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The effects of saponin, antimony and glue on zinc electrowinning from Kidd Creek electrolyte

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The effects of Saponin alone and in combination with antimony and glue 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. Saponin, at concentrations to $100\,mg\,l^{-1}$, was weakly polarizing, changed the preferred deposit orientation from basal to intermediate and decreased the current efficiency. At optimum glue + antimony levels, Saponin concentrations $\geqslant 5\,mg\,l^{-1}$ resulted in an increase in zinc deposition current efficiency and consistently gave either a $\langle 1\,1\,4\rangle\langle 1\,1\,2\rangle\langle 1\,0\,3\rangle\langle 1\,0\,2\rangle\langle 1\,0\,1\rangle$ or a $\langle 1\,0\,1\rangle\langle 1\,1\,2\rangle$ preferred deposit orientation depending on the antimony + glue combination used. Tests run for 24 h for selected combinations of Saponin, antimony and glue confirmed the results obtained for the 6 h studies.

1. Introduction

Current operating practice in the Kidd Creek zinc tankhouse includes the addition of antimony and sodium silicate to control the growth of the zinc deposit, of Dowfroth, a frothing agent, to form a layer of foam on the surface of the electrolyte to minimize acid mist formation and of $SrCO_3$ to control the level of lead in the zinc deposit. Dowfroth, however, in addition to controlling acid mist, also acts as a strong polarizer and thus affects zinc deposition current efficiency (CE) and zinc deposit morphology. Because of its strong polarizing effect, which is counteracted to some extent by the antimony added to the electrolyte, the Dowfroth concentration must be carefully controlled to avoid detrimental effects on the CE and deposit quality. Thus, the use of other foaming agents which do not strongly affect zinc deposition polarization is being considered. One such reagent is Saponin, a steroid/triterpenoid glycoside, that produces a honeycomb froth when shaken with water [1]. The use of non-polarizing foaming agents would obviate the close control necessary for Dowfroth but probably would require the presence of a polarizing additive such as animal glue to control the zinc deposit growth. Animal glue is a common addition agent in most zinc plants but is not presently added to the Kidd Creek electrolyte. Thus, a previous study [2] was done to determine the effects of glue, antimony and glue + antimony on the CE and nucleation overpotential for zinc deposition and on the morphology and orientation of zinc deposits electrowon from Kidd Creek zinc electrolyte.

The results of the previous study [2] showed that certain combinations of antimony + glue optimized the CE and consistently produced a $\langle 1\,1\,4\rangle\langle 1\,1\,2\rangle$ $\langle 1\,0\,3\rangle\langle 1\,0\,2\rangle\langle 1\,0\,1\rangle$ preferred deposit orientation. A correlation was also observed between the CE values and the nucleation overpotential (NOP) for zinc deposition such that the CE was a maximum when the NOP of the initial cell electrolyte was 120–130 mV with respect to the mercury/mercurous sulphate electrode (MSE) or when the final cell electrolyte was 100–110 mV with respect to MSE.

The present study was carried out to determine the effects of Saponin plus optimum antimony/glue combinations on the CE and nucleation overpotential for zinc depostion and on the morphology and orientation of zinc deposits electrowon from Kidd Creek zinc electrolyte.

2. Experimental details

2.1. *Experimental procedure*

The electrowinning cells and experimental procedure were described in detail in the previous paper [2]. Both feed and cell electrolytes were prepared from purified neutral and cold spent solutions received from Kidd Creek. The analyses are presented in Table 1. Each cell contained 400 ml of electrolyte at 2/3 volume. The electrolyte composition was maintained at $55\,g\,l^{-1}$ Zn and $200\,g\,l^{-1}$ H_2SO_4 throughout the electrolysis period. The various addition agents including pearl glue, potassium antimony tartrate and Saponin were supplied by Kidd Creek. These addition agents

Table 1. Analyses of neutral and cold spent solutions received from Kidd Creek Ltd

Analyte	*Neutral solution*	*Cold spent solution*
Mg ($g\,l^{-1}$)	2.3–2.5	2.5–2.8
Mn ($g\,l^{-1}$)	9.7–10.4	9.5–10.5
Na ($g\,l^{-1}$)	2.8–3.0	2.7–2.9
S ($g\,l^{-1}$)	100.7–107.9	105.9–116.9
Zn ($g\,l^{-1}$)	186.5–200.6	57.9–64.0
H_2SO_4	–	196.0–208.0
Ag ($mg\,l^{-1}$)	1	1
Al ($mg\,l^{-1}$)	16–20	28
As ($mg\,l^{-1}$)	< 0.01	0.03
Sb ($mg\,l^{-1}$)	< 0.01	< 0.01
Se ($mg\,l^{-1}$)	< 0.05	< 0.05
Sn ($mg\,l^{-1}$)	< 0.2	< 0.2
Ba ($mg\,l^{-1}$)	0.6	1
Ca ($mg\,l^{-1}$)	305–350	309–313
Cd ($mg\,l^{-1}$)	0.6	< 0.1
Co ($mg\,l^{-1}$)	0.2	0.3
Cr ($mg\,l^{-1}$)	< 0.1	< 0.1
Cu ($mg\,l^{-1}$)	0.1–0.3	0.1
Fe ($mg\,l^{-1}$)	16–20	15
Ga ($mg\,l^{-1}$)	< 1	< 1
In ($mg\,l^{-1}$)	< 1	< 1
Ni ($mg\,l^{-1}$)	< 1	< 1
Pb ($mg\,l^{-1}$)	1	1
Si ($mg\,l^{-1}$)	225–240	80–94

were added to both the feed and cell electrolytes at the desired concentrations as aliquots from their stock solutions which contained $1000\,mg\,l^{-1}$ glue, $30\,mg\,l^{-1}$ Sb and $500\,mg\,l^{-1}$ Saponin.

The 6 h electrowinning tests were carried out in four cells immersed in a temperature controlled water bath to maintain the electrolyte at 38° C. The aluminium cathodes (supplied by Kidd Creek) were masked with electroplating tape to give a 2 in^2 ($12.9 \times 10^{-4}\,m^2$) surface area. The cells were operated at $500\,A\,m^{-2}$ current density and platinum anodes were used to avoid lead contamination of the zinc deposits [3].

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 also added to the electrolyte to minimize lead contamination.

