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The effects of As(III) and As(V) on zinc electrowinning from industrial acid sulphate electrolyte

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The effects of As(III) and As(V), with and without glue and glue + antimony additions, on the current efficiency and polarization behaviour of zinc deposition and on the morphology and preferred orientation of 1-h zinc deposits electrowon from industrial acid sulphate electrolyte have been determined. As(III) had no effect on the current efficiency and did not alter significantly either the zinc deposition polarization curve or the zinc deposit morphology and orientation. Increasing concentrations of As(V) resulted in a significant decrease in the current efficiency for zinc deposition from addition-free electrolyte and from electrolytes containing added glue and glue + antimony. As(V) also changed the zinc deposit morphology and orientation, and significantly altered the shape of the zinc deposition cyclic voltammogram.

1. Introduction

During the past years reports have been published describing the effects of commonly encountered impurities on zinc electrowinning from acid sulphate electrolytes in terms of current efficiency, zinc deposition polarization, deposit morphology and orientation. Thus, the effects of antimony [1–3], cobalt and nickel [4–10], germanium [6, 7, 11], lead [12] and cadmium [13, 14] have been documented. Although these studies have provided a better understanding of impurity behaviour and have suggested the development of better control measures to counteract their deleterious effects, the mechanisms by which the impurities become activated in the electrolyte are still not fully understood.

As harmful levels of impurities such as arsenic are not usually present in zinc electrolyte, the effects of arsenic on zinc electrowinning have not been studied in detail previously. It has been stated [15], however, that arsenic is less harmful to zinc electrowinning than germanium or antimony and that its presence in the electrolyte is manifested by a pronounced corrugation and a lack of the usual luster of the zinc deposit. Weaver [16] also noted that arsenic is not as harmful as germanium or antimony and that it causes beads or sprouts to occur on the zinc deposit. Kerby and Ingraham [17] reported that As(III) had a beneficial effect on the current efficiency of zinc deposition, but Liebscher [18] reported that arsenic exerts no influence on the current efficiency even at the $5\,\mathrm{mg\,l^{-1}}$ level. Turomshina and Stender [19] also noted that arsenic had a beneficial effect on zinc deposition current efficiency and found that $10\,\mathrm{mg\,l^{-1}}$ arsenic reduced the current efficiency for hydrogen evolution. (Valence state of arsenic in [6, 18, 19] was not specified.) Fosnacht and O'Keefe [20] reported that concentrations of As(III) to $0.1\,\mathrm{mg\,l^{-1}}$ caused a slight decrease in the current efficiency for a 12-h zinc deposit, but did not change the zinc deposit morphology or orientation. They also found that there was no significant interaction between As(III) and glue under their experimental conditons. Maja *et al.* [6] found that arsenic at $50\,\mathrm{mg\,l^{-1}}$ altered the zinc deposit morphology, causing the presence of a rounded block structure.

It is possible that impurities can exist in different oxidation states in the zinc electrolyte and hence produce different electrochemical effects on zinc deposition. Recently, O'Keefe [21] compared the polarization behaviour of Sb(III) and Sb(V) using neutral and slightly acidic ($5\,\mathrm{g\,l^{-1}}$

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H_2SO_4) zinc sulphate electrolytes. It was reported that both forms of antimony caused depolarization of zinc deposition, but that Sb(III) seemed to be more potent than Sb(V) in acid solution while Sb(V) increased polarization as the pH decreased.

In the present study the effect of a less commonly encountered impurity, arsenic, on the current efficiency and polarization behaviour of zinc deposition and on the morphology and orientation of 1-h zinc deposits electrowon from industrial acid sulphate electrolyte was determined. It was felt that this information would add to the knowledge of impurity behaviour in general and might provide further insight into the mechanism of impurity interaction in the zinc electrowinning system.

2. Experimental procedure

2.1. *Electrolyte and apparatus*

The electrolyte was an industrial zinc sulphate solution prepared from hot zinc dust-purified neutral zinc electrolyte obtained from Cominco Ltd, Trail, British Columbia. The average analysis was (in $g\,l^{-1}$) Zn, 150; $MgSO_4$, 38; Mn, 1.6; (in $mg\,l^{-1}$) Cd, 0.2; Sb, 0.02; Co, 0.3; Ge, 0.01; Ni, 0.1; Cu, 0.1; Fe, 0.9; Pb, 0.2; Cl, 80; F, 3. Cell solutions were prepared by adding H_2SO_4, redistilled water and impurities to the electrolyte to give final concentrations of $55\,g\,l^{-1}$ zinc and $150\,g\,l^{-1}$ H_2SO_4. Animal glue additions were made as concentrated solutions. As(III) and As(V) were added as aliquots from their respective stock solutions. Antimony was added as a potassium antimony tartrate solution.

