

# *The effect of lead on zinc deposit structures obtained from high purity synthetic and industrial acid sulphate electrolytes*

D. J. MACKINNON, J. M. BRANNEN

*Metallurgical Chemistry Section, Physical Sciences Laboratory, Mineral Sciences Laboratories, Canada Centre for Mineral and Energy Technology (CANMET), Department of Energy, Mines and Resources, Ottawa, Canada*

R. C. KERBY

*Technical Research Centre, Cominco Ltd, Trail, British Columbia, Canada*

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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 changed the orientations from (1 1 2) to (1 0 1) to (1 0 0) to finally a poorly crystalline (0 0 2) structure. The lead content of the zinc deposits was dependent on both the concentration and chemical composition of lead added to the electrolyte, the current density and also on the presence of antimony or glue in the electrolyte. 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.

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## 1. Introduction

Recent basic studies on zinc electrolysis [1-4] 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. Apart from producing characteristic morphology changes in zinc deposits, the various additives and impurities also affect the polarization curves for zinc deposition in a characteristic manner [2-4]. As a result, it is possible to associate a given deposit morphology with a particular polarization (or overpotential) condition.

The significance of the results obtained in these related studies [1-4] is that a combination of polarization and morphology observations, or possibly either individually, may be used to obtain valuable information on zinc sulphate electrolytes for possible applications to industrial plant practice and control. However, before the full potential of this method can be realized it is necessary

to delineate the effect of lead (Pb) contamination in zinc electrolysis. As long as Pb-Ag anodes continue to be used in zinc electrowinning, the possibility of varying degrees of Pb contamination of the zinc deposits exists, either as a result of improperly conditioned anodes or because the anodes have deteriorated over a period of time. Pb is deposited at the cathode, decreasing the purity of the zinc.

During a previous study [4], it was 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. In fact it was suggested [4] that the different structures obtained by Robinson and O'Keefe [1] for deposits obtained from addition-free and balanced antimony-glue addition electrolytes were probably a result of Pb contamination of their addition-free deposit. In view of this possibility it is desirable to correlate the Pb content with the morphologies of zinc deposits obtained under controlled overpotential

conditions and, thus, obtain a more complete characterization of the system.

With the exception of some results reported by Fukubayashi *et al.* [5], information on the effect of Pb on zinc deposit morphology and orientation is lacking. Previous studies [6–12] reported the effect of Pb on the current efficiency of zinc deposition. These results indicate that Pb either has little effect [6] or else slightly increases the current efficiency of zinc deposition [7–10]. The increase in current efficiency has been attributed to the fact that the hydrogen overpotential on Pb is higher than that on zinc [6–9]. Large concentrations of Pb in the electrolyte result in the incorporation of Pb into the zinc deposit [11, 12].

Fukubayashi *et al.* [5] studied the effects of PbO<sub>2</sub> and PbSO<sub>4</sub> on the morphology and orientation of zinc deposits. Their results suggested that the level of Pb contamination in the zinc deposit was dependent on the chemical phase of Pb present in the electrolyte since the Pb levels were much higher with PbO<sub>2</sub> in the cell than with PbSO<sub>4</sub>. The surface orientation observed for Pb-contaminated zinc deposits was (1 0 2) (1 0 1) for PbSO<sub>4</sub> addition electrolytes and (1 0 3) (1 0 2) (0 0 2) for PbO<sub>2</sub> addition electrolytes. Scanning electron photomicrographs revealed that these Pb-contaminated zinc deposits had a distinctive, triangular morphology which made them easily identifiable.

The present work was undertaken to study the effect of Pb contamination on the morphology and orientation of zinc deposits obtained from acid sulphate electrolytes and to determine the effect of Pb on the polarization behaviour and current efficiency of zinc deposition in relation to any significance it may have with respect to controlling the process using polarization techniques.