At the end of the electrolysis period, the cathodes were pulled from the cells and the zinc deposits were rinsed with water, stripped, dried and weighed. The current efficiency was calculated from the weight of zinc deposited and the number of coulombs passed. A portion of the final cell electrolyte was analysed for zinc and free H_2SO_4, and the remainder was used to determine the zinc deposition polarization characteristics using cyclic voltammetry.

2.2. *Deposit examination*

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 (SE) detector to determine the deposit morphology. A portion of each 24 h zinc deposit was analysed for lead.

2.3. *Polarization studies*

Cyclic voltammetry (CV) experiments were conducted to determine the polarization characteristics of zinc deposition for both the initial and final cell electrolytes for all the tests. The CV tests were done in duplicate using 150 ml of electrolyte at room temperature. An aluminium disk cathode ($2.8\,cm^2$), a platinum foil anode and a MSE reference electrode were employed. The potential was cycled between -1.1 and -1.7 V with respect to MSE at a rate of $4\,mV\,s^{-1}$ using a potentiostat driven by a voltage scan generator. The voltammograms were recorded as i against E plots using a X–Y recorder.

3. Results and discussion

3.1. *Saponin effects*

The effect of Saponin additions from 0 to $1000\,mg\,l^{-1}$ on the CE for 6 h zinc deposits electrowon at $500\,A\,m^{-2}$ and 38° C is summarized in Table 2 and a plot of CE against Saponin concentration ($1–100\,mg\,l^{-1}$) is shown in Fig. 1. There is an initial decrease in CE from 91% at $0\,mg\,l^{-1}$ Saponin to ~88% at $10\,mg\,l^{-1}$ Saponin. Thereafter, the CE increases with increasing Saponin concentration to a maximum of ~90% at $25\,mg\,l^{-1}$ Saponin. For increasing Saponin concentrations $> 25\,mg\,l^{-1}$, the CE steadily decreases to a value of ~86% at $100\,mg\,l^{-1}$ Saponin. At $1000\,mg\,l^{-1}$ Saponin, the CE was 77.1% (Table 2) and the deposit was very brittle.

The morphologies of the 6 h zinc deposits electrowon from electrolyte containing various Saponin concentrations are shown in a series of SEM photographs, Fig. 2, and the deposit orientation results are summarized in Table 2. In the absence of Saponin, the zinc deposit consists of closely packed nodules of varying grain size, Fig. 2(a). Higher magnification indicates that these nodules consist of hexagonal zinc platelets aligned at low angles (< 30°) to the aluminium cathode, Fig. 2(b). This results in a ⟨0 0 2⟩ ⟨1 0 3⟩ preferred deposit orientation, Table 2.

The addition of low concentrations of Saponin ($1–10\,mg\,l^{-1}$) changes the preferred deposit orientation to ⟨1 1 4⟩⟨1 0 3⟩⟨1 1 2⟩⟨1 0 2⟩⟨1 0 1⟩, Table 2. This is reflected in the deposit morpholgy shown in Figs 2c and d for $10\,mg\,l^{-1}$ Saponin. In this case the nodules consist of hexagonal zinc platelets aligned at intermediate (30°–70°) angles to the aluminium cathode, Fig. 2d. Saponin concentrations in the range $15–30\,mg\,l^{-1}$ resulted in the preferred deposit orientation becoming predominantly ⟨1 1 2⟩⟨1 1 4⟩ ⟨1 0 3⟩⟨1 0 1⟩, Table 2. The morphology was characterized by the clusters of large nodules growing on the surface of a relatively smooth layer of zinc, Fig. 2e. These large nodules consist of poorly defined hexagonal

Table 2. The effect of Saponin on the current efficiency, orientation and nucleation overpotential (NOP) for 6 h zinc deposits electrowon at 500 $A\,m^{-2}$ and 38° C

Saponin ($mg\,l^{-1}$)	*CE* (%)	*Orientation**	*NOP (mV against MSE)* *Initial*	*Final*
0	91.0	002, 103	140	125
1	89.3	114, 103, 112, 102, 101	140	150
3	89.7	114, 103, 112, 102, 101	155	155
5	88.4	114, 112, 103, 102, 101	153	150
10	88.1	114, 112, 103, 102, 101	135	140
15	89.2	112, 102, 103, 114, 101	140	130
20	89.6	112, 114, 103, 101	140	140
25	90.3	112, 114, 101	150	135
30	89.5	112, 114, 103, 201, 101	150	135
40	89.0	114, 201, 112, 110, 103, 101	160	145
50	89.2	114, 110, 201, 100, 002, 112, 101	150	150
75	88.1	002, 100, 110, 114, 112, 101	165	155
100	86.0	100, 110, 002, 201	165	155
1000	77.1	110, 100, 002, 201	190	145

* Relative to ASTM standard for zinc powder

zinc platelets aligned at intermediate angles to the aluminium cathode, Fig. 2f.

For Saponin concentrations $>40\,mg\,l^{-1}$, the zinc deposit was characterized by extremes in orientation, including ⟨1 0 0⟩⟨1 1 0⟩ (zinc platelets perpendicular to the aluminium cathode) and ⟨0 0 2⟩ (zinc platelets parallel to the aluminium cathode), Table 2. This type of preferred orientation was observed previously for thiourea concentrations between 10–200 $mg\,l^{-1}$ [4], and results in the deposit morphology shown in Figs 2g and h. The deposit is characterized by the growth of non-uniform, oblong particles deposited on an underlying layer of grain-refined zinc, Fig. 2g. These particles consist of layers of poorly defined zinc platelets aligned at parallel and vertical angles to the aluminium cathode, Fig. 2h, that give rise to the extremes in orientation, Table 2.

The above results suggest that Saponin additions to zinc electrolyte have an effect on zinc deposition polarization. Zinc deposition polarization was measured using cyclic voltammetry and a typical voltammogram (CV) for addition-free elecrolyte is shown in Fig. 3a. A scan is initiated at point A, -1.1 V with respect to MSE at a scan rate of 4 $mV\,s^{-1}$. An appreciable current begins to flow at point B (zinc sulphate decomposition potential) and the scan is reversed at point C; i.e., when the current is approximately 30 mA. At point D, the so-called crossover potential, the current is zero. After crossing point D, the current becomes anodic and zinc dissolves from the cathode; the anodic current reaches a maximum at point E and upon return to point A, zinc dissolution is complete.