The electrolysis cell consisted of a 1-litre beaker fitted with a Lucite cover which had slots cut in it to mount the electrodes [3]. A three-electrode assemblage consisting of a central aluminum cathode and two platinum anodes was used. The cathode was fashioned from aluminium sheet (4.7 mm thick, purity 99.6%) obtained from Cominco. It measured 31.8 × 136.3 mm and was mounted so that zinc deposited on both sides onto a total area of $12.9\,cm^2$. The anodes were cut from a platinum sheet, 0.3 mm thick, and measured 17.9 × 109.7 mm. The platinum anodes were used to avoid lead contamination on the zinc deposits from conventional lead–silver anodes [12].

2.2. *Electrolysis*

The electrolysis experiments were run in a constant temperature bath at 35° C with stirring and at a cathode current density of $430\,A\,m^{-2}$ for a period of 1 h.

2.3. *Examination of deposits*

Sections of the zinc deposits were examined by scanning electron microscopy (SEM) to determine the surface morphology and by X-ray diffraction to determine the preferred crystal orientation relative to the ASTM standard for zinc powder. One side of the deposits electrowon from selected electrolytes was dissolved in HNO_3 for chemical analysis to determine the total arsenic content of the metal.

2.4. *Cyclic voltammetry*

Cyclic votammograms were obtained using a voltage scan generator, a potentiostat and a x–y recorder for recording current versus applied potential. The voltage scan generator was used to cycle the potential from $-0.95\,V$ to about $-1.15\,V$ versus a saturated calomel electrode (SCE). The latter limit was determined to give a maximum current of approximately 65 mA on the forward scan; hence there is some variation in the potential scan range. The scan was performed at a rate of $2\,mV\,s^{-1}$.

3. Results and discussion

3.1. *Current efficiency*

The effects of As(III) and As(V) on the current efficiency for 1-h zinc deposits electrowon at $430\,A\,m^{-2}$ from industrial acid sulphate electrolyte are shown in Figs 1 and 2, resepectively. The data presented in these figures were obtained using 'addition-free' electrolyte (i.e. containing no additions of antimony and glue), 'excess glue' electrolyte (i.e. containing $30\,mg\,l^{-1}$ glue) and 'balanced' electrolyte (i.e. containing $30\,mg\,l^{-1}$ glue and $0.08\,mg\,l^{-1}$ antimony). In agreement

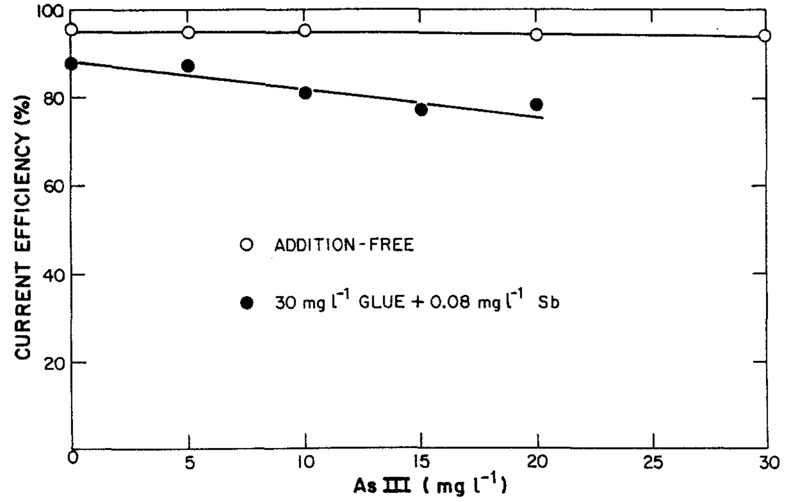

Fig. 1. The effect of increasing As(III) concentration on the current efficiency for 1-h zinc deposits electrowon at 430 A m^{-2} from various electrolytes.

with previous studies [16–20], the data in Fig. 1 indicate that the presence of up to 30 mg l^{-1} As(III) in the 'addition-free' electrolyte had no effect on the current efficiency for the 1-h zinc deposits. As(V), on the other hand, caused a significant decrease in the current efficiency for the 1-h zinc deposits as indicated by the data plotted in Fig. 2.

