# The effect of thiourea on zinc electrowinning from industrial acid sulphate electrolyte

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The effect of thiourea, with and without glue and antimony additions, on the current efficiency (CE) and polarization behaviour of zinc deposition and on the morphology and preferred orientation of the zinc deposits electrowon (at $430 \, A \, m^{-2}$ and $35° C$) from industrial acid sulphate electrolyte ($55 \, g \, l^{-1}$ Zn and $150 \, g \, l^{-1}$ $H_2SO_4$) has been determined. Increasing concentrations of thiourea in the electrolyte decreased the CE for zinc deposition; the additional presence of antimony did not significantly alter the decrease in CE but the presence of glue resulted in a further substantial decrease in CE. Thiourea changed the zinc deposit morphology and orientation, and also altered the shape of the zinc deposition cyclic voltammogram.

## 1. Introduction

Canadian zinc ores contain potentially recoverable quantities of silver, but much of this is lost either in tailings during milling or in silver-bearing zinc plant residues which cannot at present be fed to lead or copper smelters for recovery. Methods to recover the silver from these zinc residues include flotation techniques and leaching with thiourea solutions. Although data on the thiourea leaching of silver-bearing zinc residues have not been published, considerable work on the thiourea leaching of other silver-containing materials has been issued [1].

Successful application of thiourea leaching to silver-bearing zinc residues may result eventually in the presence of thiourea in the electrolyte feed to the zinc electrowinning plant. The effects of thiourea on zinc electrowinning are not known. Thiourea, however, is one of the more common additions used for electro-refining copper in acid sulphate electrolyte. The addition of a small amount of thiourea, in some cases even a fraction of a $mg \, l^{-1}$, can have a substantial influence on the polarization behaviour and the resulting copper deposit structure [2].

The present study was undertaken to obtain some basic information on the effect of thiourea on the zinc deposition current efficiency and polarization behaviour as well as on the morphology and orientation of zinc deposits electrowon from industrial acid sulphate electrolyte. In acidic solutions, thiourea is reported [3] to undergo a slow decomposition to $H_2S$ and cyanamide ($NH_2CN$) which in turn hydrolyses to urea (($NH_2)_2CO$). Consequently, the effects of cyanamide and urea on the zinc electrowinning process were also examined.

## 2. Experimental details

### 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 $55 \, g \, l^{-1}$ Zn and $150 \, g \, l^{-1}$ $H_2SO_4$. Thiourea, cyanamide, urea and glue additions were made as aliquots from their respective stock solutions. Antimony was added as a potassium antimony tartrate solution.

The electrolysis cell consisted of a 1-l beaker fitted with a Lucite cover which had slots cut in it to mount the electrodes [4]. A three electrode assemblage consisting of a central aluminium cathode and two platinum anodes was used. The anodes were spaced 7.6 cm apart. The cathode was fashioned from 4.7 mm thick Al sheet (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 0.3 mm thick Pt sheet and measured 17.9 × 109.7 mm. The platinum anodes were used to avoid Pb contamination of the zinc deposits from conventional Pb-Ag anodes [5].

### 2.2. Electrolysis

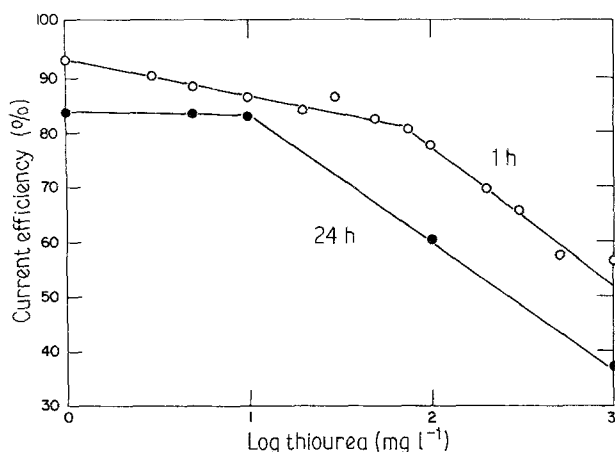The electrolysis experiments were run in a constant temperature bath at 35° C with stirring, and at a cath-