## 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 mg l<sup>-1</sup>, Sb 0.02 mg l<sup>-1</sup>, Co 0.3 mg l<sup>-1</sup>, Ge 0.01 mg l<sup>-1</sup>, Ni 0.1 mg l<sup>-1</sup>, Cu 0.1 mg l<sup>-1</sup>, Fe 0.9 mg l<sup>-1</sup>, Pb 0.2 mg l<sup>-1</sup>, Cl 80 mg l<sup>-1</sup>, F 3 mg l<sup>-1</sup>. 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<sup>-1</sup> zinc and 150 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Antimony additions were made to the electrolyte as required as a potassium antimony tartrate solution while animal glue was added as a concentrated solution. Lead was added to the electrolyte either as a lead acetate solution or as a slurry of lead sulphate or lead oxide (PbO). Additional tests were also done using synthetic electrolyte [4] to verify certain trends. One-hour zinc deposits were prepared from zinc electrolytes containing various concentrations of lead, antimony and glue. The electrolysis cell and electrode assembly was described in detail in a previous publication [4]. The anodes were 0.75 wt% Ag–Pb obtained from Cominco and measured 15.2 × 3.8 × 0.64 cm. Pt anodes, cut from 0.01 cm thick Pt sheet and measuring 15.2 × 2.5 cm, were also used in order to avoid lead contamination of the zinc deposits. The cathodes, which measured 15.2 × 3.2 × 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<sup>-2</sup> and 807 A m<sup>-2</sup> and 35°C were used for the tests. Some tests were also done at 215 A m<sup>-2</sup> to confirm certain trends. The effect of lead additions on the current efficiency (CE) for zinc deposition was also studied as a function of temperature (i.e.  $T = 35$  and 45°C).

### 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 microscopy (SEM) to determine their surface morphology. Selected deposits were also analysed for their lead content by the dithiazone method.

### 2.4. Cyclic voltammetry

Cyclic voltammetry tests for the evaluation of the effects of lead in the electrolyte on the over-

potential associated with zinc electrodeposition onto aluminum were done on 500 ml acid zinc solutions ( $55 \text{ g l}^{-1} \text{ Zn}$ ,  $150 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$ ) held at  $25^\circ \text{C}$ . The additives were introduced into the electrolyte as concentrated aqueous solutions five minutes prior to the start of the tests. High purity (99.999%) aluminum mounted in Teflon was used as the cathode substrate. The aluminum cathode was polished with 600 grit paper and washed with acetone and distilled water prior to every test. Platinum foil was used for the anode and a saturated calomel electrode for the reference electrode. The potential was cycled between  $-700 \text{ mV}$  and  $-1400 \text{ mV SCE}$  at a potential sweep rate of  $100 \text{ mV min}^{-1}$ . The cyclic voltammograms were recorded as  $i$  versus  $E$  plots on an  $X-Y$  recorder.

A typical cyclic voltammogram is shown in Fig. 1. The point B, the potential at which the curve DE crosses the zero current line, approximates to the zinc reversible potential for the solution being tested. The potential difference BC corresponds to the activation overpotential required to initiate zinc deposition onto the Al substrate. The point C corresponds to zinc deposition onto the aluminum cathode. The curve CD is the polarization overpotential associated with zinc deposition onto the aluminium substrate. The curve DB corresponds to the polarization overpotential associated with zinc deposition onto freshly deposited zinc. The curve BE represents the anodic dissolution of the previously electrodeposited zinc. The activation overpotential

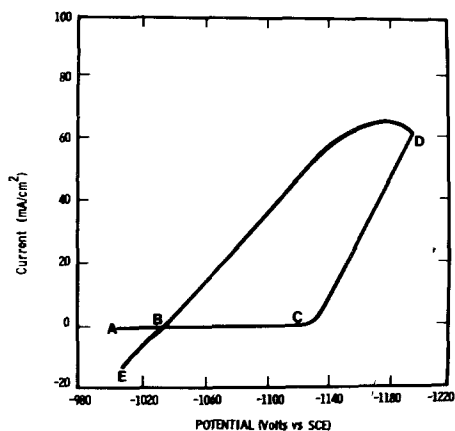


Fig. 1. Cyclic voltammogram for acidified zinc sulphate electrolyte.

required to initiate zinc deposition onto aluminium, i.e. the voltage difference between points B and C, was the measurement used to determine the effect of impurities and organic additives in zinc electrolyte. Point B was taken where line DE crosses the zero current line, while point C was taken at  $0.4 \text{ mA cm}^{-2}$  current density.

### 3. Results and discussion

#### 3.1. Identification of the lead effect

During the previous study [4], when unconditioned Pb-Ag anodes were used, SEM observations indicated that the crystal growth pattern of the zinc deposits was primarily a function of the current density. Also the zinc deposit morphology and orientation were significantly different from those for the characteristic zinc deposit described previously [4]. The series of SEM photomicrographs shown in Fig. 2 represents the general trend in zinc deposit morphology as a function of current density. At current densities  $< 538 \text{ A m}^{-2}$ , the zinc deposits obtained from addition-free Cominco and synthetic electrolytes using unconditioned Pb-Ag anodes were characterized by a poorly-defined, amorphous-type morphology and appeared to be pitted and corroded. Typical low current density structures are shown in Figs. 2a-c. These deposits are characterized by a pronounced (0 0 2) orientation. At current densities  $\geq 583 \text{ A m}^{-2}$ , the zinc deposits were composed of well-defined hexagonal platelets and exhibited a triangular-type morphology, Figs. 2d-f. These high current density deposits are characterized by a pronounced (1 0 1) (1 0 2) preferred orientation.

