

# *Zinc deposit structures obtained from high purity synthetic and industrial acid sulphate electrolytes with and without antimony and glue additions*

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A characteristic morphology and crystal orientation; namely (112) (114) (102), has been obtained for zinc deposits electrowon from high purity synthetic and industrial acid sulphate electrolytes. These deposit characteristics persisted over a wide range of experimental conditions which included variations in the applied current density and changes in the anode materials and cathode pretreatments. The addition of either antimony or glue to the electrolyte produced deposit morphologies and orientations which were distinctly different from those obtained for addition-free electrolytes. When both antimony and glue additions were made to the electrolyte, however, the deposit morphologies and crystal orientations were similar to those obtained from addition-free solutions. The various deposit morphologies and orientations obtained were shown to correlate with changes occurring in the zinc deposition overvoltage.

## 1. Introduction

The presence of impurities in zinc electrolyte is a major problem for the electrolytic zinc industry, and over the years there have been several investigations [1-4] to determine the maximum level of impurities which can be tolerated during zinc electrowinning. Although the impurities can be reduced to very low concentrations by a rigorous purification of the neutral leach solution, this does not necessarily reduce them to a harmless level in the electrowinning process owing to the synergistic effects among various impurities [5].

Some impurities exhibit an induction period before they become detrimental to the zinc electrowinning process [6]. These impurities then cause redissolution of the deposited zinc and decrease the current efficiency. Because redissolution starts in pits formed in the deposit [6], a possible means of extending the induction period to obtain better current efficiencies for longer times is to maintain a smooth, level deposit free from dendrites or pores. One method of improving the physical character of the deposit is to add organic reagents such as glue to the electrolyte.

These organic reagents tend to produce a smooth level deposit, possibly by depositing in clusters on points of high current density, thereby reducing the amount of current at these points.

There appears to be a relationship between the zinc deposit structure and current efficiency, and this suggests that proper control of crystal growth could yield high current efficiencies (> 90%) and longer plating cycles. Although the effects of impurities and addition agents on current efficiency are well established [2, 6-8], their effects on zinc deposit morphology, orientation and smoothness have only recently begun to receive some attention. These studies have been facilitated by the development of the scanning electron microscope (SEM) which has provided a suitable means for characterizing the often rough deposit surfaces [9].

Sato has recently carried out a study of the crystal growth of electrodeposited zinc from acidic zinc sulphate electrolytes with and without organic colloids [10]. His work consisted of an electron-diffraction study of the preferred orientations of zinc deposits and included electron micrographs of the deposit topography. The micro-

graphs revealed flat, well-developed, plate-like crystals. Sato found that, in the absence of organic colloids, the (114) orientation was invariably obtained except for cases where the  $\text{H}_2\text{SO}_4/\text{Zn}$  ratio was high; e.g. 5 or 10. In such cases the (101) orientation was obtained. In the presence of increasing amounts of organic colloids (glue, gelatin, dextrin, starch) the preferred orientation was found to follow the sequence: (114)→(101)→(112)→(110). He interpreted his results by assuming that the development of crystallographic planes is influenced by the absorption of hydrogen and/or organic colloids.

Cole has studied the surface morphology and orientation of zinc deposits obtained from pure, addition-free synthetic electrolytes containing  $65 \text{ g l}^{-1} \text{ Zn}^{2+}$  and  $200 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$  [11]. He observed that temperature and current density variations influenced the orientation and current efficiency (CE) in a systematic manner. Hexagonal platelets grew preferentially with the basal plane aligned parallel to the substrate at high temperature and current density (CE = 95%); they were perpendicular to the substrate at low temperature and high current density (CE = 74%), and were inclined to substrate at intermediate temperatures and current densities (CE = 93%). Furthermore, a minimum current density was observed at each temperature below which a deposit could not be obtained without its completely redissolving within a few hours. This minimum current density was  $108 \text{ A m}^{-2}$  at  $20^\circ \text{ C}$ ,  $215 \text{ A m}^{-2}$  at  $30^\circ \text{ C}$  and  $861 \text{ A m}^{-2}$  at  $50^\circ \text{ C}$ .