Fig. 1. The effect of increasing thiourea concentration on the CE for 1 and 24-h zinc deposits electrowon at $430\,A\,m^{-2}$ from industrial acid sulphate electrolyte.

ode current density of $430\,A\,m^{-2}$ for a period of 1 h. Additional tests of 24 h duration were run under selected experimental conditions to determine the long term effect of thiourea on zinc electrowinning. For the 24-h tests, the cell electrolyte composition was maintained by continuously adding zinc electrolyte containing the appropriate additives. At the end of the electrolysis period, the cathode was removed from the cell, the zinc deposits were stripped, washed, dried and accurately weighed. The current efficiency for zinc deposition was calculated from the weight of the deposits.

### 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. The samples were scanned over the eight most intense lines for zinc. The peak heights for each line were compared to the corresponding ASTM values for zinc dust. Any departure from these values indicates the type and degree of preferred orientation of the specimens.

### 2.4. Cyclic voltammetry

Cyclic voltammograms were obtained using a PAR model 175 voltage scan generator, a PAR model 173 potentiostat and a Hewlett-Packard model 7004B X-Y recorder for recording current versus applied potential. The voltage scan generator was used to cycle the potential from $-0.85$ to $-1.1\,V$ versus a saturated calomel electrode. The scan was done at a rate of $2\,mV\,sec^{-1}$ to approximate steady state conditions.

## 3. Results and discussion

### 3.1. Current efficiency

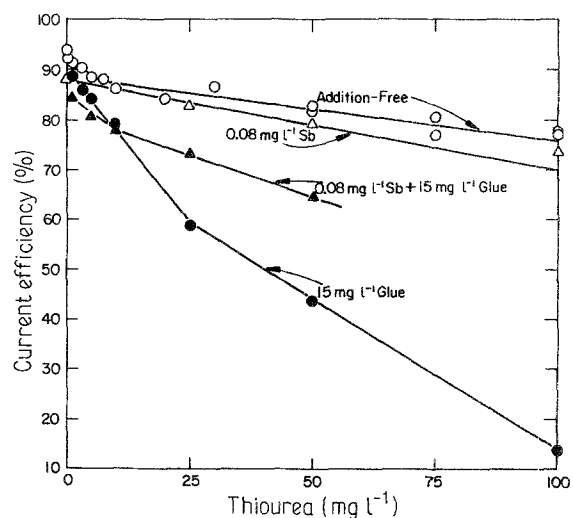The effect of thiourea ($tu$) on the CE (for zinc deposition) for 1 and 24-h zinc deposits electrowon at



Fig. 2. The effect of increasing thiourea concentration on the CE for 1-h zinc deposits electrowon at $430\,A\,m^{-2}$ from industrial acid sulphate electrolyte in the presence and absence of glue, antimony, and glue + antimony.

$430\,A\,m^{-2}$ from industrial acid sulphate electrolyte is shown in Fig. 1. For the 1-h deposits, the CE decreased from 93% at $0\,mg\,l^{-1}$ $tu$ to $\sim 78\%$ at $100\,mg\,l^{-1}$ $tu$. For $tu > 100\,mg\,l^{-1}$, the CE for zinc deposition continues to decrease, becoming $\sim 55\%$ at $1000\,mg\,l^{-1}$ $tu$. For the 24-h deposits, the initial CE was 84% and remained constant for $tu < 10\,mg\,l^{-1}$; at $tu > 10\,mg\,l^{-1}$, the CE decreased rapidly reaching a low value of 37% at $1000\,mg\,l^{-1}$ $tu$. The decrease in zinc deposition CE with increasing $tu$ concentration, in the electrolyte indicates that the rate of hydrogen evolution is increased under these experimental conditions.

Both glue and glue-antimony are added to zinc electrolyte to counteract the effect of impurities [4, 6]. The effect of these additives in combination with increasing concentrations of $tu$ on the CE for the 1-h zinc deposits is compared to the effect of $tu$ alone in Fig. 2. Increasing $tu$ concentration in an electrolyte containing $15\,mg\,l^{-1}$ glue $+ 0.08\,mg\,l^{-1}$ Sb gives an effect between that observed for the glue-containing and Sb-containing electrolytes. The combined presence of glue and $tu$ is very detrimental to zinc electrowinning whereas the presence of Sb counteracts the adverse effect of glue to some extent.