Fig. 3 shows a plot of the current efficiency as a function of the current density. As indicated by this plot, the CE values below  $430 \text{ A m}^{-2}$  are poor; i.e.,  $< 80\%$ . As the current density is increased beyond  $430 \text{ A m}^{-2}$ , the CE increases linearly from  $85\%$  at  $430 \text{ A m}^{-2}$  to  $98\%$  at  $2152 \text{ A m}^{-2}$ . This trend in the CE as a function of current density essentially follows that observed for the zinc deposit morphology as a function of current density. Thus, at the high current densities, the zinc deposits which consist of well-defined hexagonal platelets, reflect high CE values whereas at the lower current densities, the poorly developed, pitted structures correspond to low CE values.

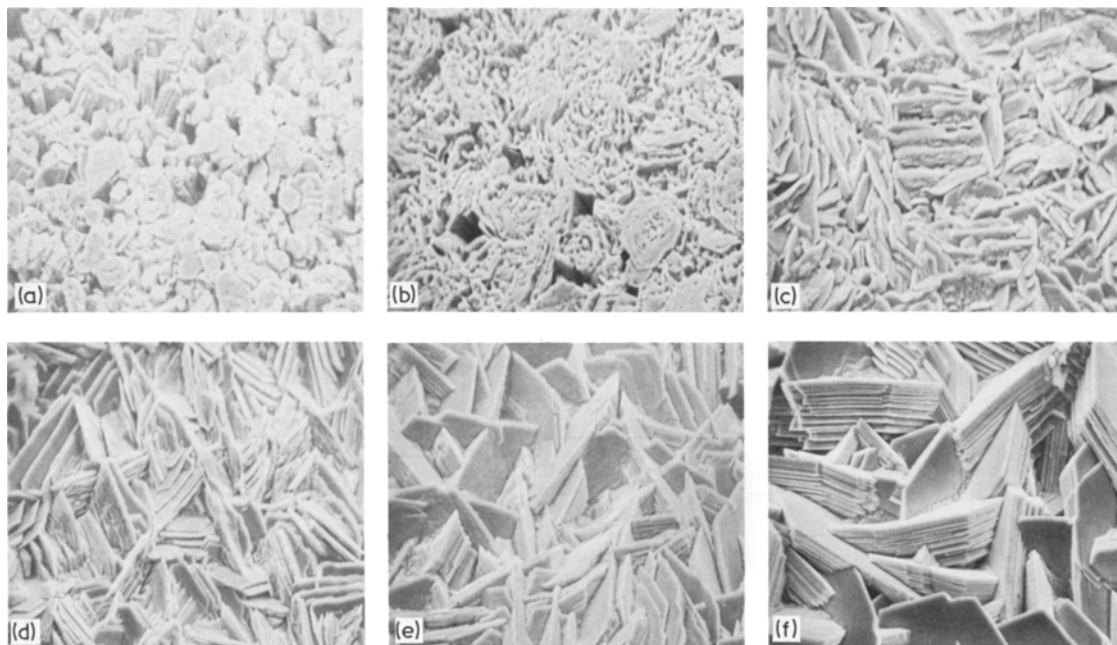


Fig. 2. SEM photomicrographs ( $\times 385$ ) showing the effect of current density on the morphology of zinc deposits from addition-free electrolyte using unconditioned Pb-Ag anodes. (a)  $215 \text{ A m}^{-2}$ , 60 min, 0.125% Pb; (b)  $323 \text{ A m}^{-2}$ , 60 min, 0.076% Pb; (c)  $430 \text{ A m}^{-2}$ , 60 min, 0.04% Pb; (d)  $538 \text{ A m}^{-2}$ , 60 min, 0.021% Pb; (e)  $1076 \text{ A m}^{-2}$ , 30 min, 0.019% Pb; (f)  $2152 \text{ A m}^{-2}$ , 15 min, 0.011% Pb.

