# The effect of cadmium on zinc deposit structures obtained from high purity industrial acid sulphate electrolyte

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The effect of cadmium on cathodic zinc crystal growth was studied in high purity industrial electrolyte, with and without additives, in an attempt to establish a correlation between morphology, polarization and the extent of cadmium contamination. Cadmium additions to acid zinc sulphate electrolyte did not have a significant effect on the zinc deposit orientation but did substantially refine the deposit grain size. The refinement in deposit grain size is directly related to the level of cadmium in the zinc deposits. Cadmium, in combination with glue and optimum amounts of glue and antimony, also reduced the deposit grain size: the preferred deposit orientation remained  $(1\ 1\ 2)$  with a slight tendency to  $(1\ 0\ 1)$  at high glue concentrations. Cadmium in combination with antimony resulted in an increased depolarization of zinc deposition and a basal  $(0\ 0\ 2)$  deposit orientation. Lead additions to zinc electrolyte containing cadmium resulted in increased deposition overpotentials and intermediate to vertical deposit orientations.

## 1. Introduction

Zinc electrocrystallization from acid sulphate electrolyte is affected by a number of process parameters, including the presence of impurities and organic colloids in the electrolyte. Recent fundamental studies on zinc electrolysis [1-5] have shown that there is a definite correlation between zinc deposit morphology and the type and concentration of additives and/or impurities present in the electrolyte. These studies further revealed that the characteristic zinc deposit morphology changes, which result from the presence of impurities and/or additives in the electrolyte, are associated with particular zinc deposition overpotential conditions. Lead and cadmium are both found as impurities in zinc electrolyte and are known to affect adversely zinc electrowinning by contaminating the cathode zinc.

The effect of lead on the electrocrystallization

of zinc was discussed in a previous publication [5]. Zinc deposits contaminated with lead were found to have characteristic morphologies and orientations which were dependent on the amount of lead present in the zinc deposits and to a lesser extent on the presence of other impurities such as antimony and glue in the deposits. Increasing lead in the zinc deposits progressively changes the orientations from  $(1 \ 1 \ 2)$  to  $(1 \ 0 \ 1)$  to  $(1 \ 0 \ 0)$  to, finally, a poorly crystalline  $(0 \ 0 \ 2)$  structure.

A relationship was shown to exist between the effect of lead contamination on zinc deposit morphology and orientation, and on the overpotentials associated with zinc electrodeposition in the presence of lead. Deposition overpotentials increased for conditions which gave increased lead contamination of electrodeposited zinc. Antimony or glue additions to the electrolyte decreased the observed overpotential effects.

The effect of cadmium on the electrocrystal-

lization of zinc has received scant attention. Fukubavashi et al. [6] briefly studied the effect of cadmium on zinc crystallization using synthetic acid sulphate electrolytes containing 65 g  $l^{-1}$  Zn and 200 g  $l^{-1}$  H<sub>2</sub>SO<sub>4</sub>. At 40° C, zinc deposits obtained at 807 A  $m^{-2}$  from electrolytes containing  $2.5-50 \text{ mg l}^{-1}$  Cd showed a preferred (002), (102), (103) orientation. They reported that impurities such as Cd usually gave fine facets with increasing amounts of cadmium; sometimes a pitted or waffled structure was obtained, the degree of waffling being dependent on the amount of cadmium and the electrolysis time. For solutions containing 50 mg  $l^{-1}$  Cd, the presence of Cd was detected in the pitted regions of the zinc deposit by non-dispersive X-ray analysis.

The present work was undertaken to study the effect of cadmium alone and in combination with other impurities and additives on the morphology and orientation of zinc deposits obtained from industrial acid sulphate electrolyte; a further objective was to determine the effect of Cd on the polarization behaviour of zinc deposition.