### 3.2. Deposit morphology and orientation

The effect of $tu$ on the morphology of the 1-h zinc deposits electrowon at $430\,A\,m^{-2}$ from industrial acid sulphate electrolyte is shown in the series of SEM photomicrographs, Fig. 3. The zinc deposit morphology obtained in the absence of $tu$ is characterized by hexagonal platelets aligned at intermediate angles to the aluminium cathode, Fig. 3(a); the preferred orientation is $\{112\}$ $\{114\}$ $\{102\}$, Table 1.

For $tu = 10\,mg\,l^{-1}$, the zinc deposit morphology consists of pyramidal-like stacks of hexagonal platelets which are oriented at angles of $0$–$90°$ to one another, Fig. 3(b). This morphology type is charac-
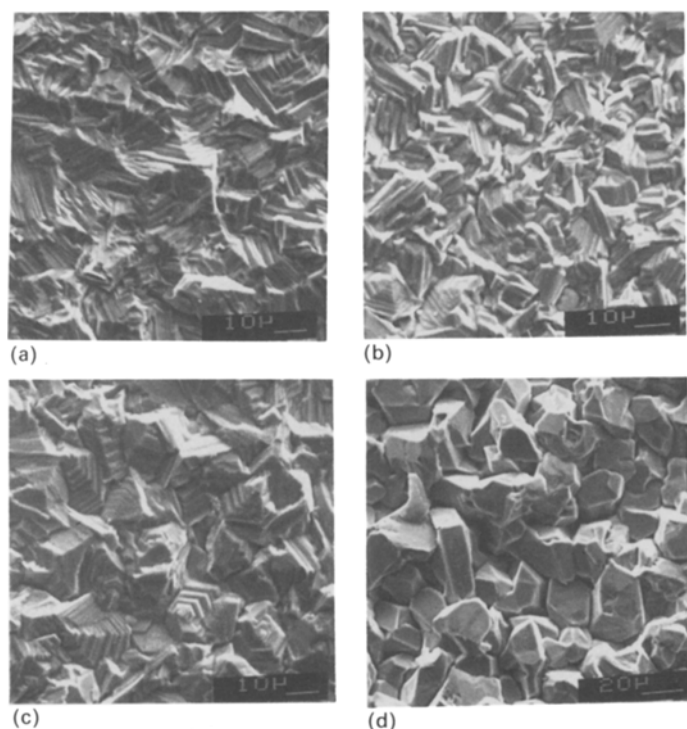
Fig. 3. SEM photomicrographs showing the effect of thiourea on the morphology of 1-h zinc deposits electrowon at 430 A m$^{-2}$ from industrial acid sulphate electrolyte. (a) Addition-free; (b) 10 mg l$^{-1}$ tu; (c) 200 mg l$^{-1}$ tu; (d) 1000 mg l$^{-1}$ tu.

terized by extremes in orientations, Table 1, including {110} (zinc platelets perpendicular to the Al cathode) and {002} (zinc platelets parallel to the Al cathode). This morphology type with its mixture of orientations persists for tu concentrations to 200 mg l$^{-1}$, Fig. 3(c) and Table 1. At 1000 mg l$^{-1}$ tu, the morphology no longer consists of distinct stacks of hexagonal platelets, but rather large blocky crystals indicative of Zn re-solution, Fig. 3(d). The preferred orientation in this case is {002}, Table 1.

The zinc deposit morphology obtained from electrolyte containing tu in various combinations with glue and Sb is shown in Fig. 4. The morphology shown in Fig. 4(a), 50 mg l$^{-1}$ tu + 15 mg l$^{-1}$ glue, is typical of that found for all the tu-glue combinations