The triangular-type morphology exhibited by the high current density zinc deposits (see Figs. 2e and f) compares closely with that obtained under similar experimental conditions by Fukubayashi *et al.* [5] for electrolytes containing lead. This suggested that the deposit morphology and CE trends observed in the present work might be associated with Pb contamination of the zinc deposits which could result from the use of uncon-

ditioned Pb-Ag anodes. Thus, the zinc deposits were analysed for their Pb content and the results are reported in the caption of Fig. 2. These results are also shown in Fig. 3 as a plot of Pb percentage in the zinc deposits versus current density. It can be seen that the Pb content of the zinc deposits increases abruptly as the current density decreases below  $538 \text{ A m}^{-2}$ . The increase in the Pb content of the zinc deposits (Fig. 3) occurs with a corre-

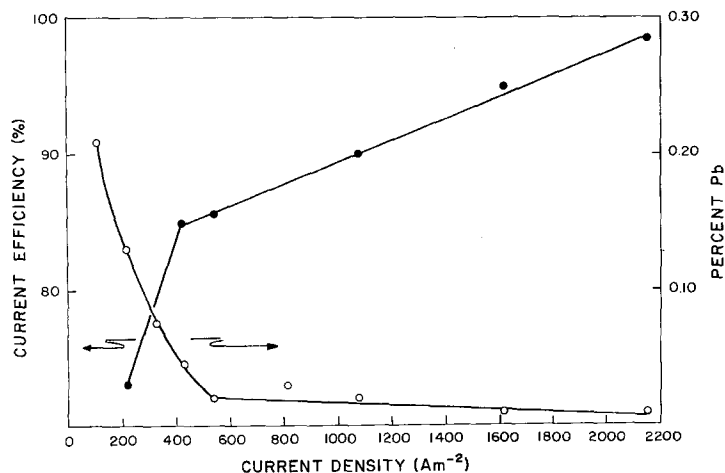


Fig. 3. Plots of zinc deposition current efficiency and lead content of zinc deposits as a function of current density.

spending decrease in zinc deposition current efficiency.

Thus it appears that the observed changes in zinc deposit morphology and orientation and zinc deposition CE may be directly related to the Pb content of the zinc deposits. Based on these findings a detailed investigation was made into the effect of Pb contamination in zinc electrolysis, the results of which are presented in the following sections of this paper. Pt anodes were used throughout these subsequent studies to ensure that the anodes would not be a source of lead contamination [4]. Selected zinc deposits were assayed for platinum to ensure no significant contamination was taking place. The assays which were sensitive to at least 0.001 wt% Pt, indicated that no Pt was present in zinc deposits produced either with conditioned 0.75 wt% Ag-Pb or Pt anodes.

### 3.2. Characterization of the lead effect

#### 3.2.1. 'Addition-free' and 'balanced' electrolytes.

(a) The addition of lead as a lead acetate solution to acid zinc electrolyte produced significant changes in the morphology and orientation of zinc deposits obtained from addition-free zinc electrolyte (i.e. containing no additions of antimony and glue) at all current densities studied (Table 1). The lead acetate additions had an appreciable effect on the morphology but not the orientation of zinc deposits obtained from balanced electrolyte (i.e. containing both antimony and glue additions in proportions that give an optimum in levelling properties and current efficiency of zinc deposition) at high current density ( $807 \text{ A m}^{-2}$ ). However, at low current densities ( $215 \text{ A m}^{-2}$ ) lead acetate additions to a balanced electrolyte effected both the morphology and orientation of the zinc deposits.

In a previous publication [4] it was reported that, in the absence of lead contamination, zinc deposits having the same characteristic morphology and orientation were obtained from both addition-free and balanced electrolytes for a wide range of experimental conditions, including various anode materials and significant variations in current density. This characteristic zinc deposit morphology is effected by lead contamination as shown in the series of SEM photomicrographs in Fig. 4. Figs. 4a-d indicate the effect of increasing

lead in solution on the morphology of zinc deposits obtained at  $807 \text{ A m}^{-2}$ . As shown in Table 1, there is a corresponding increase in the lead content of the zinc deposits. It can readily be seen (Fig. 4b) that the addition of  $1 \text{ mg l}^{-1}$  Pb (as lead acetate) to the electrolyte substantially increases the size of the individual zinc platelets and also changes the preferred orientation from (1 1 2) (1 1 4) (1 0 2) to (1 0 1) (1 0 2). Increasing the Pb concentration to  $3 \text{ mg l}^{-1}$  (Fig. 4c) and  $9 \text{ mg l}^{-1}$  (Fig. 4d) results in the zinc platelets having a more vertical alignment with respect to the Al cathode giving preferred orientations, respectively (1 0 1) (1 0 0) and (1 0 0) (1 0 1).