Fukubayashi has recently studied the effects of various impurities and additives on the morphology and orientation of electrodeposited zinc [12]. He observed that increasing concentrations of most cationic impurities tend to produce (002) preferred orientations whereas organic additives polarized the electrode to a greater extent than inorganic additives and shifted the orientations to (101), in agreement with Sato's observation [10]. He also observed that the deposit morphology was characteristic of the type and concentration of the impurity present in the electrolyte. Thus it was possible to determine approximately the impurities active in the electrolyte by examining the deposits using the SEM. Fukubayashi [12] showed that the induction time [6] could be determined as a function of the impurity concentration and

that it was inversely proportional to the impurity concentration and temperature. Furthermore, the deposit morphology had an important influence on the induction time since rough, irregular or pitted deposits presented conditions much more conducive to the initiation of zinc redissolution.

Robinson and O'Keefe have recently shown that correlations of SEM observations with current efficiency results can provide an insight into what constitutes the desirable deposit structure characteristics [13]. The basis for their work was the fact that at the zinc plant of Cominco Ltd at Trail, B.C.,  $15\text{--}30 \text{ mg l}^{-1}$  of animal glue and  $0.04\text{--}0.08 \text{ mg l}^{-1}$  of antimony are added to the purified electrolyte to obtain an empirically determined maximum metal recovery [14]. Robinson and O'Keefe found that the current efficiency was maximized for antimony–glue combinations of  $0.04 \text{ mg l}^{-1} \text{ Sb} + 15 \text{ mg l}^{-1}$  glue and  $0.08 \text{ mg l}^{-1} \text{ Sb} + 30 \text{ mg l}^{-1}$  glue and that a characteristic zinc deposit morphology resulted for these conditions. They also observed characteristic zinc deposit morphologies for addition-free, antimony-addition and glue-addition electrolytes.

Zinc deposits obtained from addition-free electrolytes were characterized by large hexagonal platelets which grew at random angles to the aluminium substrate. The preferred orientations were (101) (102) (103). Glue additions ( $50 \text{ mg l}^{-1}$ ) caused a decrease in the zinc platelet size and the platelets were oriented at  $90^\circ$  angles to the substrate. The observed orientation was (110). Antimony additions ( $0.04 \text{ mg l}^{-1}$ ) also resulted in a decrease in zinc platelet size but, in this case, the platelets were aligned parallel to the substrate. The preferred orientation was (002). Combinations of antimony and glue in solution gave platelets with intermediate angles.

There is some indication that the results obtained by Robinson and O'Keefe [13] may have been influenced by lead contamination\* of the zinc deposit; certainly the morphology of their addition-free deposits suggests this to be the case.

\* During the course of the present work it has been observed that the zinc deposit morphology and orientation are extremely sensitive to lead levels as low as  $1 \text{ mg l}^{-1}$  in the electrolyte. The conventional Pb–Ag anodes used by Robinson and O'Keefe are a possible source of lead in the electrolyte. The effects of lead contamination of zinc on the morphology and orientation of zinc deposits will be discussed in detail in the next paper in this series.

Thus, the object of the present study, done in collaboration with Cominco Ltd, was to determine under conditions similar to those employed in commercial zinc electrowinning operations, the characteristic structures for zinc deposits containing less than 15 ppm lead, which consistently yielded smooth deposits and high current efficiencies ( $> 90\%$ ).

## 2. Experimental

### 2.1. Materials and apparatus

The electrolyte was prepared from hot-zinc-dust purified neutral zinc electrolyte obtained from Cominco Ltd. It had the following average analysis: Zn 150, Mg 38, Mn  $1.6 \text{ g l}^{-1}$  (respectively), Cd 0.3, Sb 0.02, Co 0.3, Ge 0.01, Ni 0.1, Cu 0.1, Fe 0.9, Pb 0.2, Cl 80, F  $3 \text{ mg l}^{-1}$  (respectively). Cell solutions were prepared by adding  $\text{H}_2\text{SO}_4$ , water and the desired addition agents to neutral electrolyte to give concentrations of  $55 \text{ g l}^{-1}$  zinc and  $150 \text{ g l}^{-1}$   $\text{H}_2\text{SO}_4$ . Additional tests were done using synthetic electrolyte [11, 12] containing  $65 \text{ g l}^{-1}$  zinc and  $200 \text{ g l}^{-1}$   $\text{H}_2\text{SO}_4$  to verify certain trends.

The synthetic electrolyte was prepared by dissolving stoichiometric amounts of lead-free photoconductive zinc oxide in ultrapure sulphuric acid according to the procedure outlined by Cole [11].