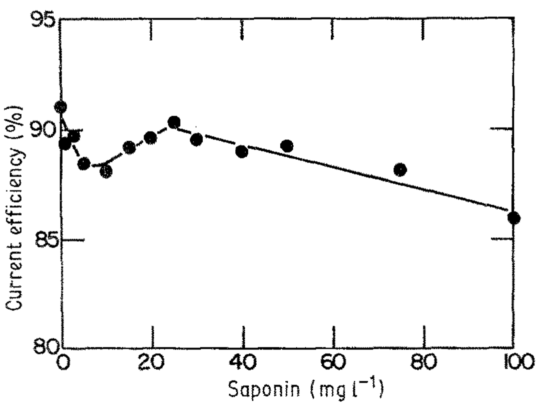

Fig. 1. Plot of current efficiency against Saponin concentration for 6 h zinc deposits electrowon at 500 $A\,m^{-2}$ and 38°C.

The region B–D is termed nucleation overpotential (NOP) and it is the difference between the crossover potential D and the point B at which zinc begins to deposit. In the present work the point B was arbitrarily chosen to be the value of the potential when a current of 2.5 mA was reached in the forward scan.

The addition of Saponin to the electrolyte did not significantly change the shape of the CV, but did result in some variations in the B–D portion of the curve; i.e., in the NOP, Fig. 3b. The NOP values for the initial and final electrolytes were obtained for Saponin additions from 0 to 1000 $mg\,l^{-1}$. These values are listed in Table 2 and are shown as plots of NOP vs Saponin concentration in Fig. 4. These data indicate an increase in both the initial and final NOPs with increasing Saponin concentrations to 5 $mg\,l^{-1}$. Both NOP values then decrease to a minimum value at 10 to 15 $mg\,l^{-1}$ Saponin. Increasing the Saponin concentration to values $>15\,mg\,l^{-1}$ results in an increase in the NOP values which gradually level off at 40–50 $mg\,l^{-1}$ Saponin. At 1000 $mg\,l^{-1}$ Saponin the initial NOP is very high; i.e., 190 mV (Table 2) although the final NOP is only 145 mV. For Saponin concentrations $>10\,mg\,l^{-1}$, the final NOP values are generally less than the initial NOP.

3.2. *Saponin + antimony effect*

Antimony, at concentrations $\leqslant 0.02\,mg\,l^{-1}$, is usually added to purified zinc electrolyte because it is thought to reduce zinc deposit adherence to the aluminium cathode blank 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

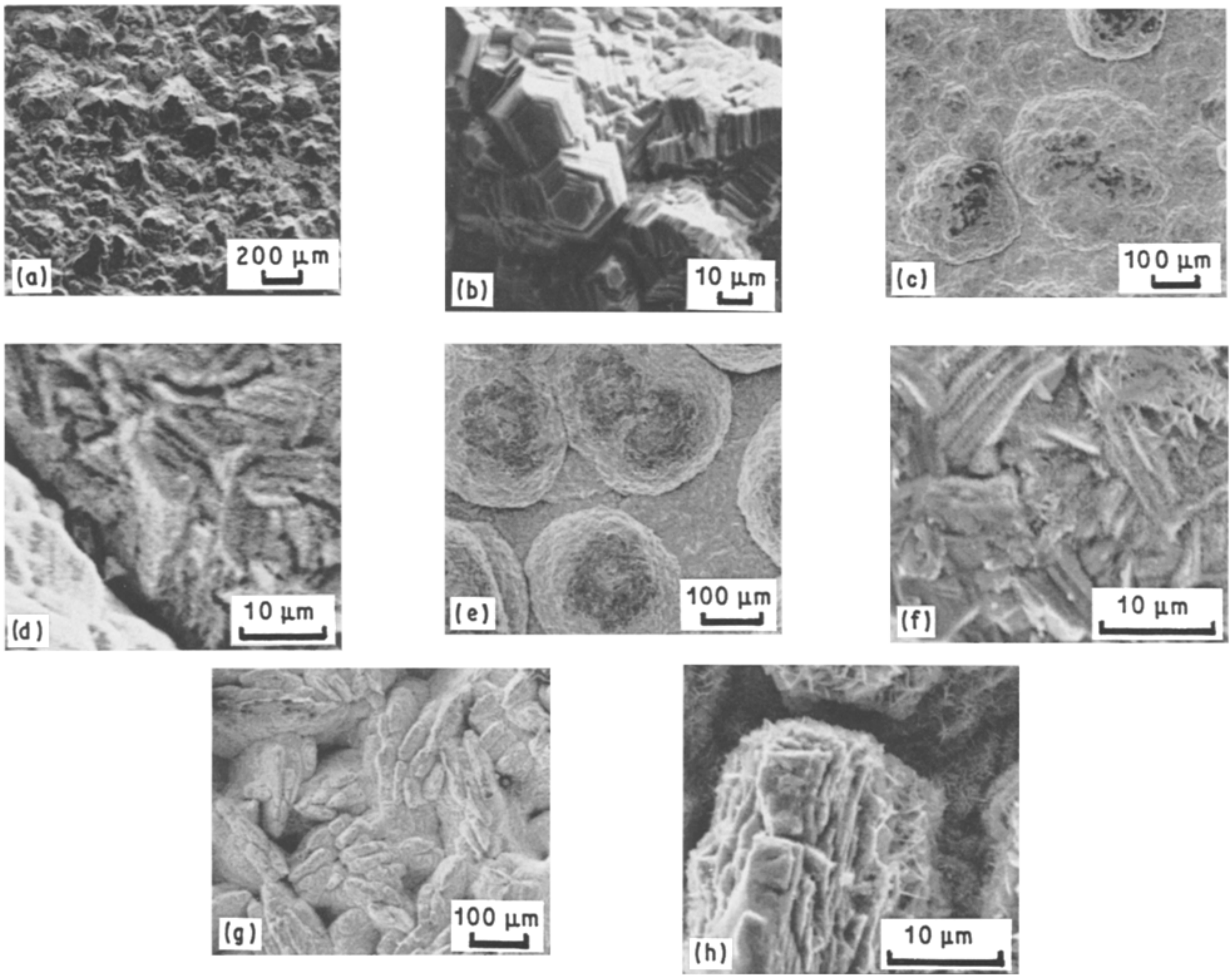

Fig. 2. SE micrographs showing the morphology of 6 h zinc deposits electrowon at 500 A m^{-2} and 38° C from electrolytes containing 0, 10, 20 and 100 mg l^{-1} Saponin. (a) and (b) Addition-free; (c) and (d) 10 mg l^{-1} Saponin; (e) and (f) 20 mg l^{-1} Saponin; (g) and (h) 100 mg l^{-1} Saponin.

it is desirable to determine its interaction with Saponin. The effect of increasing antimony concentrations to 0.03 mg l^{-1} with 1–10 mg l^{-1} Saponin on the CE for 6 h zinc deposts electrowon at 500 A m^{-2} and 38° C is summarized in Table 3 and a plot CE against antimony concentration is presented in Fig. 5.