Both glue and glue + antimony are added to zinc electrolyte to counteract the effect of impurities [1, 3, 22]. Increasing additions of As(III) to an electrolyte containing 30 mg l^{-1} glue + 0.08 mg l^{-1} antimony caused a gradual decrease in the current efficiency for zinc deposition (Fig. 1). Similar additions of As(V) to electrolytes containing 30 mg l^{-1} glue and 30 mg l^{-1} glue + 0.08 mg l^{-1} antimony resulted in a more dramatic decrease in current efficiency (Fig. 2).

Fig. 3 presents the data obtained for the current efficiency of zinc deposition resulting from increasing glue concentration in addition-free electrolyte and in electrolytes containing 40 mg l^{-1} As(III) or 10 mg l^{-1} As(V). In every case, the current efficiency decreases with increasing glue concentration. Thus the interaction of As(III) and As(V) with glue and glue + antimony is more detrimental to the current efficiency of zinc deposition than either impurity alone.

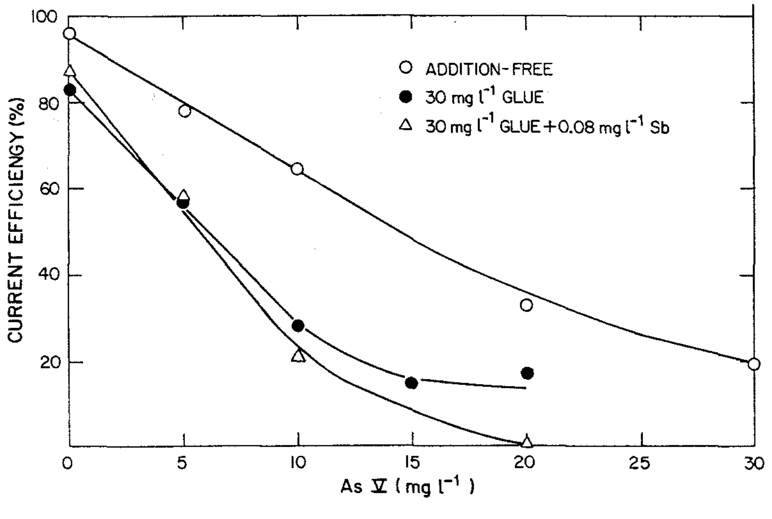

Fig. 2. Plots showing the effect of increasing As(V) concentration on the current efficiency for 1-h zinc deposits electrowon at 430 A m^{-2} from various electrolytes.

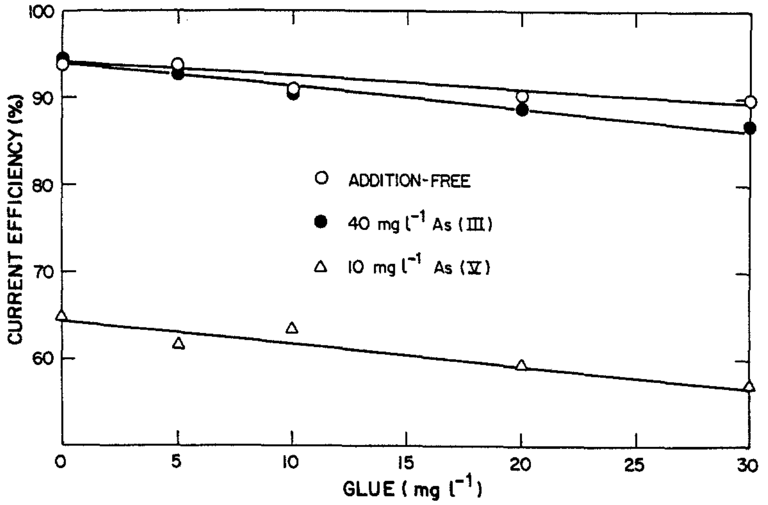

Fig. 3. The effect of increasing glue concentration on the current efficiency for 1-h zinc deposits electrowon at 430 A m^{-2} from electrolytes with and without antimony additions.