The electrolysis cell consisted of a 1 l beaker fitted with a 0.95 cm thick lucite cover which was used to hold and space the electrodes. The lucite cover was 12.7 cm in diameter with two  $3.8 \times 0.64$  cm slots cut exactly 7.6 cm apart to accommodate the anodes. Centred between the anode slots was a third  $3.8 \times 1.9$  cm slot into which was fitted a T-shaped plug containing the cathode. This design enabled the cathode plus deposit to be conveniently removed from the cell after the desired time without disturbing the anodes or the cell cover.

Pt anodes were used in order to avoid lead contamination of the zinc deposits. The anodes were cut from 0.01 cm thick Pt sheet and they measured  $15.2 \times 2.5$  cm. Conditioned 0.75 wt.% Ag-Pb anodes [15] and graphite anodes were used in some tests to verify certain trends.

The cathodes which measured  $15.2 \times 3.2 \times 0.32$  cm thick were fabricated from commercial purity Al sheet (99.6%) obtained from Cominco

and were mounted in the cell so that the total deposit area was  $10.2 \text{ cm}^2$ . In some cases, certain cathodes were treated to increase the Al grain size while others were soaked in the electrolyte for various time periods in order to examine the effects of such cathode conditioning procedures on the zinc deposit morphology.

### 2.2. Electrolysis

Operating conditions of  $807 \text{ A m}^{-2}$  and  $35^\circ \text{ C}$  were used for most of the experiments although additional tests were conducted at 215 and  $430 \text{ A m}^{-2}$ . The principal variables studied were the anode materials (e.g. Pt, Pb-Ag, graphite) cathode conditioning, current density, electrolyte type and composition, antimony concentrations ( $0-0.10 \text{ mg l}^{-1}$ ) added as potassium antimony tartrate solution and glue concentration ( $0-50 \text{ mg l}^{-1}$ ) added as a water solution to the electrolyte. Unless otherwise specified, the duration of electrolysis was 1 h.

### 2.3. Deposit examination

Sections of the deposits were examined by X-ray diffraction (XRD) to determine their preferred orientation relative to the ASTM standard for zinc powder and by scanning electron microscope (SEM) to determine their surface morphology.

### 2.4. Cyclic voltammetry

Cyclic voltammetry experiments were conducted to determine the polarization characteristics of zinc deposition in the presence of antimony and glue. The same electrolysis cell and electrolyte composition used in obtaining the one hour zinc deposits were employed to obtain the voltammograms. A Wenking model VSG72 voltage scan generator was used to drive a Wenking Potentiostat model 70HP10, and the cyclic voltammograms were recorded with a Brinkmann model 2551 X-Y recorder. A sweep rate of  $1 \text{ mV s}^{-1}$  was found to give consistent results. The cycle was started at  $-0.9 \text{ V}$  versus SCE with the upper cathodic potential limit set to a value capable of producing a total current of about 50 mA. At this point the potential was reversed and driven anodically to the point of zero net current flow. Thus only the cathodic portion of the voltammogram was recorded.

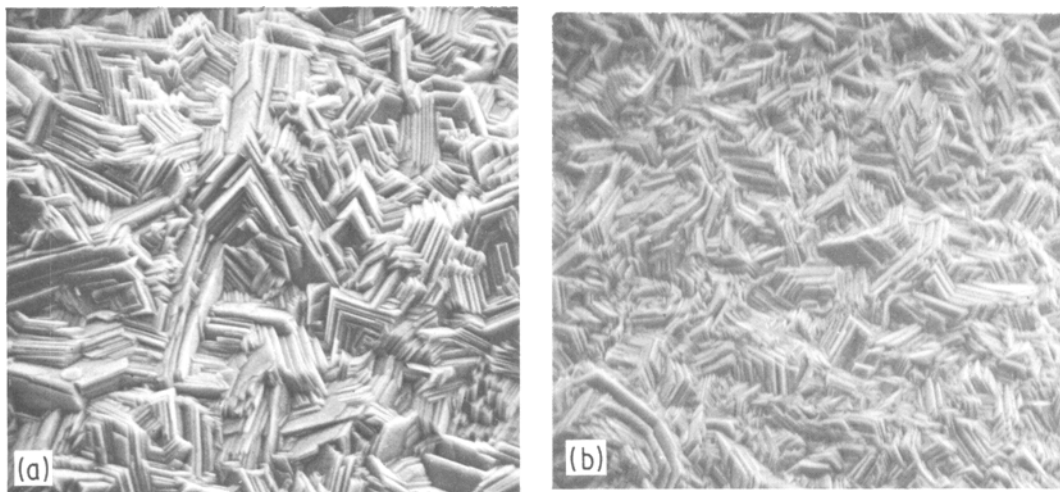


Fig. 1. SEM photomicrographs (X 1400) showing the preferred zinc deposit morphology (see Table 1 for conditions). (a) Addition-free electrolyte; (b) balanced Sb-glue addition electrolyte.