The CE increased with increasing antimony concentration to 0.01 mg l^{-1} for all Saponin concentrations

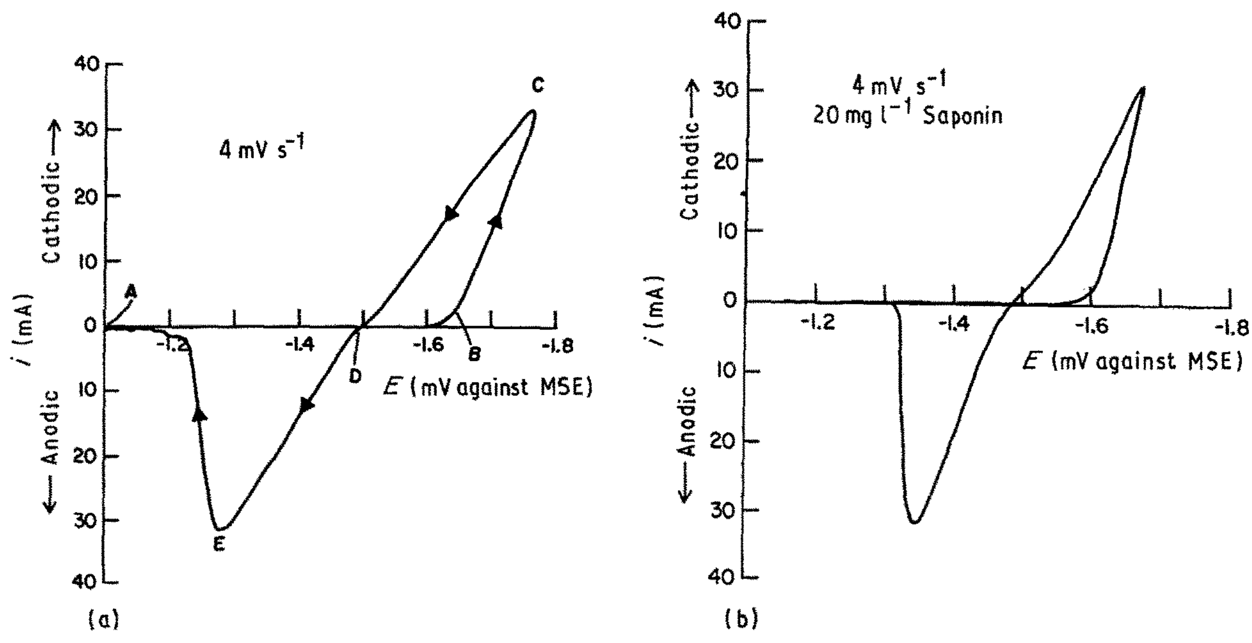

Fig. 3. Typical cyclic voltammograms for Kidd Creek zinc electrolyte containing 0 and 20 mg l^{-1} Saponin. (a) No additions; (b) 20 mg l^{-1} Saponin.

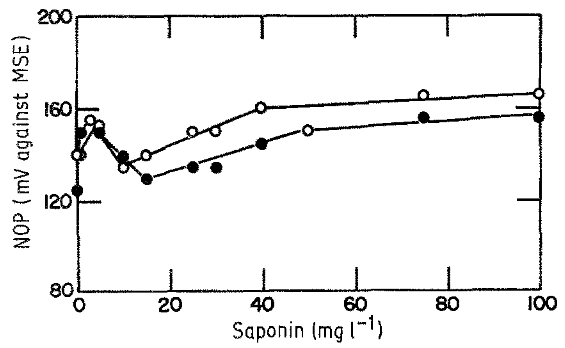

Fig. 4. Plots of nucleation overpotential against Saponin concentration for initial and final cell electrolyses. (○) initial, (●) final.

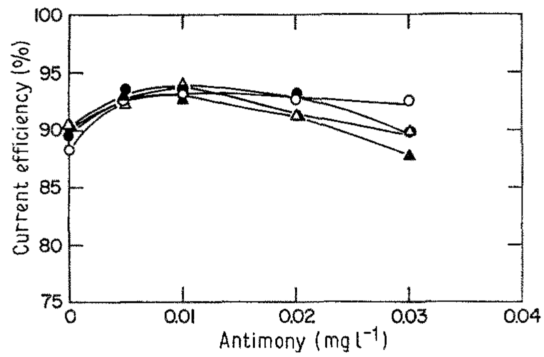

Fig. 5. Plots of current efficiency vs antimony concentration for 6 h zinc deposits electrowon at 500 A m^{-2} and 38° C from electrolytes containing (▲) 1, (△) 3, (●) 5 and (○) 10 mg l^{-1} Saponin.

reaching a maximum of 93.9% for 0.01 mg l^{-1} antimony and 3 mg l^{-1} Saponin, Table 3, Fig. 5. For antimony concentrations $\geqslant$ 0.02 mg l^{-1}, the CE began to decrease with the rate of decrease being greatest for the lowest Saponin concentration. For example, at 0.03 mg l^{-1} antimony, the CE was 87.7% for 1 mg l^{-1} Saponin but was 92.5% for 10 mg l^{-1} Saponin, Table 3.

In the absence of antimony, the preferred deposit orientation for each Saponin concentration was essentially ⟨1 1 4⟩⟨1 0 3⟩⟨1 1 2⟩⟨1 0 2⟩⟨1 0 1⟩, Table 3. The addition of 0.005 and 0.01 mg l^{-1} antimony changed the deposit orientation to ⟨1 0 1⟩⟨1 1 2⟩; at the higher antimony concentrations, the orientation was either ⟨1 1 2⟩⟨1 0 1⟩⟨1 0 2⟩⟨1 0 3⟩⟨1 1 4⟩ or ⟨1 1 4⟩⟨1 0 3⟩⟨1 1 2⟩⟨1 0 2⟩⟨1 0 1⟩, Table 3. The final NOP values were higher than the initial values but, as expected, both decreased with increasing Sb concentration. The deposit morphologies obtained for the various Saponin and antimony combinations are typical of that shown in Fig. 6a and b. The deposit consists of distinct, relatively uniform nodules, Fig. 6a, that are composed of well-defined hexagonal zinc platelets aligned at intermediate angles to the aluminium cathode, Fig. 6b.