Table 1. The effect of thiourea and its interaction with glue and antimony on the preferred orientation of 1-h zinc deposits electrowon from industrial acid sulphate electrolyte

| Thiourea (mg l$^{-1}$) | Glue (mg l$^{-1}$) | Sb (mg l$^{-1}$) | Orientation[1] |
|---|---|---|---|
| 0 | 0 | 0 | {112}{114}{102} |
| 5 | 0 | 0 | {112}{114}{110} |
| 10 | 0 | 0 | {110}{102}{114}{105}{002} |
| 50 | 0 | 0 | {114}{110}{102}{103} |
| 75 | 0 | 0 | {110}{103}{102}{114} |
| 100 | 0 | 0 | {110}{102}{114}{112}{105}{002} |
| 200 | 0 | 0 | {110}{103}{105}{002}{114} |
| 1000 | 0 | 0 | {002} |
| 25 | 15 | 0 | {112}{101}{102} |
| 50 | 15 | 0 | {101} |
| 50 | 0 | 0.08 | {112}{101}{114} |
| 100 | 0 | 0.04 | {112}{101}{114} |
| 100 | 0 | 0.08 | {112}{101}{114} |
| 50 | 15 | 0.08 | {101} |

[1] Relative to ASTM standard for zinc powder.
Electrolysis conditions: 55 g l$^{-1}$ Zn; 150 g l$^{-1}$ H$_2$SO$_4$; 35° C; 430 A m$^{-2}$.

examined. The preferred orientation, Table 1, is {101}, and this is typical of electrolytes containing glue. The surface morphology, Fig. 4(a), however, is not that usually observed for glue-containing electrolytes [4]. In this case it consists of nodular clusters of grain-refined, poorly defined zinc platelets growing out of relief on the surface. This surface shows evidence of zinc re-solution in agreement with the low CE, 44%, obtained under these experimental conditions; zinc resolution is usually a result of the co-evolution of hydrogen.

The combined presence of tu and Sb in the electrolyte results in a zinc deposit morphology, Fig. 4(b), which is very similar to that obtained from addition-free electrolyte, cf. Fig. 3(a). The preferred orientation consists of {112}, {101}, {114}, Table 1, and this indicates that the presence of Sb removes the perpendicular orientations (i.e., {110}) which are significant for electrolytes containing tu alone.

The combined presence of glue and Sb in an electrolyte containing tu results in the deposit morphology shown in Fig. 4(c). The preferred orientation is {101}, Table 1, and the morphology is very similar to that obtained for the glue + tu case, Fig. 4(a). The presence of Sb, however, raised the CE from 44.0 to 64.7%; cf., Fig. 2.

### 3.3. Polarization effects

The cyclic voltammograms obtained for addition-free, purified industrial acid sulphate electrolyte, in the presence and absence of various concentrations of tu, are shown in Fig. 5. A cycle starting point A (−0.85 V vs SCE) goes through a region of low current until point B where zinc deposition commences. The current increases to point C where the scan is reversed. The current then decreases, reaches zero at point D where it becomes anodic corresponding to the dissolu-
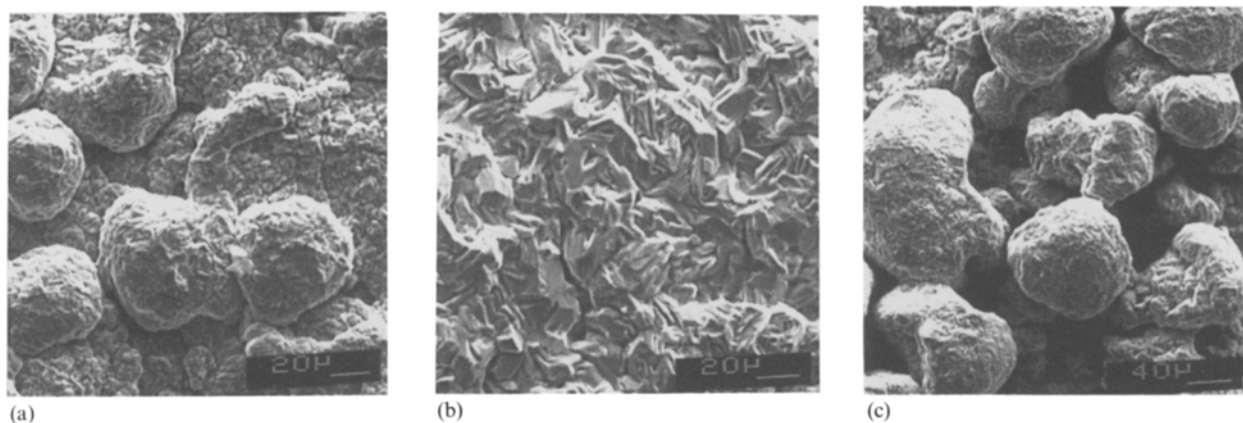
(a)    (b)    (c)