For comparison, the effect of Pb on the morphology of zinc deposits obtained at  $807 \text{ A m}^{-2}$  from balanced electrolyte is shown in Figs. 4e-h. Under these conditions the addition of lead has virtually no effect on the deposit orientation which remains strongly preferred (1 1 2). The morphology is effected, however, with the individual zinc platelets becoming less distinct and their edges becoming rounded as lead in solution and in the deposit increases. The lead content of the zinc deposits (Table 1) obtained from balanced electrolyte is generally less than that for zinc deposits obtained from addition-free electrolyte under similar conditions.

The series of SEM photomicrographs shown in Fig. 5 indicate that Pb additions have a more drastic and detrimental effect on the morphology and orientation of zinc deposits obtained at  $215 \text{ A m}^{-2}$ . This corresponds to higher lead contents in the zinc deposits (Table 1). For the addition-free electrolyte the deposits obtained for 1 and  $9 \text{ mg l}^{-1}$  Pb, Figs. 5a and b respectively, are composed of poorly-defined zinc platelets; the preferred orientation tends to be basal, i.e., (0 0 2).

For the balanced electrolyte, at  $215 \text{ A m}^{-2}$ , the zinc deposit orientation obtained in the presence of  $1 \text{ mg l}^{-1}$  Pb (Fig. 5c) remains essentially the same as the characteristic lead-free deposit (Fig. 4e). However, some change in morphology is observed. In the presence of  $9 \text{ mg l}^{-1}$  Pb (Fig. 5d) the Pb effect on the deposit morphology, i.e. rounding of the platelet edges, is obvious and the deposit orientation changes to (0 0 2).

At  $807 \text{ A m}^{-2}$  (Table 1), increasing Pb additions to the addition-free electrolyte causes a change in deposit orientation from intermediate to perpen-

Table 1. Crystallographic orientation and lead content of zinc deposits obtained from 'addition-free' and balanced electrolytes (electrolysis conditions: 55 g l<sup>-1</sup> Zn; 150 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; 35° C; Pt anodes)

| Corresponding figure in text          | Current density (A m <sup>-2</sup> ) | Additives (mg l <sup>-1</sup> ) |      | Glue | Crystallographic orientation† | Cathode lead (%) |
|---------------------------------------|--------------------------------------|---------------------------------|------|------|-------------------------------|------------------|
|                                       |                                      | Pb*                             | Sb   |      |                               |                  |
| <i>A. 'Addition-free' electrolyte</i> |                                      |                                 |      |      |                               |                  |
| 4a                                    | 807                                  | 0                               | 0.00 | 0    | (1 1 2) (1 0 2)               | 0.0040           |
| 4b                                    | 807                                  | 1                               | 0.00 | 0    | (1 0 1)                       | 0.0047           |
| 4c                                    | 807                                  | 3                               | 0.00 | 0    | (1 0 1) (1 0 0)               | 0.0164           |
| 4d                                    | 807                                  | 9                               | 0.00 | 0    | (1 0 0) (1 0 1)               | 0.0465           |
| —                                     | 430                                  | 0                               | 0.00 | 0    | (1 1 2) (1 0 2)               | 0.0024           |
| —                                     | 430                                  | 3                               | 0.00 | 0    | (1 0 0) (1 0 1)               | 0.0399           |
| —                                     | 430                                  | 9                               | 0.00 | 0    | (1 0 0) (1 0 1)               | 0.1535           |
| 5a                                    | 215                                  | 1                               | 0.00 | 0    | (1 0 1)                       | 0.0285           |
| 5b                                    | 215                                  | 9                               | 0.00 | 0    | (1 0 1) (1 0 0)               | 0.0680           |
| 6a                                    | 807                                  | 3‡                              | 0.00 | 0    | (1 0 1) (1 1 2)               | 0.0023           |