3.3. *Saponin + antimony + glue effects*

In a previous paper [2] it was reported that certain glue + antimony combinations; e.g., 5 mg l^{-1} glue + 0.02 mg l^{-1} Sb and 30 mg l^{-1} glue + 0.04 mg l^{-1} Sb, resulted in maximum CE values. The effect of Saponin additions (0–50 mg l^{-1}) to electrolytes containing these optimum glue + antimony combinations was studied, and the results are presented in Tables 4 and 5 and as plots of CE against Saponin concentration, Fig 7. As indicated by the plots in Fig. 7, the CE begins to increase for Saponin concentrations $\geqslant$ 5 mg l^{-1} and reaches a maximum value at ~ 20 mg l^{-1} Saponin. For the 5 mg l^{-1} glue + 0.02 mg l^{-1} antimony solutions,

Table 3. The effect of Saponin and antimony on the current efficiency, orientation and nucelation overpotential (NOP) for 6 h zinc deposits electrowon at 500 A m^{-2} and 38° C

Saponin (mg l^{-1})	*Sb (mg l^{-1})*	*CE (%)*	*Orientation**	*NOP (mV against MSE) Initial*	*Final*
1	0	90.5	114, 103, 112, 102, 101	143	145
1	0.005	93.1	101, 112	110	135
1	0.010	92.8	101, 112	100	135
1	0.020	91.2	112, 101, 102, 103, 114	80	120
1	0.030	87.7	112, 114, 103, 102, 101	85	125
3	0	90.5	114, 103, 112, 102, 101	145	143
3	0.005	92.1	101, 112	115	130
3	0.010	93.9	101, 112	100	135
3	0.020	91.2	101, 112	80	110
3	0.030	89.7	114, 112, 103, 102, 101	85	125
5	0	89.4	114, 112, 103, 102, 101	153	147
5	0.005	93.5	101, 112	125	130
5	0.010	93.5	101, 112	95	130
5	0.020	93.1	112, 101	95	135
5	0.030	89.7	112, 114, 103, 102, 101	80	120
10	0	88.1	114, 112, 103, 102, 101	135	140
10	0.005	92.6	101, 112	125	135
10	0.010	93.1	114, 112, 101	110	125
10	0.020	92.6	114, 101	85	90
10	0.030	92.5	114, 103, 112, 102, 101	85	120

* Relative to ASTM standard for zinc powder

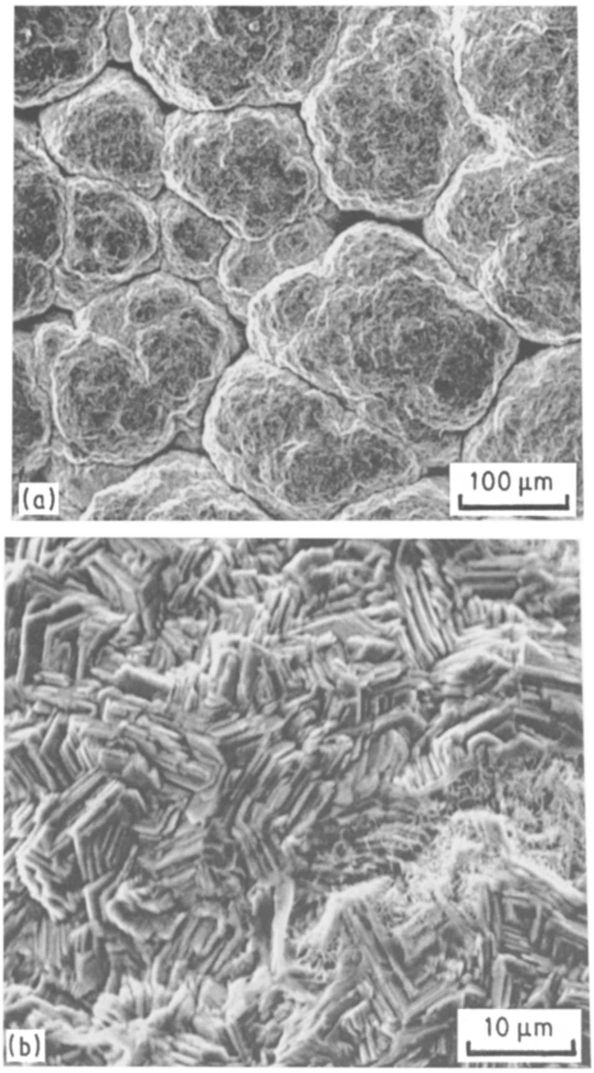

Fig. 6. SE micrographs showing the morpholgy of a 6 h zinc deposit electrowon at 500 A m^{-2} and 38° C from an electrolyte containing (a) and (b) 10 mg l^{-1} Saponin + 0.01 mg l^{-1} antimony.

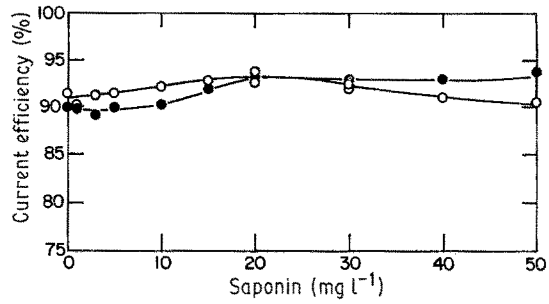

Fig. 7. Plots of current efficiency against Saponin concentration at optimum levels of antimony + glue for 6 h zinc deposits electrowon at 500 A m^{-2} and 38° C. (○) 0.02 mg l^{-1} Sb + 5 mg l^{-1} glue; (●) 0.04 mg l^{-1} Sb + 30 mg l^{-1} glue.

the CE begins to decrease at > 20 mg l^{-1} Saponin, Table 4 and for the 30 mg l^{-1} glue + 0.04 mg l^{-1} antimony solutions, the CE remains at its maximum value at least up to 50 mg l^{-1} Saponin, Table 5.