3.2. *Deposit morphology and orientation*

The effects of As(III) and As(V) on the morphology of the 1-h zinc deposits electrowon at 430 A m^{-2} from the various electrolytes are shown in a series of SEM photomicrographs (Fig. 4). The effects of these impurities in the presence and absence of glue and glue + antimony on the preferred deposit orientation are summarized in Table 1.

As indicated in Fig. 4a, the presence of 40 mg l^{-1} As(III) in the 'addition-free' electrolyte had no effect on the morphology of the 1-h zinc deposit which was identical to that obtained from 'addition-free' electrolyte containing no added impurities [3]. Similarly, the deposit

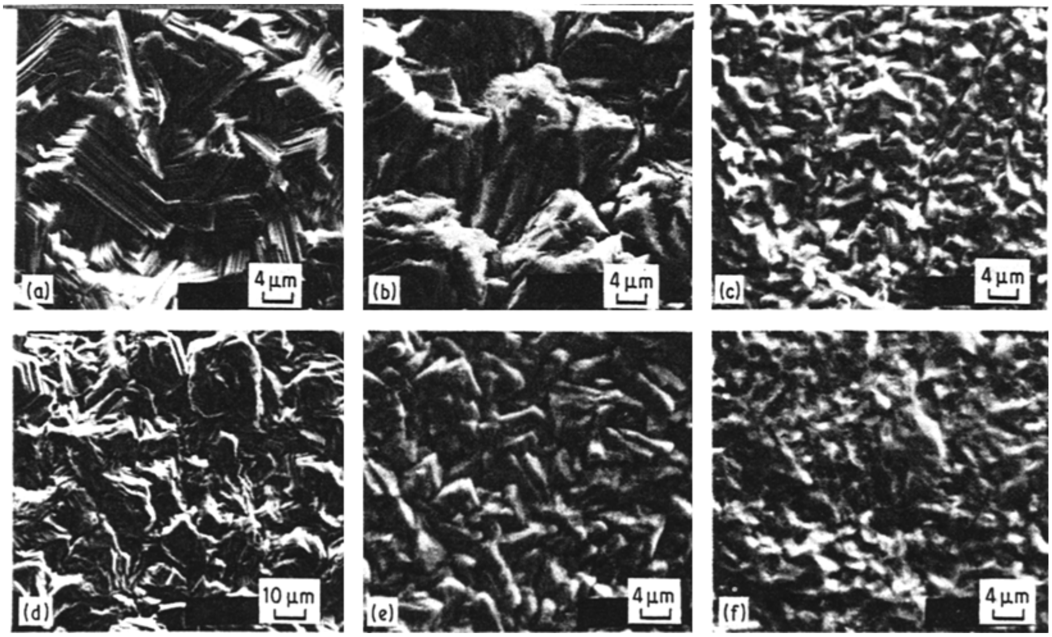

Fig. 4. SEM photomicrographs showing the effects of As(III) and As(V) on the morphology of 1-h zinc deposits electrowon at 430 A m^{-2} from various electrolytes. (a) 40 mg l^{-1} As(III); (b) 40 mg l^{-1} As(III) + 20 mg l^{-1} glue; (c) 20 mg l^{-1} As(III) + 30 mg l^{-1} glue + 0.08 mg l^{-1} antimony; (d) 10 mg l^{-1} As(V); (e) 5 mg l^{-1} As(V) + 30 mg l^{-1} glue; (f) 10 mg l^{-1} As(V) + 30 mg l^{-1} glue + 0.08 mg l^{-1} antimony.

Table 1. The effect of As(III) and As(V) and their interaction with glue and glue + antimony on the preferred orientation of 1-h zinc deposits electrowon from industrial acid sulphate electrolyte

