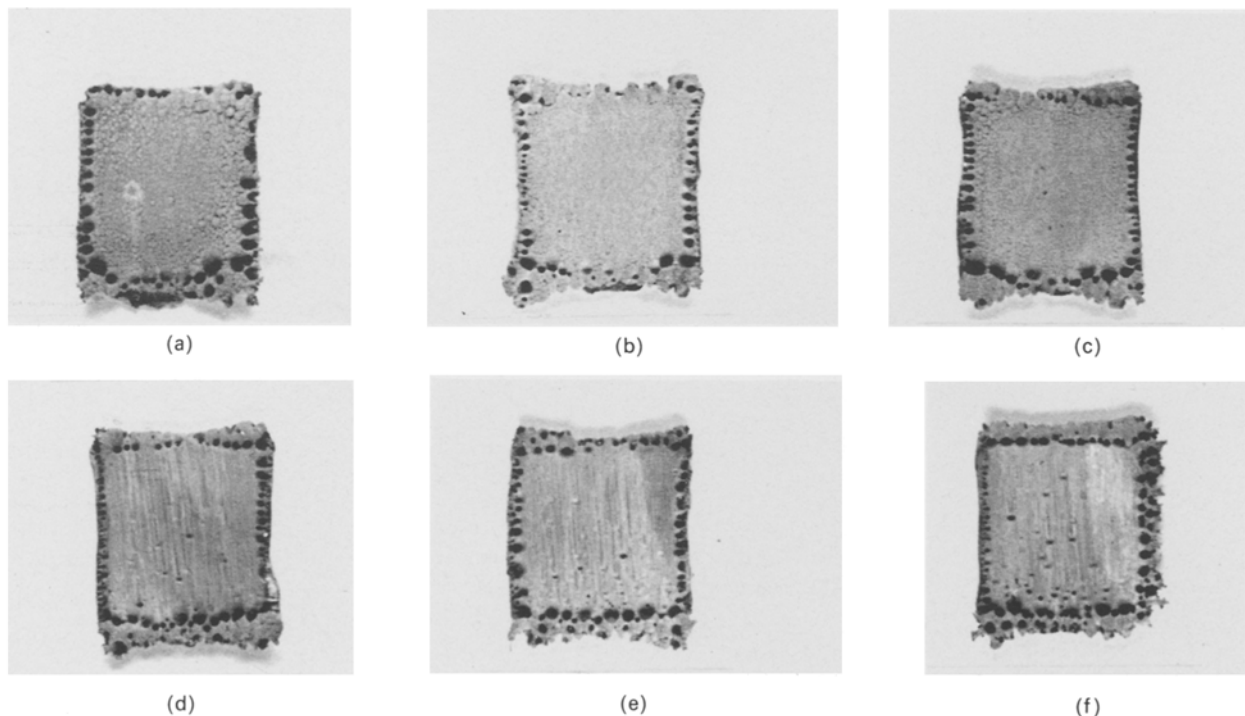


Fig. 8. Photographs ($\approx 1\times$) of 24 h zinc deposits electrowon at 500 A m^{-2} and 38°C from electrolytes containing various combinations of Dowfroth, antimony and Saponin. (a) 3 mg dm^{-3} Dowfroth + 0.01 mg dm^{-3} Sb; 92.6% CE, (b) 3 mg dm^{-3} Dowfroth + 0.01 mg dm^{-3} Sb + 1 mg dm^{-3} Saponin; 91.4% CE, (c) 3 mg dm^{-3} Dowfroth + 0.01 mg dm^{-3} Sb + 3 mg dm^{-3} Saponin; 91.5% CE, (d) 7 mg dm^{-3} Dowfroth + 0.015 mg dm^{-3} Sb; 90.0% CE (e) 7 mg dm^{-3} Dowfroth + 0.015 mg dm^{-3} Sb + 1 mg dm^{-3} Saponin; 89.8% CE and (f) 7 mg dm^{-3} Dowfroth + 0.015 mg dm^{-3} Sb + 3 mg dm^{-3} Saponin; 90.4% CE.

zinc deposition current efficiency. At optimum antimony + Dowfroth combinations, the addition of Saponin did not affect significantly the current efficiency or deposit morphology.

Tests run for 24 h for selected combinations of Dowfroth, antimony and Saponin confirmed the results obtained for the 6 h studies.

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