### 3. Results and discussion

#### 3.1. The characteristic zinc deposit structure

**3.1.1. Addition-free acid sulphate electrolyte.** The SEM photomicrograph in Fig. 1(a) shows the typical morphology of zinc deposits obtained under a variety of experimental conditions using addition-free acid sulphate electrolyte; these conditions are summarized in Table 1. Because this morphology was consistently obtained for a range of current densities, including those normally used in zinc electrowinning plants, and with various anode materials (i.e., Pt, graphite, conditioned Ag–Pb) which would not significantly contaminate zinc with lead, we have termed it a characteristic or

Table 1. Zinc deposit morphology, Fig. 1— Experimental conditions

Current density (A m <sup>-2</sup> )	Additives (mg l <sup>-1</sup> )		Anodes
	Sb	Glue	
215, 430, 807	0.00	0	Pt, Pb–Ag* graphite†
215, 430, 807	0.04	15	Pt, Pb–Ag*
215, 430, 807	0.08	30	Pt, Pb–Ag*

Electrolysis conditions: 55 g l<sup>-1</sup> Zn<sup>2+</sup>; 150 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; 35° C; commercial Al cathode.

\* Conditioned anodes [15].

† The graphite anodes were 'bagged' to prevent contamination of the zinc deposit by carbon. See [11] p. 72 for the effects of carbon on zinc deposit morphology.

preferred zinc deposit morphology. The essential feature to note here is that this characteristic morphology is very similar to that obtained by Robinson and O'Keefe [13] for their balanced antimony-glue additions, but different from their addition-free deposit morphology. Our work with Pb–Ag anodes has shown that unless extreme care is taken to condition properly\* these anodes, zinc deposit morphologies similar to those obtained for the addition-free deposit of Robinson and O'Keefe [13] result because of lead contamination of the deposit [16].

The crystallographic orientations for this characteristic type zinc deposit morphology which were obtained for a variety of experimental conditions, are listed in Table 2. The various peak intensities are presented as ratios to the ASTM standard values for zinc powder. As indicated by the results in Table 2, the deposit orientation is generally highly preferred (112) (114) (102).

#### 3.1.2. Balanced additions of antimony and glue.

Balanced additions of antimony and glue; e.g. 0.04 mg l<sup>-1</sup> Sb + 15 mg l<sup>-1</sup> glue (see Robinson and O'Keefe [13]) to the electrolyte produced the deposit morphology type shown in the SEM photomicrograph Fig. 1(b) for the experimental conditions summarized in Table 1. This morphology type is very similar to that obtained for depos-

\* The anode conditioning procedure is that presently used by Cominco as outlined by Farmer [15].

Table 2. Zinc deposit crystallographic orientations

Electrolyte type	Additives (mg l <sup>-1</sup> )		Anodes	Surface orientation (ratio to ASTM standard)*							
	Sb	Glue		(002)	(101)	(102)	(103)	(100)	(110)	(112)	(114)
Cominco	0.00	0	Pt	0.04	1.0	1.9	0.9	0.13	0.24	1.9	1.5
Cominco	0.04	15	Pt	0.04	1.0	1.4	1.4	0.05	0.6	2.8	0.9
Synthetic	0.00	0	Pt	0.04	1.0	1.9	1.5	0.2	0.5	2.0	2.2
Synthetic†	0.00	0	Pt	0.06	1.0	1.9	1.4	0.3	0.5	3.0	3.5
Cominco	0.00	0	Pb-Ag‡	0.04	1.0	0.8	0.6	0.13	0.5	1.2	0.4
Cominco	0.04	15	Pb-Ag‡	0.04	1.0	1.7	1.0	0.05	0.14	13.0	3.3

Electrolysis conditions: 55 g l<sup>-1</sup> Zn<sup>2+</sup>; 150 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; 35° C.; 807 A cm<sup>-2</sup>; Commercial Al cathode.

\* (002)50; (101)100; (102)28; (103)25; (100)40; (110)21; (112)23; (114)11.

† 65 g l<sup>-1</sup> Zn; 200 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

‡ Conditioned anodes [15].

its from the addition-free electrolyte [compare with Fig. 1(a)] except for a refined platelet size. The crystallographic orientations for this type of zinc deposit morphology are listed in Table 2. The deposit orientation is generally highly preferred (112) (114) (102) as it was for the addition-free electrolyte. Thus, the balanced antimony-glue additions, which were shown to optimize the current efficiency for zinc deposition [13], also produce essentially the same characteristic zinc deposit morphology as the addition-free electrolyte.