As(III) *($mg\,l^{-1}$)*	*As(V)* *($mg\,l^{-1}$)*	*Glue* *($mg\,l^{-1}$)*	*Antimony* *($mg\,l^{-1}$)*	*Orientation*[a]
0	0	0	0	[1 1 2] [1 1 4] [1 0 2]
5	0	0	0	[1 0 1]
10	0	0	0	[1 1 2] [1 0 1]
10	0	30	0.08	[1 0 1]
20	0	30	0.08	[1 0 1]
40	0	5	0	[1 0 1]
40	0	20	0	[1 0 1]
50	0	0	0	[1 1 2]
0	5	0	0	[1 1 2] [1 1 0]
0	5	30	0.08	[1 0 1]
0	10	0	0	[1 1 4] [1 1 2]
0	10	5	0	[1 1 2]
0	10	10	0	[1 0 1]
0	10	30	0	[1 0 1]
0	20	0	0	[0 0 2] [1 0 5]

[a] Relative to ASTM standard for zinc powder. Electrolysis conditions: $55\,g\,l^{-1}$ Zn; $150\,g\,l^{-1}$ H_2SO_4; 35° C; $430\,A\,m^{-2}$.

orientation (Table 1) remained essentially unchanged, with the hexagonal zinc platelets being aligned at intermediate angles to the aluminim cathode, Fig. 4a.

The presence of glue in the electrolyte containing $40\,mg\,l^{-1}$ As(III) resulted in a typical glue-type morphology (Fig. 4b), having a preferred [1 0 1] deposit orientation (Table 1). The addition of As(III) to a 'balanced' electrolyte resulted in the deposit morphology shown in Fig. 4c. This morphology is somewhat similar to that obtained from the 'addition-free' electrolyte (cf. Fig. 4a) except that the platelet size is reduced. The preferred orientation was [1 0 1] (Table 1).

Increasing As(V) concentrations in 'addition-free' electrolyte resulted in a change in preferred orientation according to the sequence, [1 1 2] → [1 1 4] → [0 0 2] (Table 1). The deposit morphology obtained for $10\,mg\,l^{-1}$ As(V) is shown in Fig. 4d and consists of a large proportion of flat, rounded platelets oriented at low angles to the aluminium cathode. The addition of As(V) to the 'excess-glue' electrolyte resulted in a glue-type deposit morphology (Fig. 4e), similar to that obtained for As(III) + glue (cf. Fig. 4b). The addition of As(V) to the 'balanced' electrolyte resulted in the zinc deposit morphology shown in Fig. 4f. It consists of poorly-defined platelets which may be indicative of zinc resolution. However, the preferred orientation is [1 0 1] (Table 1) and this suggests that the platelets are oriented at intermediate angles to the aluminium cathode.

3.3. *Polarization effects*

A typical cyclic voltammogram obtained for addition-free, purified industrial acid sulphate electrolyte is shown in Fig. 5. A cycle starting from point A (−0.95 V versus SCE) goes through a region of low current until point B where zinc

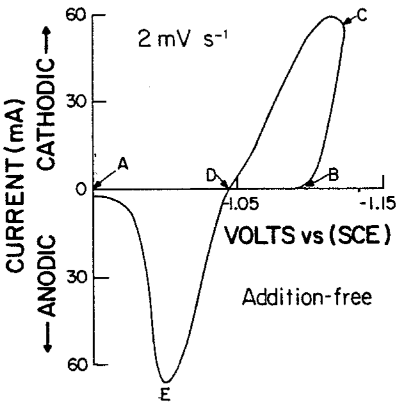

Fig. 5. Characteristic cyclic voltammogram obtained from addition-free industrial acid zinc sulphate electrolyte.

deposition commences. The current increases to point C where the scan is reversed. The current then decreases and reaches zero at point D where it becomes anodic corresponding to the dissolution of deposited zinc. The anodic peak is reached at E and dissolution is complete on return to A.

The region BCD is called a nucleation hysteresis loop and is characterized by several important features. The current for the initial deposition of zinc (point B) does not become appreciable until well beyond the zinc reversible potential. The point B has been used to define a 'nucleation overpotential', B–D. However, as noted by Biegler [23], the position of B can be defined only loosely as it appears to shift with the sensitivity at which the current is recorded and with the sweep rate. The position of B also shifts when certain impurities and/or organics are added to the electrolyte. For example, relative to the addition-free electrolyte, the point B occurs at a less negative potential when antimony is present in the electrolyte, but becomes more negative for glue-containing electrolytes [2, 3].