The increase in the Saponin concentration results in a change in the preferred deposit orientation from ⟨1 1 4⟩⟨1 1 2⟩⟨1 0 3⟩⟨1 0 2⟩⟨1 0 1⟩ at low Saponin concentrations to ⟨1 0 1⟩⟨1 1 2⟩ at higher Saponin levels when the CE is maximized, Tables 4 and 5. The typical deposit morphology obtained from Saponin additions to electrolytes containing optimum glue + antimony is shown in Figs 8a and b. The deposit surface consists of relatively uniform nodules, Fig. 8a, composed of well-defined hexagonal zinc platelets aligned at intermediate angles to the aluminium cathode, Fig. 8b.

Both the initial and final NOP values gradually increase with increasing Saponin concentration, and this shows that zinc deposition polarization increases with increasing Saponin in both the 0.02 mg l^{-1} antimony + 5 mg l^{-1} glue and the 0.04 mg l^{-1} antimony + 20 mg l^{-1} glue-containing electrolytes, Tables 4 and 5.

Various other combinations of glue and antimony with 10 mg l^{-1} Saponin also were studied, and the results are summarized in Table 6. As noted earlier, the combination of 10 mg l^{-1} Saponin with 0.01 mg l^{-1} Sb resulted in a high CE, 93.1%, Table 3. The additional presence of 5 mg l^{-1} glue maintained the high CE, 93.2% Table 6, and resulted in a smoother deposit. The deposit morphology is shown in Figs 9a and b and indicates a surface composed of uniform, closely packed nodules, Fig. 9a, which are composed of well-defined hexagonal platlets aligned at inter-

Table 4. The effect of saponin with optimum antimony + glue on the current efficiency, orientation and nucleation overpotential (NOP) for 6 h zinc deposits electrowon at 500 A m^{-2} and 38° C

Saponin (*mg* l^{-1})	*Glue* (*mg* l^{-1})	*Sb* (*mg* l^{-1})	*CE* (*%*)	*Orientation**	*NOP* (*mV against MSE*) *Initial*	*Final*
0	5	0.02	91.4	114, 112, 103, 102, 101	83	81
1	5	0.02	90.2	114, 103, 112, 102, 101	85	80
3	5	0.02	91.2	114, 103, 112, 102, 101	85	85
5	5	0.02	91.5	114, 103, 112, 102, 101	90	90
10	5	0.02	92.2	101, 112	95	95
15	5	0.02	92.7	101, 112	110	100
20	5	0.02	93.7	101, 112	115	130
20	5	0.02	92.7	112, 101	95	125
30	5	0.02	92.1	101	120	135
30	5	0.02	92.6	112, 101	100	130
40	5	0.02	91.1	112, 101	115	140
50	5	0.02	90.6	112, 101	125	135

* Relative to ASTM Standard for zinc powder

Table 5. The effect of Saponin with optimum antimony + glue on the current efficiency, orientation and nucleation overpotential (NOP) for 6 h zinc deposits electrowon at 500 $A\,m^{-2}$ and 38° C

Saponin ($mg\,l^{-1}$)	Glue ($mg\,l^{-1}$)	Sb ($mg\,l^{-1}$)	CE (%)	Orientation*	NOP (mV against MSE) Initial	Final
0	30	0.04	89.9	114, 112, 103, 102, 101	125	100
1	30	0.04	89.9	114, 103, 112, 102, 101	130	100
3	30	0.04	89.1	114, 112, 103, 102, 101	130	95
5	30	0.04	89.9	114, 112, 103, 102, 101	130	90
10	30	0.04	90.3	114, 112, 103, 102, 101	130	120
15	30	0.04	92.0	112, 114, 101	130	120
20	30	0.04	93.2	101, 112	95	120
30	30	0.04	92.8	101, 112	105	130
40	30	0.04	93.0	112, 101	115	135
50	30	0.04	93.7	112, 101	120	135

*Relative to ASTM standard for zinc powder

mediate angles to the aluminium cathode, Fig. 9b. The CE remained >92% for the other antimony + glue combinations with 10 $mg\,l^{-1}$ Saponin, Table 6, and the deposit morphologies were similar to that depicted in Figure 9. The preferred orientations remains essentially unchanged at ⟨114⟩⟨101⟩⟨112⟩; i.e., intermediate, although both the initial and final NOP values increased with increasing glue, Table 6.

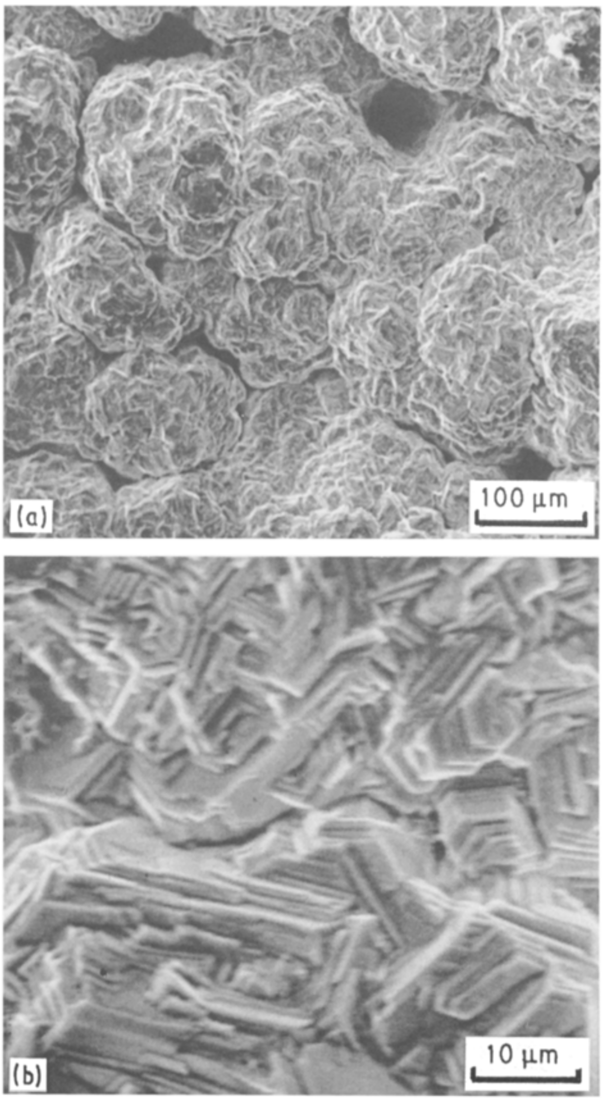

Fig. 8. SE micrographs showing the morphology of a 6 h zinc deposit electrowon at 500 $A\,m^{-2}$ and 38° C from electrolyte containing (a) and (b) 5 $mg\,l^{-1}$ Saponin with optimum glue + antimony (0.02 $mg\,l^{-1}$ + 5 $mg\,l^{-1}$ glue).