#### 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 g l<sup>-1</sup>, MgSO<sub>4</sub> 38 g l<sup>-1</sup>, Mn 1.6 g l<sup>-1</sup>, Cd  $0.2 \text{ mg l}^{-1}$ , Sb  $0.02 \text{ mg l}^{-1}$ , Co  $0.3 \text{ mg l}^{-1}$ , Ge  $0.01 \text{ mg } l^{-1}$ , Ni  $0.1 \text{ mg } l^{-1}$ , Cu  $0.1 \text{ mg } l^{-1}$ , Fe 0.9 $mg l^{-1}$ , Pb 0·2  $mg l^{-1}$ , Cl 80  $mg l^{-1}$ , F 3  $mg l^{-1}$ . Cell solutions were prepared by adding H<sub>2</sub>SO<sub>4</sub> and water to neutral electrolyte to give concentrations of 55 g  $l^{-1}$  zinc and 150 g  $l^{-1}$  H<sub>2</sub>SO<sub>4</sub>. Antimony additions were made to the electrolyte as a potassium antimony tartrate solution and animal glue was added as a concentrated solution. Cadmium was added to the electrolyte as a cadmium sulphate solution and lead as a solution of lead acetate. One hour zinc deposits were prepared from zinc electrolytes containing various concentrations of cadmium, antimony, glue and lead. The electrolysis cell and electrode assembly have been described in detail in previous publications [4, 5].

Pt anodes were used in order to avoid lead con-

tamination of the zinc deposits [4, 5]. The anodes were cut from 0.01 cm thick Pt sheet and measured  $15.2 \times 2.5$  cm. 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 cm<sup>2</sup>.

#### 2.2. Electrolysis

Operating conditions of 430 A  $m^{-2}$  and 807 A  $m^{-2}$  and 35° C were used for the tests. Some tests were also done at 215 A  $m^{-2}$  to confirm certain trends.

#### 2.3. Deposit examination

Sections of 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. Selected deposits were also analysed for their cadmium content by atomic absorption spectrophotometry and for their lead content by the Dithiazone method.

#### 2.4. Cyclic voltammetry

The cyclic voltammetry tests for the evaluation of the effect of cadmium in the electrolyte on the overpotential associated with zinc electrodeposition onto aluminum were described in a previous publication [5].

#### 3. Results and discussion

#### 3.1. Characterization of the cadmium effect

3.1.1. 'Addition-free' and 'balanced' electrolytes. Unlike impurities such as antimony and lead [4, 5], cadmium additions to the 'addition-free' acid zinc sulphate electrolyte (i.e. containing no additions of antimony and glue) did not result in significant changes in the zinc deposit orientation but did decrease the zinc platelet size. The effect of cadmium on the morphology of zinc deposits obtained from 'addition-free' electrolyte is shown in Figs. 1a-c inclusive. Fig. 1a shows the morphology of the characteristic zinc deposit structure which has been discussed in detail in a previous



Fig. 1. SEM photomicrographs ( $\times$  770) showing the effect of cadmium on the preferred structure of zinc deposits: (a)–(c) addition-free electrolyte; (d)–(f) balanced electrolyte; 807 A m<sup>-2</sup>. (a) 0 mg l<sup>-1</sup> Cd; (b) 10 mg l<sup>-1</sup> Cd; (c) 50 mg l<sup>-1</sup> Cd; (d) 0 mg l<sup>-1</sup> Cd, 0.04 mg l<sup>-1</sup> Sb, 15 mg l<sup>-1</sup> glue; (e) 10 mg l<sup>-1</sup> Cd, 0.04 mg l<sup>-1</sup> Sb, 15 mg l<sup>-1</sup> glue; (f) 50 mg l<sup>-1</sup> Cd, 0.04 mg l<sup>-1</sup> Sb, 15 mg l<sup>-1</sup> glue.

publication [4]. Figs. 1b and c show the effect of cadmium additions of 10 and 50 mg  $l^{-1}$ , respectively, on the morphology of zinc deposits obtained at 807 A m<sup>-2</sup> current density. It can be seen (Figs. 1a-c), that there is a substantial reduction in the size of the zinc platelets with increasing cadmium concentration in the electrolyte. Variations in the applied current density resulted in a similar trend in zinc deposit morphology with respect to cadmium additions. The addition of 10 and 50 mg  $l^{-1}$  cadmium to a 'balanced' electrolyte (i.e. containing both antimony and glue additions in proportions which give an optimum in levelling properties and current efficiency of zinc deposition) also decreased the size of the zinc platelets (Figs. 1d-f).