In addition to the conditions listed in Table 1, other factors such as the grain size of the aluminium cathode and various cathode conditioning procedures (e.g. soaking the cathode in the cell electrolyte for various times prior to depositing the zinc) had no significant effect on either the morphology or the orientation of the 1 h deposits. These procedures will be considered in more detail in the paper dealing with Pb effects [16].

### 3.2. Antimony, glue effects

The effects of various antimony and glue concentrations on the morphology and orientation of the preferred zinc deposit structure were determined using Pt anodes to avoid the possibility of lead contamination.

The effect of 0.04 and 0.08 mg l<sup>-1</sup> antimony on the zinc deposit morphology is shown in the

SEM photomicrographs (Figs. 2(a) and (b), respectively). At 0.04 mg l<sup>-1</sup> antimony, the deposit appears to be more compact and of finer grain size than the deposits from addition-free electrolytes. This morphology type is characterized by a significant increase in the (112) and (103) preferred orientations. The effect of increasing amounts of antimony on the crystallographic orientation of the zinc deposits is summarized in Table 3.

At higher antimony concentrations, e.g. 0.08 and 0.10 mg l<sup>-1</sup>, the zinc deposit is seen to consist of large, rounded platelets [Fig. 2(b)] having a preferred (103), (002) orientation (Table 3). The trend to increased (002) preferred orientation and flat platelets with increasing antimony concentrations is in agreement with the results obtained by Fukubayashi [12] under similar experimental conditions.

Glue additions resulted in a pronounced (101) preferred zinc orientation even at the 7.5 mg l<sup>-1</sup> level as indicated in Table 3. Fukubayashi [12] reported (101) oriented zinc deposits for the addition of 10 mg l<sup>-1</sup> animal glue to the electrolyte. The degree of (101) preferred orientation increased as the glue concentration was increased to 50 mg l<sup>-1</sup>. Figs. 3(a) and (b) show the zinc deposit morphology obtained when the electrolyte contained 15 and 50 mg l<sup>-1</sup> glue, respectively. With glue in the electrolyte the resulting deposit had a smooth surface and the deposit grain size generally decreased with an increase in the amount of additive.

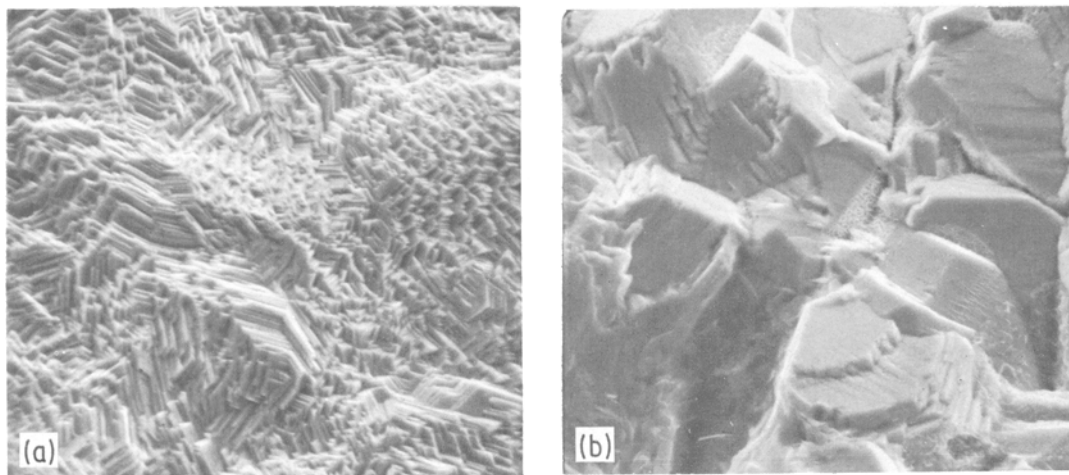


Fig. 2. SEM photomicrographs (X 1400) showing the effect of antimony additions on the preferred zinc deposit morphology. (a)  $0.04 \text{ mg l}^{-1} \text{ Sb}$ ; (b)  $0.08 \text{ mg l}^{-1} \text{ Sb}$ .