Fig. 4. SEM photomicrographs showing the effect of various combinations of *tu*, glue and Sb on the morphology of 1-h zinc deposits electrowon at 430 A m$^{-2}$ from industrial acid sulphate electrolyte. (a) 50 mg l$^{-1}$ *tu*; 15 mg l$^{-1}$ glue; (b) 50 mg l$^{-1}$ *tu*; 0.08 mg l$^{-1}$ Sb; (c) 50 mg l$^{-1}$ *tu*; 15 mg l$^{-1}$ glue; 0.08 mg l$^{-1}$ Sb.

tion of the 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. As noted by Biegler [7], however, 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. It can be seen from Fig. 5 that the position of B also is sensitive to the *tu* concentration in the electrolyte. Under otherwise similar experimental conditions, point B occurs at a less negative potential with increasing *tu* concentration.

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 whereas the charge-transfer rate constant is the same. The cathodic overpotential in this region is associated essentially with the zinc deposition onto freshly deposited zinc and has been termed 'plating overpotential' [8]. It appears Fig. 5, that the
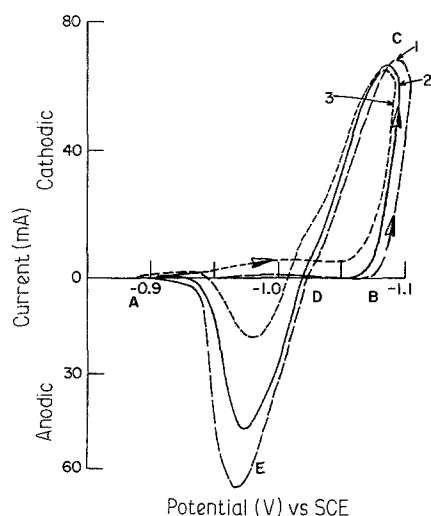
plating overpotential also is sensitive to the presence of *tu* in the electrolyte.

The descending branch crosses the zero current axis at point D, the crossover potential, at or close to the reversible potential of the system. The crossover potential also becomes less negative with increasing *tu* concentration in the electrolyte, Fig. 5.

The anodic portion of the cyclic voltammogram, DEA, likewise is affected by the presence of *tu* in the electrolyte. The loop, DEA, Fig. 5, is considerably reduced with increasing *tu* concentration, indicating either that extensive zinc re-solution has occurred prior to the current becoming anodic or that a significant part of the cathodic current (BCD) is due to hydrogen evolution.

The presence of 75 mg l$^{-1}$ *tu* in the electrolyte resulted in a significant cathodic current (AB section of the voltammogram) prior to the zinc decomposition potential, Fig. 5. This current may be a result of increased H$_2$ evolution on the aluminium cathode prior to zinc decomposition. As indicated by the cyclic galvanograms, Fig. 6, increasing concentrations of *tu* in the electrolyte depolarize the H$_2$ evolution reaction on the aluminium cathode. The increase in H$_2$ evolution prior to Zn deposition may have an effect on the nucleation of Zn and hence the zinc deposit morphology.

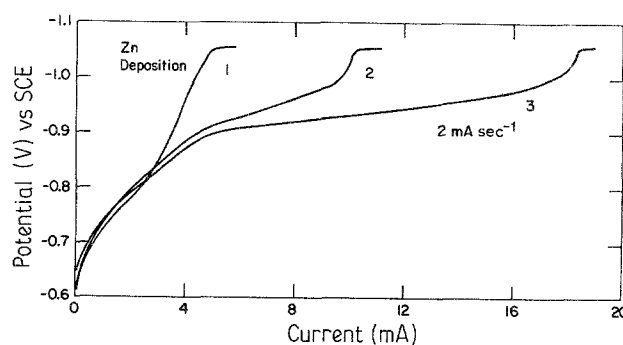The cyclic voltammograms obtained for an electrolyte containing *tu* with and without Sb and glue



Fig. 5. Cyclic voltammograms showing the effect of thiourea on zinc deposition polarization. (1) No addition; (2) 10 mg l$^{-1}$ *tu*; (3) 75 mg l$^{-1}$ *tu*.