The effect of cadmium additions on the crystallographic orientation and cadmium content of zinc deposits obtained from both addition-free and balanced electrolytes at various current densities is summarized in Table 1. The data obtained for the addition-free and balanced electrolytes indicate that the deposit orientation remains essentially unchanged and similar to that noted for the characteristic deposit structures described previously [4]. The cadmium content of the zinc deposits increases with increasing cadmium in the electrolyte and with decreasing current density. Zinc deposits obtained from balanced electrolyte had higher cadmium levels than those obtained from addition-free electrolyte under similar experimental conditions.

3.1.2. 'Excess antimony' and 'excess glue' electrolytes. Cadmium additions to an excess antimony electrolyte (i.e., containing added antimony but no glue) gave a more basal orientation at 430 A  $m^{-2}$  but did not affect the orientation at 807 A  $m^{-2}$  (Table 2). The effect of cadmium additions on the morphology of zinc deposits obtained at 430 A  $m^{-2}$  from excess antimony electrolyte is shown in Figs. 2a-c. The SEM photomicrographs (Figs. 2b and c) show an increase in the growth of flat platelets with rounded edges with increasing cadmium content in the zinc deposits. This type of platelet growth may also be related to increased antimony in the zinc deposits [1, 3] with increasing antimony in solution. At 807 A

Corresponding figure in text	<i>Current density</i> (A m <sup>-2</sup> )	Additives (mg l <sup>-1</sup> )			Court llos on his	Cathode
		Cd	Sb	Glue	orientation <sup>†</sup>	caamium (%)
A. 'Addition-free' electrolyte						
1a	807	0	0.00	0	(112)(102)	0.0003
		5	0.00	0	(112)(101)	0.024
1b		10	0.00	0	(112)(101)	0.050
1c		50	0.00	0	(114) (112)	0.30
	430	0	0.00	0	(112) (102)	_
_		5	0.00	0	(112)(110)	0.025
_		10	0.00	0	(112)(114)	0.092
		50	0.00	0	(112) (114)	0.42
	215	0	0.00	0	(112)(114)	
		5	0.00	0	$(1\ 1\ 2)\ (1\ 0\ 1)$	0.072
-		10	0.00	0	(112)(102)	0.14
		50	0.00	0	(1 1 2) (1 1 4)	0.70
B. 'Balanced' electrolyte						
2d	807	0	0.04	15	(112)(102)	0.029
_		5	0.04	15	(112)	_
2e		10	0.04	15	(112)(114)	0.070
2f		50	0.04	15	(112) (114)	0.40
_	430	0	0.04	15	(112)(102)	-
		5	0.04	15	$(1\ 1\ 2)\ (1\ 0\ 1)$	0.048
_		10	0.04	15	(101)(112)	0.11
_		50	0.04	15	(101)(112)	0.54

Table 1. Crystallographic orientations and cadmium contents of zinc deposits obtained from 'addition-free' and 'balanced' electrolytes\*

\* Electrolysis conditions: 55 g  $l^{-1}$  Zn; 150 g  $l^{-1}$  H<sub>2</sub>SO<sub>4</sub>; 35° C; Pt anodes † Relative to ASTM standard for zinc powder.

 $m^{-2}$  the zinc deposit grain size decreased in a manner similar to that previously observed with addition-free and balanced electrolytes.

The crystallographic orientation and cadmium content zinc deposits obtained from excess antimony electrolyte containing cadmium additions are summarized in Table 2. As indicated by the data in Table 2, all deposits obtained at 430 A  $m^{-2}$  show a predominant (002) orientation in excellent agreement with the morphologies shown in Figs. 2b and c. The deposits obtained at 807 A  $m^{-2}$  have a (114) (112) orientation similar to that observed when no cadmium was present. The cadmium content of the zinc deposits increased with increasing antimony concentration, with increasing cadmium concentration and with decreasing current density.