### 3.3. Polarization studies

The cathodic portions of the cyclic voltammograms obtained for zinc deposition in the presence of antimony and glue are compared to the corresponding curve for the addition-free electrolyte in Fig. 4. The point on the voltammograms during the increase in cathodic potential at which the current begins to flow is the decomposition potential; whereas, the point at which the current becomes zero after the reversal in potential is the cross-over potential [17]. The difference between the cross-over and decomposition potentials is a

measure of the activation overpotential for zinc deposition on to an aluminium substrate. It can be seen from Fig. 4 that the cross-over potential is essentially the same for each voltammogram whereas the decomposition potential varies depending on the type of addition made to the electrolyte.

As indicated by Fig. 4, the addition of  $0.04 \text{ mg l}^{-1}$  antimony depolarizes the electrodeposition reaction (compare curves A and B), whereas the addition of  $30 \text{ mg l}^{-1}$  glue results in a significant polarization of the reaction (compare curves A and C). The combined addition of  $0.04 \text{ mg l}^{-1}$  antimony and  $30 \text{ mg l}^{-1}$  glue results in curve D,

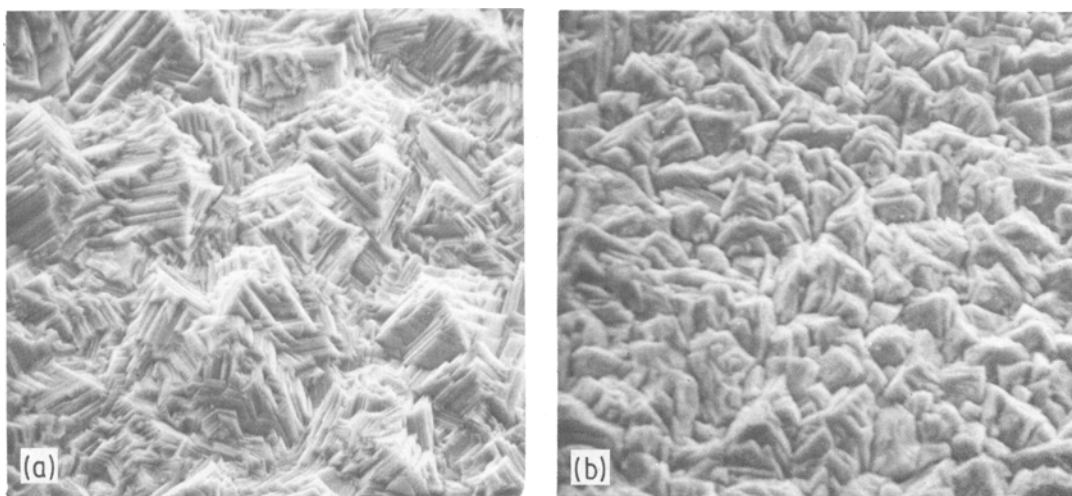


Fig. 3. SEM photomicrographs (X 1400) showing the effect of glue additions on the preferred zinc deposit morphology. (a)  $15 \text{ mg l}^{-1}$  glue; (b)  $50 \text{ mg l}^{-1}$  glue.

Table 3. Zinc deposit crystallographic orientations

Electrolyte type	Additives ( $\text{mg l}^{-1}$ )		Anodes	Surface orientation (ratio to ASTM standard)*							
	Sb	Glue		(002)	(101)	(102)	(103)	(100)	(110)	(112)	(114)
Cominco	0.02	0	Pt	—	1.0	3.8	8.2	—	2.7	13.3	1.7
Cominco	0.04	0	Pt	0.3	1.0	2.0	2.8	0.08	0.90	7.9	1.4
Cominco	0.06	0	Pt	0.3	1.0	1.0	1.1	0.08	0.70	2.8	0.2
Cominco	0.08	0	Pt	0.8	1.0	1.2	1.3	0.05	0.43	1.0	1.0
Cominco	0.10	0	Pt	1.3	1.0	1.0	1.2	0.10	0.29	0.5	0.7
Cominco	0.00	7.5	Pt	0.06	1.0	0.5	0.48	0.15	0.30	0.57	0.36
Cominco	0.00	15	Pt	0.06	1.0	0.6	0.4	0.15	0.28	0.7	0.5
Cominco	0.00	30	Pt	0.03	1.0	0.28	0.2	0.03	0.07	0.3	0.2
Cominco	0.00	50	Pt	—	1.0	0.1	—	0.05	0.10	0.09	—

Electrolysis conditions:  $55 \text{ g l}^{-1} \text{ Zn}^{2+}$ ;  $150 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$ ;  $35^\circ \text{ C}$ .;  $807 \text{ A m}^{-2}$ ; Commercial Al cathode.