Fig. 6. Cyclic galvanograms showing the effect of thiourea on zinc deposition polarization. (1) No addition; (2) 10 mg l$^{-1}$ *tu*; (3) 20 mg l$^{-1}$ *tu*.
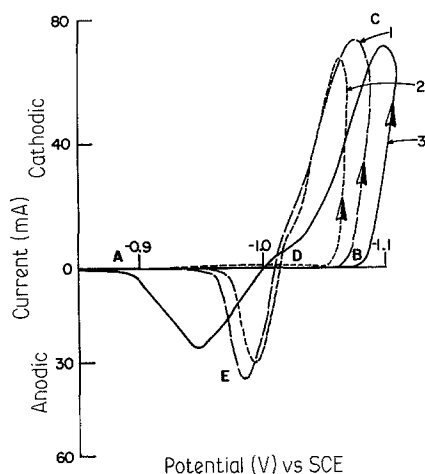
Fig. 7. Cyclic voltammograms showing the effect of thiourea in the presence of antimony, and glue + antimony on zinc deposition polarization. (1) $50\,mg\,l^{-1}$ $tu$; (2) $50\,mg\,l^{-1}$ $tu$ + $0.08\,mg\,l^{-1}$ Sb; (3) $50\,mg\,l^{-1}$ $tu$ + $0.08\,mg\,l^{-1}$ Sb + $15\,mg\,l^{-1}$ glue.

addition, are shown in Fig. 7. The voltammogram obtained for an electrolyte containing $50\,mg\,l^{-1}$ $tu$, curve 1, Fig. 7, is similar to that for an electrolyte containing $10\,mg\,l^{-1}$ $tu$; $cf$. Fig. 5. The combination of $50\,mg\,l^{-1}$ $tu$ + $0.08\,mg\,l^{-1}$ Sb resulted in voltammogram 2, Fig. 7. It can be seen that, relative to curve 1, the presence of $0.08\,mg\,l^{-1}$ Sb shifts point B to a less negative potential and point D to a more negative potential. Thus, Sb depolarizes the Zn deposition reaction in the presence of $tu$ and this may account for the change in deposit morphology, Fig. 4(b), and in preferred orientation, Table 1.

The combination of $50\,mg\,l^{-1}$ $tu$ + $0.08\,mg\,l^{-1}$ Sb + $15\,mg\,l^{-1}$ glue, curve 3, Fig. 7, shifts point B to a more negative potential and point D to a less negative potential relative to curve 1. Thus glue completely counteracts the effect of Sb and results in the morphology type shown in Figs 4(a) and (c) and a preferred {101} orientation, Table 1.

### 3.4. Effect of cyanamide and urea

Increasing concentrations of cyanamide in the range $0$–$100\,mg\,l^{-1}$ in the electrolyte resulted in only a slight decrease in the CE. The morphology of the zinc deposits electrowon from electrolytes containing cyanamide was very similar to the addition-free morphology; however, at $100\,mg\,l^{-1}$ cyanamide, the preferred orientation had a significant {110} compo-

nent. Increasing concentrations of urea ($0$–$100\,mg\,l^{-1}$) had no effect on either the CE or the zinc deposit morphology.

### 4. Conclusions

The effect of thiourea, with and without glue, antimony and glue + antimony additions, on the current efficiency and polarization behaviour of zinc deposition and on the morphology and orientation of the zinc deposits electrowon from industrial acid sulphate electrolyte has been determined. Increasing concentrations of thiourea in the electrolyte decreased the current efficiency for zinc deposition; the decrease in CE was more pronounced for the 24-h zinc deposits. The additional presence of antimony did not significantly alter the decrease in CE but the presence of glue resulted in a further substantial decrease in CE. Thiourea changed the zinc deposit morphology and orientation and also altered zinc deposition polarization. Possible thiourea decomposition products, e.g. cyanamide and urea, had no significant effect on the CE or on morphology of the 1-h zinc deposits.

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