The addition of cadmium to excess glue elec-

trolyte (i.e., containing added glue but no added antimony) resulted in zinc deposit morphologies which were very similar to those obtained for cadmium additions to addition-free and balanced electrolytes. The SEM photomicrographs, Figs. 2d-f, show the effect of cadmium additions to excess glue electrolyte on the zinc deposit morphology. The main feature of this morphology type is the substantial reduction in the size of the zinc platelets.

The crystallographic orientations and cadmium contents of zinc deposits obtained from excess glue electrolyte containing various amounts of cadmium are also summarized in Table 2. At 430 A  $m^{-2}$ , the cadmium additions resulted in a (112) oriented deposit; generally zinc deposits obtained from excess glue electrolytes are (101) oriented [4]. At 807 A  $m^{-2}$ , the zinc deposits were (101)

Table 2. Crystallographic orientations and cadmium contents of zinc deposits obtained from 'excess antimony' and 'excess glue' electrolytes\*

Corresponding figure in text	<i>Current density</i> (A m <sup>-2</sup> )	Additives (mg l <sup>-1</sup> )				Cathode
		Cd	Sb	Glue	crystallographic orientation <sup>†</sup>	caamium (%)
A. 'Excess antimony' electroly	te					
	807	0	0.04	0	(1 1 2) (1 0 3)	
		10	0.04	0	(114)(112)	0.07
_		50	0.04	0	(114) (112)	0.38
2a	430	0	0.04	0	(1 1 2) (1 0 1)	0.0005
2b		10	0.04	0	(002)(103)	0.12
2c		50	0.04	0	(002)(114)	0.59
_		10	0.08	0	(002)(103)	0.13
		50	0.08	0	(002)(103)	0.69
		10	0.10	0	(002)(105)	0.14
		50	0.10	0	(0 0 2) (1 0 3)	0.88
B. 'Excess glue' electrolyte						
_	807	0	0.00	15	(101)	0.0002
		5	0.00	15	(101)	0.023
_		10	0.00	15	(101)	0.040
_		50	0.00	15	(101)	0.41
-		5	0.00	30	(1 0 1)	0.026
_		10	0.00	30	(101)	0.058
_		50	0.00	30	(101)	0.33
2d	430	0	0.00	15	(101)	0.0018
		5	0.00	15	(112)(102)	0.049
2e		10	0.00	15	(112)	0.11
2f		50	0.00	15	(103)(112)	0.68
_		5	0.00	30	(101)	0.050
		10	0.00	30	(112)(101)	0.082
-		50	0.00	30	(1 1 2) (1 0 1)	0.35

\* Electrolysis conditions: 55g1<sup>-1</sup> Zn; 150g1<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; 35°C; Pt anodes † Relative to ASTM standard for zinc powder.

oriented for all combinations of glue and cadmium used in the tests. This suggests an overriding glue effect at this current density due to lower cadmium levels in the zinc deposits as compared to those obtained at 430 A m<sup>-2</sup> under similar conditions (Table 2). The cadmium content of the zinc deposits increased with decreasing glue concentration, decreasing current density and with increasing cadmium content in the electrolyte.

### 3.2. The effect of lead and cadmium additions

The combined effect of lead and cadmium additions to 'addition-free' electrolyte on the zinc deposit morphology is shown in the series of SEM

photomicrographs in Fig. 3. The presence of Cd in the electrolyte tends to moderate the Pb effect on the zinc deposit morphology to some extent at the lower current density, i.e., at 430 A  $m^{-2}$ , by decreasing zinc platelet size. This is particularly evident in the series of SEM photomicrographs, Figs. 3a-c which show the effect of increasing Cd additions on the morphology of zinc deposits obtained at 430 A m<sup>-2</sup> from an electrolyte containing 3 mg  $l^{-1}$  Pb. However, when the electrolyte contained 9 mg  $l^{-1}$  Pb, the addition of Cd to the  $50 \text{ mg l}^{-1}$  level had less effect on the zinc deposit morphology as indicated by Figs. 3d-f. The distinct triangular morphology obtained under these conditions (Figs. 3d-f) indicates the dominant