The current on the descending branch of the loop (CD) is higher than on the ascending branch because, at a given potential, there are more and larger zinc nuclei available while the charge-transfer rate constant is the same. The cathodic overpotential in this region is associated essentially with zinc deposition onto freshly deposited zinc and has been termed 'plating overpotential'. The plating overpotential has been found to be sensitive to the presence of certain organic additives in both lead and copper electrorefining [24]. The descending branch crosses the zero current axis at point D, the crossover potential [2], at or close to the reversible potential of the system.

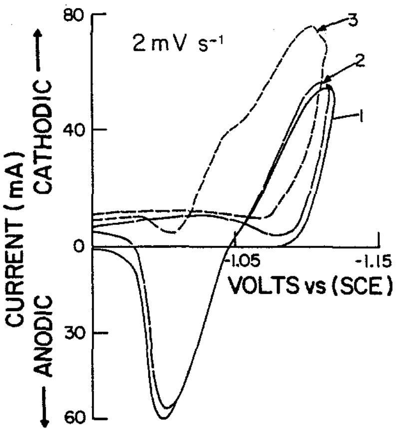

Fig. 6. Cyclic voltammogram showing the effects of As(III) and As(V) on zinc deposition polarization. 1, Addition-free; 2, $50\,\mathrm{mg\,l^{-1}}$ As(III); 3, $9\,\mathrm{mg\,l^{-1}}$ As(V).

The cyclic voltammograms obtained from electrolytes containing $50\,\mathrm{mg\,l^{-1}}$ As(III) and $9\,\mathrm{mg\,l^{-1}}$ As(V) are compared to that obtained from an 'addition-free' electrolyte (Fig. 6). The presence of $50\,\mathrm{mg\,l^{-1}}$ As(III) in the electrolyte results in a significant cathodic current prior to the zinc decomposition potential; however, the remainder of the voltammogram is similar to the 'addition-free' case, except that following the anodic dissolution of zinc, the current again becomes cathodic.

The initial stage of the voltammogram obtained in the presence of $9\,\mathrm{mg\,l^{-1}}$ As(V) is similar to that for As(III). As(V), however, causes a significant decrease in the zinc decomposition potential. Also, the reverse scan is characterized by a plateau region; there is no anodic current and the crossover potential is shifted to less negative values. The absence of an anodic current indicates that all the previously deposited zinc has dissolved while the current was cathodic. Thus, during the reverse scan, the plateau region and beyond is probably due to H_2 evolution (vigorous gassing occurs in this region) with concomitant zinc dissolution as the corresponding anodic half-reaction.

The main difference between the As(III) and As(V) voltammograms is shown more clearly in Fig. 7 in which only the descending cathodic branches ('CD' position of the curves) are shown as a function of increasing As(III) and As(V) concentrations. As indicated in Fig. 7a, increasing the As(III) concentration to $50\,\mathrm{mg\,l^{-1}}$ has no significant effect on the 'CD' portion of the voltammogram, i.e. on the zinc plating overpotential. Increasing the As(V) concentration (Fig. 7b), on the other hand, has a significant effect on both the shape and position of the 'CD' curves relative to that for an electrolyte containing no added arsenic. Thus, it appears that the plating overpotential [24] for zinc deposition is sensitive to As(V) but not to As(III). Analysis of selected zinc deposits indicates that both As(III)

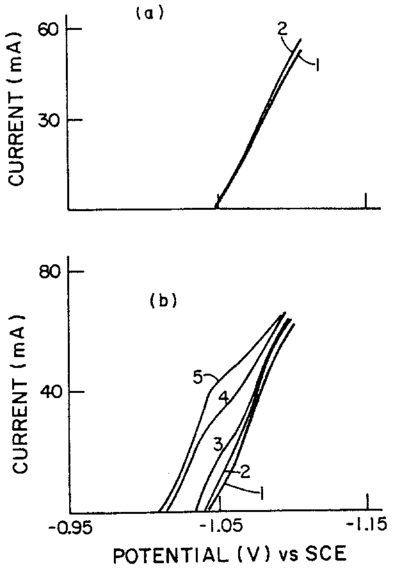

Fig. 7. The 'CD' portions of cyclic voltammograms showing the effect of (a) As(III) concentration and (b) As(V) concentration on the plating overpotential for zinc deposition from 'addition-free' electrolyte. (a) Concentrations of As(III): 1, 0 mg l^{-1}; 2, 50 mg l^{-1}. (b) Concentrations of As(V): 1, 0 mg l^{-1}; 2, 1 mg l^{-1}; 3, 6 mg l^{-1}; 4, 9 mg l^{-1}; 5, 12 mg l^{-1}.

and As(V) co-deposit with zinc (Table 2). However, the nature of the co-deposited arsenic may be different, i.e. As(V) may form an intermetallic zinc compound, for example Zn_3As_2, which may have a significantly lower hydrogen overvoltage than metallic arsenic. Because of the low As(V) concentrations employed, however, such intermetallic compounds were not directly observed in this study.