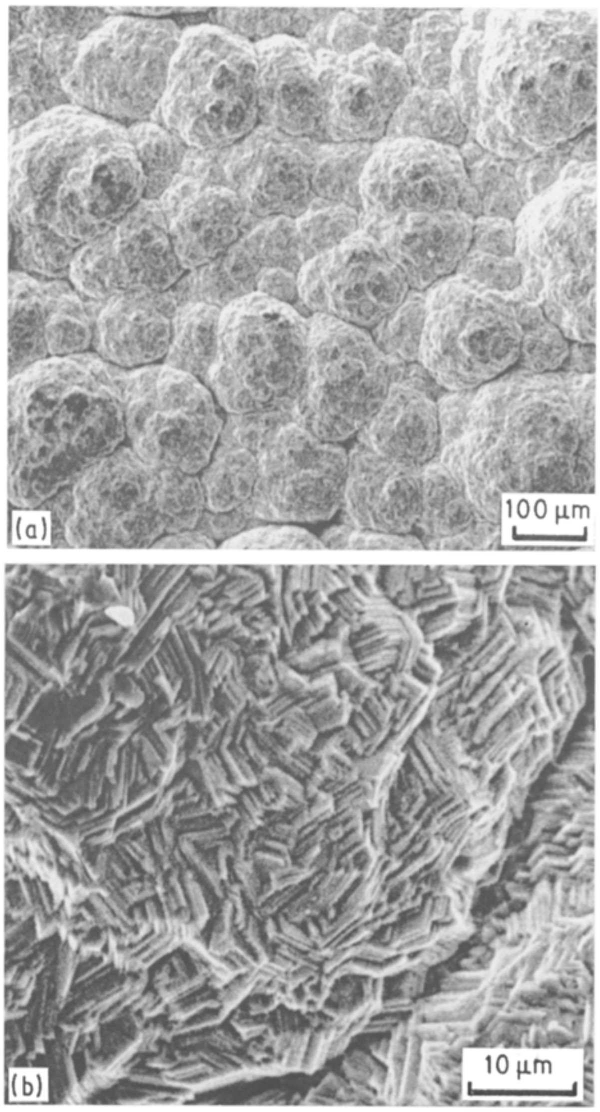

Fig. 9. SE micrographs showing the morphology of a 6 h zinc deposit electrowon at 500 $A\,m^{-2}$ and 38° C from electrolyte containing (a) and (b) 10 $mg\,l^{-1}$ Saponin + 0.01 $mg\,l^{-1}$ Sb + 5 $mg\,l^{-1}$ glue.

Table 6. The effect of Saponin with various antimony + glue additions on the current efficiency, orientation and nucleation overpotential (NOP) for 6 h zinc deposits electrowon at 500 $A\,m^{-2}$ and 38° C

Saponin ($mg\,l^{-1}$)	*Glue* ($mg\,l^{-1}$)	*Sb* ($mg\,l^{-1}$)	*CE* (%)	*Orientation**	*NOP (mV against MSE)* *Initial*	*Final*
10	5	0.01	93.2	114, 101, 112	115	135
10	5	0.02	92.2	101, 112, 114	95	95
10	5	0.03	92.9	114, 112, 103, 102, 101	85	130
10	10	0.02	92.6	112, 114, 101	110	95
10	15	0.02	92.6	101, 114	120	110
10	20	0.02	92.3	101, 112, 114	130	120
10	30	0.02	92.9	101, 112, 114	140	135

* Relative to ASTM standard for zinc powder

3.4. 24 *h confirmation tests*

A series of 24 h tests was run for selected combinations of additives to confirm the results obtained in the 6 h experiments. The selected conditions together with the test data are presented in Table 7. A 24 h test without additions was also run for comparison purposes. The CE for the addition-free 24 h deposit was 90.6%. The presence of various additives in the electrolyte increased the CE ~93%, Table 7.

The presence of the additives changes the preferred deposit orientation from ⟨2 0 1⟩⟨1 0 1⟩ to ⟨1 0 1⟩ ⟨1 1 2⟩; i.e., to more intermediate, Table 7. This is probably a result of the decrease in the NOP values that occurs in the presence of these particular combinations of addition agents, Table 7.

The deposit morphology changes significantly when the additives are present in the electrolyte, Fig. 10. The surface of the addition-free deposit, Fig. 10a, consists of large, coarse, irregular nodules which in turn are