| 6b                                    | 807                                  | 9‡                              | 0.00 | 0    | (1 0 2) (1 0 1)               | 0.0056           |
| 6c                                    | 430                                  | 9‡                              | 0.00 | 0    | (1 0 1) (1 1 2)               | 0.0155           |
| 6d                                    | 807                                  | 3§                              | 0.00 | 0    | (1 0 1)                       | 0.0032           |
| 6e                                    | 807                                  | 9§                              | 0.00 | 0    | (1 0 1)                       | 0.0063           |
| 6f                                    | 430                                  | 9§                              | 0.00 | 0    | (1 0 1) (1 1 2)               | 0.0149           |
| <i>B. 'Balanced' electrolyte</i>      |                                      |                                 |      |      |                               |                  |
| —                                     | 807                                  | 0                               | 0.04 | 15   | (1 1 2) (1 0 2)               | 0.0024           |
| —                                     | 807                                  | 3                               | 0.04 | 15   | (1 1 2) (1 1 4)               | 0.0069           |
| —                                     | 807                                  | 9                               | 0.04 | 15   | (1 0 1) (1 0 2)               | 0.0320           |
| —                                     | 430                                  | 0                               | 0.04 | 15   | (1 1 2) (1 0 3)               | 0.0020           |
| —                                     | 430                                  | 3                               | 0.04 | 15   | (1 1 2) (1 0 1)               | 0.0251           |
| —                                     | 430                                  | 9                               | 0.04 | 15   | (1 0 1) (1 1 0)               | 0.0556           |
| —                                     | 807                                  | 3                               | 0.04 | 30   | (1 0 1)                       | 0.0130           |
| —                                     | 430                                  | 3                               | 0.04 | 30   | (1 0 1)                       | 0.0285           |
| —                                     | 430                                  | 9                               | 0.04 | 30   | (1 0 1)                       | 0.0500           |
| 4e                                    | 807                                  | 0                               | 0.08 | 30   | (1 1 2) (1 0 1)               | 0.0004           |
| 4f                                    | 807                                  | 1                               | 0.08 | 30   | (1 1 2)                       | 0.0062           |
| 4g                                    | 807                                  | 3                               | 0.08 | 30   | (1 1 2)                       | 0.0065           |
| 4h                                    | 807                                  | 9                               | 0.08 | 30   | (1 1 2) (1 0 1)               | 0.0180           |
| —                                     | 430                                  | 0                               | 0.08 | 30   | (1 0 1) (1 0 2)               | —                |
| —                                     | 430                                  | 3                               | 0.08 | 30   | (1 1 2) (1 1 4)               | 0.0045           |
| —                                     | 430                                  | 9                               | 0.08 | 30   | (1 0 3) (1 0 1)               | 0.0220           |
| 5c                                    | 215                                  | 1                               | 0.08 | 30   | (1 0 3) (1 1 4)               | 0.0040           |
| 5d                                    | 215                                  | 9                               | 0.08 | 30   | (0 0 2) (1 0 3)               | 0.0135           |
| —                                     | 430                                  | 3                               | 0.10 | 45   | (1 1 2) (1 1 0)               | 0.0135           |
| —                                     | 430                                  | 9                               | 0.10 | 45   | (1 0 1)                       | 0.0165           |