\* (002)50; (101)100; (102)28; (103)25; (100)40; (110)21; (112)23; (114)11.

which lies very close to curve A, the addition-free curve. It will be recalled that the deposit structure obtained from addition-free electrolyte and from electrolytes containing balanced antimony-glue additions were very similar. The overvoltages for zinc deposition estimated from the voltammograms in Fig. 4 are listed in Table 4.

The results obtained from the above polarization studies suggest a correlation between the observed zinc deposit morphologies (orientation) and the deposition overvoltage. The morphology obtained with additives or impurities such as anti-

mony which depolarize the reaction (lower the overvoltage) is characterized by large crystal facets which appear to have a slight preferred orientation parallel to the aluminium substrate compared with that for pure addition-free zinc electrolytes. Antimony can depolarize the reaction by interfering with the adsorption of hydrogen ions on the various zinc crystal planes. Metals such as arsenic, germanium and antimony which are capable of forming volatile hydrides, can do so by combining with hydrogen ions in the double layer [2] and thus provide an alternate path for hydro-

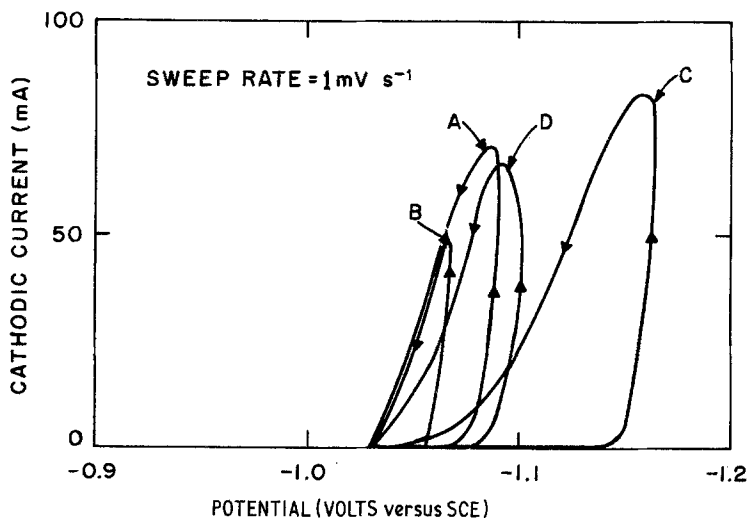


Fig. 4. Cyclic voltammograms for acidified zinc sulphate electrolyte ( $55 \text{ g l}^{-1} \text{ Zn}^{2+}$ ,  $150 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$ ). (A) addition-free; (B)  $0.04 \text{ mg l}^{-1} \text{ Sb}$ ; (C)  $30 \text{ mg l}^{-1} \text{ glue}$ ; and (D)  $0.04 \text{ mg l}^{-1} \text{ Sb} + 30 \text{ mg l}^{-1} \text{ glue}$ .

Table 4. Zinc deposition overvoltage and deposit orientations

Voltammogram (see Fig. 4)	Additives (mg l <sup>-1</sup> )		Orientation	Overvoltage (mV)
	Sb	Glue		
A	0.00	0	(112) (114) (102)	44
B	0.04	00	(103) (002)	26
C	0.00	30	(101)	144
D	0.04	30	(112) (114) (102)	54

Electrolysis conditions: 55 g l<sup>-1</sup> Zn<sup>2+</sup>; 150 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; 35° C.

gen evolution. Since it is likely that hydrogen ion adsorption occurs to a different extent on different zinc crystal planes, any additive or impurity that interferes with hydrogen ion adsorption could also modify the deposit orientation. Also, the fact that depolarization causes a decrease in nucleation accounts for the increase in size of the zinc platelets observed with the addition of antimony to the electrolyte.

The zinc deposit morphology obtained when glue was added to the electrolyte was characterized by a strong preference for (101) orientations. The substantial increase in overvoltage (Table 4) observed for glue additions may result from the zinc having to deposit through a glue adsorption layer [18]. The preferred (101) orientation may result from the glue increasing the overvoltage on preferentially selected planes [10]. The increased polarization observed in the presence of glue leads to increased nucleation resulting in a substantial decrease in zinc facet size.

The balanced antimony-glue additions resulted in an overvoltage and deposit morphology very similar to those obtained for the addition-free electrolyte. This suggests that the opposing influences of antimony and glue on the overpotential tend to counteract one another, resulting in an overvoltage which is indicative of the preferred morphology. The proper combinations of antimony and glue which give rise to the preferred morphology have also been shown to optimize the current efficiency for zinc deposition under similar conditions [13].