Fig. 2. SEM photomicrographs ( $\times$  770) showing the effect of cadmium on zinc deposit structures obtained from excess antimony (a)–(c) and excess glue (d)–(e) electrolytes at 430 A m<sup>-2</sup>. (a) 0 mg l<sup>-1</sup> Cd, 0.04 mg l<sup>-1</sup> Sb; (b) 10 mg l<sup>-1</sup> Cd, 0.04 mg l<sup>-1</sup> Sb; (c) 50 mg l<sup>-1</sup> Cd, 0.04 mg l<sup>-1</sup> Sb; (d) 0 mg l<sup>-1</sup> Cd, 15 mg l<sup>-1</sup> glue; (e) 10 mg l<sup>-1</sup> Cd, 15 mg l<sup>-1</sup> glue; (f) 50 mg l<sup>-1</sup> Cd, 15 mg l<sup>-1</sup> glue.



Fig. 3. SEM photomicrographs ( $\times$  770) showing the combined effect of cadmium and lead on the morphology of zinc deposits obtained from addition-free electrolyte at 430 A m<sup>-2</sup>. (a) 3 mg l<sup>-1</sup> Pb, 0 mg l<sup>-1</sup> Cd; (b) 3 mg l<sup>-1</sup> Pb, 10 mg l<sup>-1</sup> Cd; (c) 3 mg l<sup>-1</sup> Pb, 50 mg l<sup>-1</sup> Cd; (d) 9 mg l<sup>-1</sup> Pb, 0 mg l<sup>-1</sup> Cd; (e) 9 mg l<sup>-1</sup> Pb, 10 mg l<sup>-1</sup> Cd; (f) 9 mg l<sup>-1</sup> Pb, 50 mg l<sup>-1</sup> Cd; (d) 9 mg l<sup>-1</sup> Pb, 0 mg l<sup>-1</sup> Cd; (e) 9 mg l<sup>-1</sup> Pb, 10 mg l<sup>-1</sup> Cd; (f) 9 mg l<sup>-1</sup> Pb, 50 mg l<sup>-1</sup> Cd; (f) 9 mg l<sup>-1</sup> Pb, 50 mg l<sup>-1</sup> Pb,

Corresponding figures in text	<i>Current density</i> (A m <sup>-2</sup> )	Additives (mg 1 <sup>-1</sup> )		Court II an abia	Cathode	
		Pb	Cd	orientation <sup>†</sup>	Pb (%)	Cd (%)
	807	3	0	(101)(100)	0.0164	
		3	10	(101)		
		3	50	(103)(101)		
		9	0	(100)(101)	0.0465	
		9	10	(100)(101)		
		9	50	(101) (102)		
3a	430	3	0	$(1\ 0\ 0)\ (1\ 0\ 1)$	0.0230	0.0007
3b		3	10	(101)	0.0220	0.092
3c		3	50	(103)(102)	0.0220	0.43
3d		9	0	$(1\ 0\ 0)\ (1\ 0\ 1)$	0.1535	_
3e		9	10	(101)(100)	0.0650	0.079
3f		9	50	(101) (102)	0.0520	0.35

Table 3. Crystallographic orientations and cadmium and lead contents of zinc deposits obtained from 'addition-free' electrolyte\*

\* Electrolysis conditions: 55 g  $l^{-1}$  Zn; 150 g  $l^{-1}$  H<sub>2</sub>SO<sub>4</sub>; 35° C; Pt anodes † Relative to ASTM standard for zinc powder.

effect of Pb [5]. Zinc deposits obtained at 807 A  $m^{-2}$  showed this triangular-type morphology for all Pb-Cd combinations studied. The dominance of either the cadmium or lead effects is related to the relative concentrations of these impurities in the zinc deposits (Table 3). For a given level of lead addition, the lead content of the zinc deposit decreased with increasing cadmium addition to the electrolyte.

The crystallographic orientation data for zinc deposits obtained in the presence of Cd and Pb are summarized in Table 3 and are in good agreement with the morphology results presented in Fig. 3. The orientation data indicate that lead in zinc results in more vertical orientations and that cadmium in zinc results in more intermediate orientations. The predominance of either type of orientation depends on the relative concentrations of lead and cadmium in the zinc deposits.