\* Pb added as lead acetate.

† Relative to ASTM standard for zinc powder.

‡ Pb added as lead sulphate.

§ Pb added as lead oxide (PbO).

dicular and increasing Pb contamination of the zinc deposits, while for similar Pb additions to the balanced electrolyte, the deposit orientation remains as intermediate. At 430 A m<sup>-2</sup>, the zinc deposit orientation for the addition-free electrolyte changes from intermediate to perpendicular

to basal as the lead content of the electrolyte is increased. For this current density, a similar trend is also observed for the balanced electrolyte. At 215 A m<sup>-2</sup>, the zinc deposit orientation becomes (0 0 2) for both electrolytes.

Lead contamination of the zinc deposits

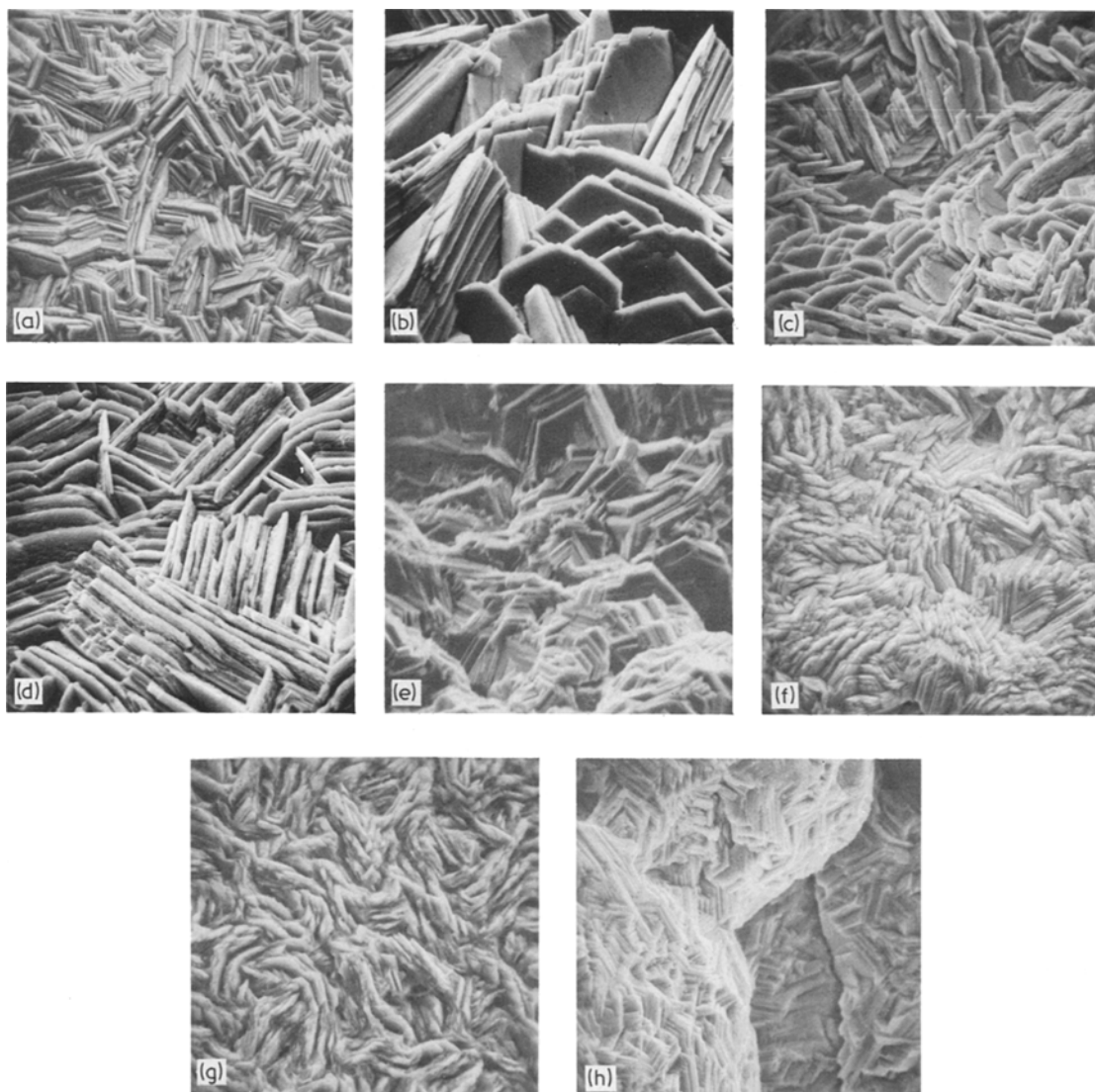


Fig. 4. SEM photomicrographs ( $\times 770$ ) showing the effect of lead on the preferred zinc deposit structure. (a)–(d) addition-free electrolyte, (e)–(f) balanced electrolyte. Current density  $807 \text{ A m}^{-2}$ . (a)  $0 \text{ mg l}^{-1} \text{ Pb}$ ; (b)  $1 \text{ mg l}^{-1} \text{ Pb}$ ; (c)  $3 \text{ mg l}^{-1} \text{ Pb}$ ; (d)  $9 \text{ mg l}^{-1} \text{ Pb}$ ; (e)  $0 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.08 \text{ mg l}^{-1} \text{ Sb}$ ,  $30 \text{ mg l}^{-1} \text{ glue}$ ; (f)  $1 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.08 \text{ mg l}^{-1} \text{ Sb}$ ,  $30 \text{ mg l}^{-1} \text{ glue}$ ; (g)  $3 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.08 \text{ mg l}^{-1} \text{ Sb}$ ,  $30 \text{ mg l}^{-1} \text{ glue}$ ; (h)  $9 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.08 \text{ mg l}^{-1} \text{ Sb}$ ,  $30 \text{ mg l}^{-1} \text{ glue}$ .

increases with increasing Pb in solution and with decreasing current density (Table 1). This dependence of the Pb contamination on current density is in agreement with the results described in the previous section (Section 3.1) for zinc deposits obtained using non-conditioned Pb–Ag anodes and is likely related to both the position of lead and zinc in the electromotive series and their concentrations in solution. Lead, being more noble, should deposit preferentially to zinc. However, the low

concentration of lead relative to zinc ensures that increased zinc deposition will occur relative to lead deposition with increasing current density due to diffusion limitations [3].