The relationships between zinc deposit preferred orientation, electrolyte additions such as antimony and glue, and the overpotentials associated with zinc deposition can be summarized as follows:

Excess Antimony (002) ← (103) ← (112)(114)(102) → (101) → (110)  
 Addition-free or Sb + glue      Excess glue

decreasing overpotential increasing  
 ←-----→

#### 4. Conclusions

Zinc deposits having a characteristic morphology and preferred orientation, (112) (114) (102), have been obtained on a consistent basis from high purity synthetic zinc electrolyte, from addition-free electrolyte prepared from Cominco purified neutral zinc electrolyte, and from zinc electrolyte containing balanced additions of antimony and glue. These deposits were obtained from laboratory studies using zinc electrowinning conditions similar to those practised by Cominco Ltd, Trail, B.C.

Variations in current density (215, 430, 807 A m<sup>-2</sup>), anode material (Pt, graphite, conditioned Pb-Ag) and cathode pretreatment produced no significant changes in the deposit characteristics.

The addition of either antimony or glue to the electrolyte produced deposit morphologies and orientations which were strikingly different from those for the addition-free or balanced Sb/glue addition electrolyte. These changes in deposit characteristics were related to the changes in zinc deposition overvoltage which also occurred when these additives were present in the electrolyte. Addition-free and balanced antimony-glue addition electrolytes had similar zinc deposition overvoltages which occurred between those for high-antimony or high-glue electrolytes.

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J. M. Stewart and E. J. Murray, Canmet, did the X-ray diffraction measurements.

## References

- [1] F. Laist, F. F. Frick, J. O. Elton and R. B. Caples, *Trans. AIME*, **64** (1921) 699.
- [2] U. F. Turonshina and V. V. Stender, *J. Appl. Chem. (U.S.S.R.)* **28** (1955) 151, 347, 447.
- [3] D. P. Zosimovich and N. F. Bogatova, *Zhur. priklad. Khim.* **33** (1959) 1324.
- [4] C. L. Mantell, "Electrochemical Engineering", McGraw-Hill Book Co., Inc., New York (1960) pp. 210-4.
- [5] G. T. Wever, *J. Metals*, Feb. (1959) 130.
- [6] M. Maja and P. Spinelli, *J. Electrochem. Soc.* **118** (1971) 1538.
- [7] A. D'Este and R. Guerriero, *Montvecchio* **16** (1965) 1.
- [8] R. C. Kerby and T. R. Ingraham, Research Report R243, Dept. of Energy, Mines and Resources, Ottawa, Canada, April (1971) pp. 35.
- [9] H. Fukubayashi, H. Kenworthy, L. W. Higley and T. J. O'Keefe, 'Some Surface Variations Resulting From Additives In The Electrowinning of Zinc', Proc. Second Annual Scanning Electron Microscope Symposium, IIT Research Institute, Chicago, April (1969) pp. 285-94.
- [10] R. Sato, *J. Electrochem. Soc.* **106** (1959) 206.
- [11] E. R. Cole, Jr., Ph.D. Thesis, University of Missouri-Rolla (1970) 144.
- [12] H. Fukubayashi, Ph.D. Thesis, University of Missouri-Rolla (1972) 63. See also, H. Fukubayashi, T. J. O'Keefe and W. C. Clinton, *U.S.B.M. Report Investigations*, **RI 7966** (1974) 26.
- [13] D. J. Robinson and T. J. O'Keefe, *J. Appl. Electrochem.* **6** (1976) 1.
- [14] C. H. G. Bushell, C. J. Krauss and S. C. Liang, 'Effect of Some Trace Impurities On The Zinc Electrowinning Process', Paper presented at CIMM Conference Of Metallurgists, Ottawa, Sept. 1-3, (1965).
- [15] R. Farmer, 'Electrometallurgy', Proc. Extractive Metallurgy Division Symposium on Electrometallurgy, Cleveland, Ohio, Dec. 2-3 (1968) pp. 242-50.
- [16] D. J. MacKinnon and J. M. Brannen (in preparation).
- [17] B. A. Lamping and T. J. O'Keefe, *Metallurgical Transactions*, **7B** (1976) 551.
- [18] B. N. Kabanov, 'Electrochemistry of Metals and Adsorption', Freund Publishing House, Holon, Israel (1969), pp. 43, 66-77.