## 3.3. Polarization behaviour resulting from cadmium in zinc electrolyte

The effect of cadmium additions to four types of acid zinc sulphate electrolytes on the activation overpotential for zinc deposition onto aluminium was measured by cyclic voltammetry. The data are listed in Table 4 and illustrated graphically in Fig. 4.

As the data indicate, the addition of cadmium

to 'excess antimony' electrolyte had only a small effect on the activation overpotential for zinc deposition, with the overpotential actually decreasing when 50 mg  $l^{-1}$  Cd was added to the electrolyte. This finding is in good agreement with the basal orientation observed for zinc deposits obtained under these conditions as discussed earlier in this report. It was previously shown [2-5]that zinc deposits having platelets aligned parallel to the aluminium cathode and having predominant (002) orientation occurred from electrolysis carried out under low polarization conditions.

The addition of cadmium to the 'balanced' electrolyte resulted in a slight increase in the activation overpotential for zinc deposition. This small increase in overpotential is in accordance with the observed change in orientation; i.e., from (112) to (101) for deposits obtained under these conditions (see Table 1). As noted in previous publications [4, 5] the trend in deposit orientation as a function of activation overpotential is as follows:

 $(002) \leftarrow (114) \leftarrow (103) \leftarrow (102)(114)(112)$ decreasing overpotential  $\xrightarrow{\longrightarrow (1 \ 0 \ 1) \rightarrow (1 \ 1 \ 0) (1 \ 0 \ 0)}_{\text{increasing}} \xrightarrow{\text{overpotential}}$ 

The presence of cadmium in the 'addition-free' and

Electrolyte	Cd	Pb <sup>†</sup>	Sb	Glue	(mV)
'addition-free'	0	0	0	0	73
	10	0	0	0	86
	50		0	0	73
	50	9	0	0	127
'excess glue'	0	0	0	15	133
U	10	0	0	15	145
	50	0	0	15	145
'excess antimony'	0	0	0.04	0	47
	10	0	0.04	0	49
	50	0	0.04	0	41
'balanced'	0	0	0.04	15	107
	10	õ	0.04	15	112
	50	Ő	0.04	15	112

Table 4. Zinc deposition activation overpotential as measured by cyclic voltammetry\*

\* Electrolysis conditions: 55 g  $l^{-1}$  Zn; 150 g  $l^{-1}$  H<sub>2</sub>SO<sub>4</sub>; 25° C; Pt anodes. † Pb added as lead acetate.





'excess glue' electrolytes resulted in somewhat larger activation overpotentials for zinc deposition at 10 mg l<sup>-1</sup> cadmium, followed by a decrease in activation overpotential at 50 mg l<sup>-1</sup> cadmium. A similar trend was observed in the orientation of the zinc deposits obtained from these solutions, with the orientations becoming slightly more vertical at 10 mg l<sup>-1</sup> Cd and more basal at 50 mg l<sup>-1</sup> Cd.

The combined presence of Pb and Cd in the 'addition-free' electrolyte resulted in a significant increase in activation overpotential for zinc deposition (Table 4). The presence of Pb in 'additionfree' electrolyte was previously reported to increase the zinc deposition overpotential [5]. This increased overpotential indicates a strong lead effect in agreement with the morphology and orientation results presented earlier.

#### 4. Conclusions

The following conclusions were reached:

- (a) Zinc deposits contaminated with cadmium were found to have a characteristic morphology; i.e., a substantial reduction in grain size with increasing cadmium content.
  Only small changes in deposit orientations were observed with increasing cadmium content.
- (b) The amount of cadmium present in the zinc deposits increased with decreasing current density, increasing levels of cadmium or antimony in the electrolyte and decreasing concentration of glue in the electrolyte.
- (c) A relationship was shown to exist between

the activation overpotential of zinc deposition and the observed orientations of the zinc deposits. Increased contamination of zinc deposits by cadmium resulted in lower overpotentials and basal (002) deposit orientations. The presence of lead counteracted these effects to some extent.

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