As discussed earlier, the presence of arsenic in 'balanced' electrolyte was more detrimental to zinc deposition current efficiency than equivalent concentrations of arsenic in 'addition-free' electrolyte. Cyclic voltammograms obtained for 'balanced' electrolyte containing As(III) and As(V) also indicate that arsenic interactions with glue + antimony are detrimental to zinc electrowinning. The results are illustrated in Fig. 8 which shows the effect of increasing concentrations of As(III) and As(V) on the 'CD' portion of the cyclic voltammograms.

Table 2. Arsenic content of selected zinc deposits

As(III) (*mg l^{-1}*)	*As(V)* (*mg l^{-1}*)	*Glue* (*mg l^{-1}*)	*Antimony* (*mg l^{-1}*)	*Arsenic (total)* (*p.p.m.*)
50	0	0	0	10
40	0	30	0	10
20	0	30	0.08	20
0	10	30	0.08	< 6

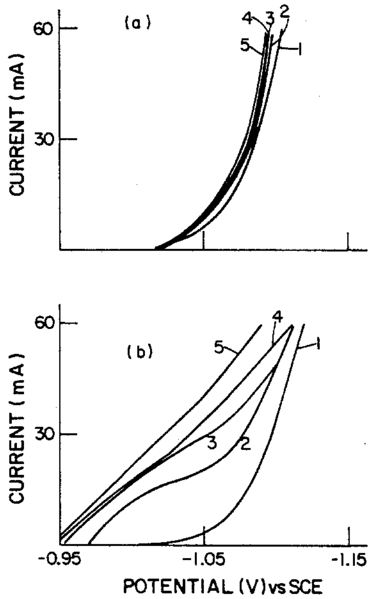

Fig. 8. The 'CD' portion of cyclic voltammograms showing the effect of (a) As(III) concentration and (b) As(V) concentration on the plating overpotential for zinc deposition from 'balanced' electrolyte. (a) Concentrations of As(III): 1, 0 mg l^{-1}; 2, 5 mg l^{-1}; 3, 10 mg l^{-1}; 4, 15 mg l^{-1}; 5, 20 mg l^{-1}. (b) Concentrations of As(V): 1, 0 mg l^{-1}; 2, 5 mg l^{-1}; 3, 10 mg l^{-1}; 4, 15 mg l^{-1}; 5, 20 mg l^{-1}.

As indicated by Fig. 8a, increasing concentrations of As(III) have only a slight effect on the CD portion of the voltammogram. Compared to the 'addition-free' electrolyte (cf. Fig. 7a), however, the curves are shifted to less negative potentials and this may account for the decrease in current efficiency observed for the presence of increasing As(III) in the 'balanced' electrolyte. Similar curves are shown in Fig. 8b for increasing As(V) concentrations in the 'balanced' electrolyte. The effect of As(V) on the 'CD' portion of the voltammograms is more pronounced than that observed for the 'addition-free' electrolyte (cf. Fig. 7b).

4. Conclusions

The effects of As(III) and As(V), with and without glue and glue + antimony additions, on the current efficiency and polarization behaviour of zinc deposition and on the morphology and orientation of zinc deposits electrowon from industrial acid sulphate electrolyte have been determined. Whereas As(III) has virtually no effect on any aspect of zinc electrowinning, the presence of small concentrations of As(V) ($\geqslant 5\,\mathrm{mg\,l^{-1}}$) proved to be very detrimental. As(V) produced changes in the morphology and orientation of the 1-h zinc deposits and also caused a dramatic decrease in zinc deposition current efficiency and significant changes in the zinc deposition cyclic voltammograms. The presence of either glue or glue + antimony in the electrolyte further aggravated the effect of As(V). These additives also produced negative interactions with As(III) although the effects were much less pronounced.

Acknowledgements

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