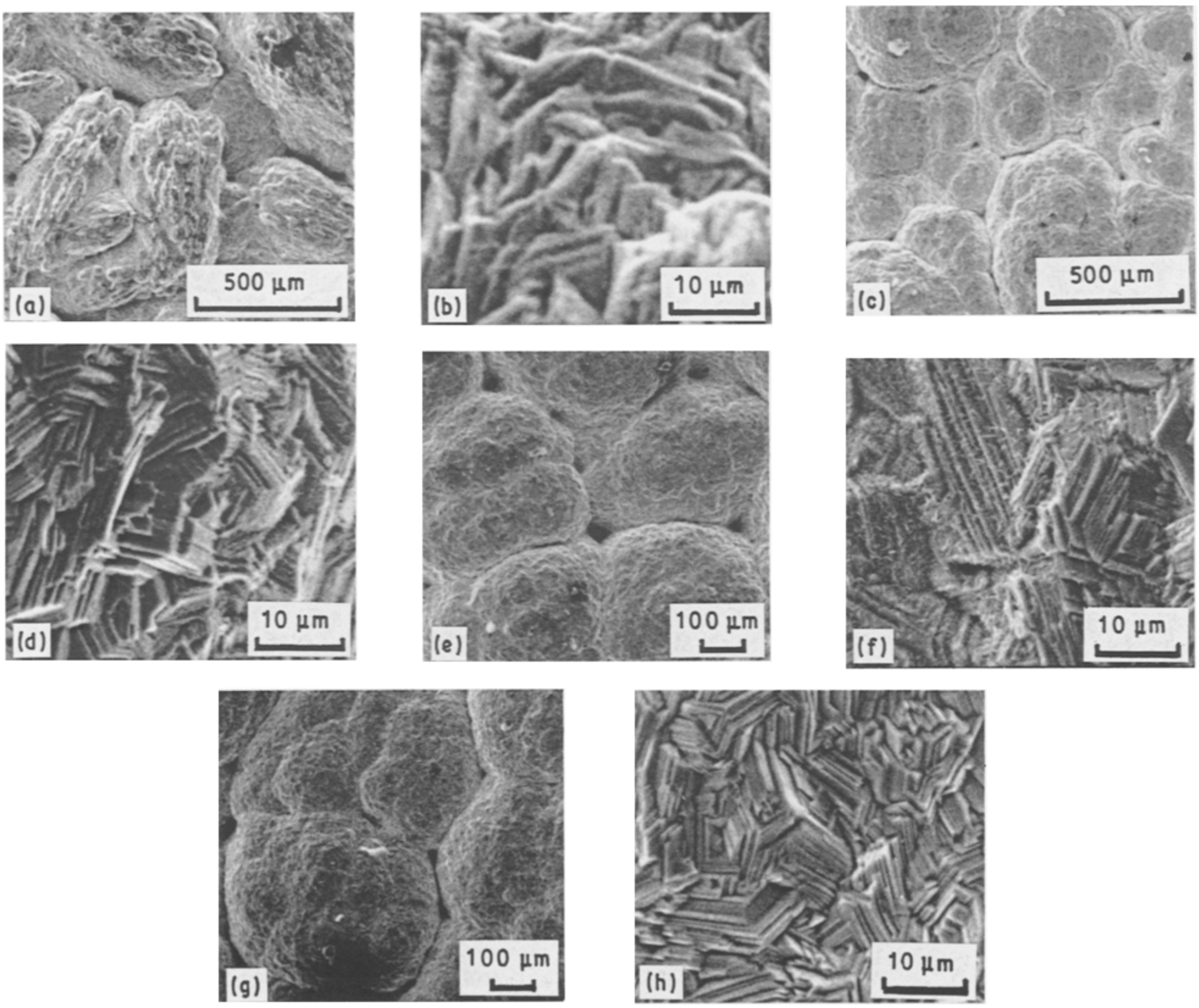

Fig. 10. SE micrographs showing the morphology of 24 h zinc deposits electrowon at 500 $A\,m^{-2}$ and 38° C from electrolytes containing various combinations of Saponin, antimony and glue: (a) and (b) addition free; (c) and (d) 10 $mg\,l^{-1}$ Saponin + 0.01 $mg\,l^{-1}$ Sb; (e) and (f) 10 $mg\,l^{-1}$ Saponin + 0.01 $mg\,l^{-1}$ Sb + 5 $mg\,l^{-1}$ glue; (g) and (h) 10 $mg\,l^{-1}$ Saponin + 0.01 $mg\,l^{-1}$ Sb + 15 $mg\,l^{-1}$ glue.

Table 7. The effect of saponin, antimony and glue on the current efficiency, orientation, nucleation overpotential (NOP) and lead content of 24 h zinc deposits electrowon at 500 A m^{-2} and 38° C

Saponin (mg l^{-1})	*Glue (mg l^{-1})*	*Sb (mg l^{-1})*	*CE (%)*	*Orientation**	*NOP (mV against MSE) Initial*	*Final*	*Pb (p.p.m)*
0	0	0	90.6	201, 101	125	140	43
10	0	0.01	93.0	101, 112	100	125	23
10	5	0.01	93.1	101, 112	100	120	26
10	15	0.01	92.9	101, 112	110	125	15
10	15	0.02	92.5	101, 112	90	115	16

* Relative to ASTM standard for zinc powder

composed of poorly defined hexagonal platelets aligned vertically to the aluminium cathode, Fig. 10b. The addition of 10 mg l^{-1} Saponin + 0.01 mg l^{-1} antimony to the electrolyte results in a 24 h deposit consisting of more uniform, smooth, rounded nodules, Fig. 10c that are composed of sharply defined zinc platelets aligned at intermediate angles to the aluminium cathode, Fig. 10d. The additional presence of 5 mg l^{-1} glue does not change significantly the deposit morphology, Figs 10e and f; increasing the glue to 15 mg l^{-1} results in a slightly reduced zinc platelet size, Fig. 10h.

Portions of the 24 h zinc deposits were analysed for lead and these results are also given in Table 7. With the exception of the addition-free test which gave a zinc deposit containing > 30 p.p.m. lead, the assays indicate that these zinc deposits are well within the special high grade zinc specification for lead.

4. Conclusions

The effects of Saponin alone and in combination with antimony and glue 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. Saponin alone was weakly polarizing, changed the preferred deposit orientation from ⟨0 0 2⟩⟨1 0 3⟩ (basal) to ⟨1 1 4⟩⟨1 0 3⟩⟨1 1 2⟩⟨1 0 2⟩ ⟨1 0 1⟩ (intermediate) and decreased the current efficiency. A minimum CE value occurred at 10 mg l^{-1} Saponin; the addition of 0.01 mg l^{-1} antimony, however, resulted in a substantial increase in the CE.

Saponin concentrations $\geqslant$ 5 mg l^{-1} added to electrolytes already containing optimum antimony + glue combinations resulted in an increase in zinc deposition current efficiency. For both 0.02 mg l^{-1} antimony + 5 mg l^{-1} glue and 0.04 mg l^{-1} antimony + 30 mg l^{-1} glue solutions the CE was maximized at 20 mg l^{-1} Saponin.

Tests run for 24 h for selected Saponin, antimony and glue combinations confirmed the results of the 6 h experiments.

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References

[1] S. Sotheeswaran, *J. Chem. Ed.* **65** (1988) 161.
[2] D. J. MacKinnon, R. M. Morrison, J. E. Mouland and P. E. Warren, *J. Appl. Electrochem.*, submitted.
[3] D. J. MacKinnon, J. M. Brannen and R. C. Kerby, *ibid.* **9** (1979) 71.
[4] D. J. MacKinnon, J. M. Brannen and R. M. Morrison, *ibid.* **18** (1988) 252.
[5] D. J. Robinson and T. J. O'Keefe, *ibid.* **6** (1976) 1.
[6] D. J. MacKinnon and J. M. Brannen, *ibid.* **7** (1977) 451.