A qualitative relationship between the Pb contamination and the observed morphology and orientation of the zinc deposits obtained under various conditions from addition-free electrolyte is summarized in Table 2. With respect to the alignment of the zinc platelets to the Al cathode, the

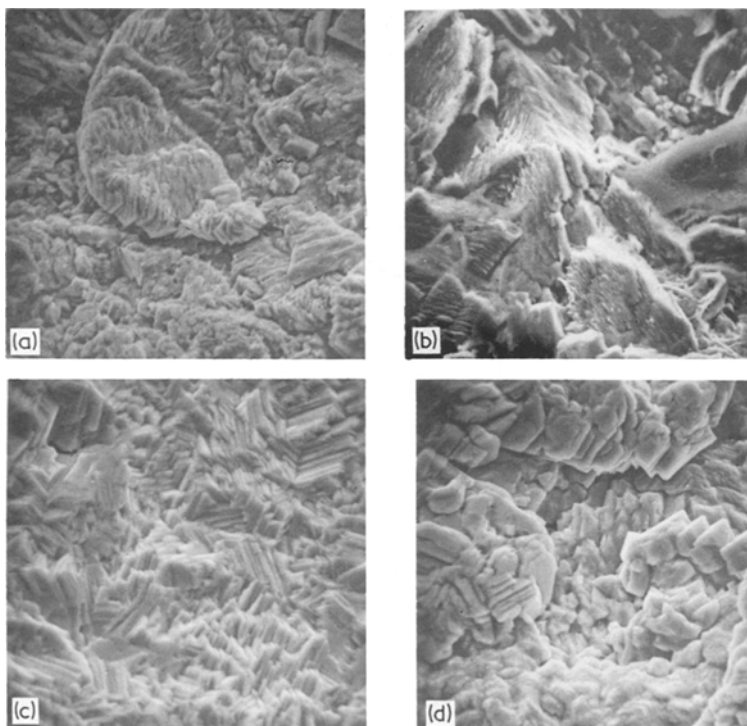
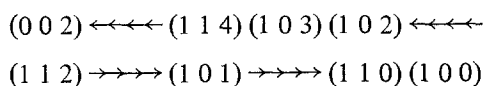


Fig. 5. SEM photomicrographs ( $\times 770$ ) showing the effect of lead on the preferred deposit structure (a), (b) addition-free electrolyte, (c), (d) balanced electrolyte. Current density  $215 \text{ A m}^{-2}$ . (a)  $1 \text{ mg l}^{-1} \text{ Pb}$ ; (b)  $9 \text{ mg l}^{-1} \text{ Pb}$ ; (c)  $1 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.08 \text{ mg l}^{-1} \text{ Sb}$ ,  $30 \text{ mg l}^{-1} \text{ glue}$ ; (d)  $9 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.08 \text{ mg l}^{-1} \text{ Sb}$ ,  $30 \text{ mg l}^{-1} \text{ glue}$ .

various orientations can be classified as follows:  
basal (or parallel)  $\leftarrow$  intermediate  $\rightarrow$  perpendicular



Thus, increased lead contamination of zinc deposits from addition-free electrolytes changes the orientation from intermediate to perpendicular. At very high levels of lead contamination, the apparent orientation changes from perpendicular

Table 2. Morphology and orientation of zinc deposits obtained from addition-free electrolyte in relation to Pb content of the zinc deposits

| Morphology type  | Crystallographic orientation* | Pb content (%) | Conditions  |
|--|-------------------------------|----------------|---|
| preferred  | (112) (102) (114)             | < 0.005        | Pt anodes. Pb-free solution; all current density values; conditioned Pb-Ag anodes.                  |
| triangular   | (101) (102)                   | < 0.02         | Unconditioned Pb-Ag anodes; current density $> 50 \text{ A ft}^{-2}$ Pt anodes + Pb in soln.        |
| poorly defined platelets; vertical orientation; serrated edges | (100) (101)                   | 0.02-0.05      | Unconditioned Pb-Ag anodes; Pt anodes + Pb in solution. current density = $40-50 \text{ A ft}^{-2}$ |
| poorly crystalline to amorphous; pitted-corroded structure     | (002)                         | > 0.07         | Unconditioned Pb-Ag anodes; current density $< 30 \text{ A ft}^{-2}$ Pt anodes + Pb in soln.        |

\* Relative to ASTM standard for zinc powder.



to basal, although the morphological features (Figs. 2a and b) appear to indicate a perpendicular growth.

(b) Lead added to the addition-free electrolyte as a slurry of  $\text{PbSO}_4$  or  $\text{PbO}$  had only a slight effect on the zinc deposit morphology as indicated by the SEM photomicrographs shown in Fig. 6. For example, the addition of  $9 \text{ mg l}^{-1}$   $\text{PbSO}_4$  or  $\text{PbO}$  at  $870 \text{ A m}^{-2}$ , Fig. 6b and Fig. 6e, resulted in a zinc deposit morphology very similar to that obtained for the addition of  $1 \text{ mg l}^{-1}$  Pb (as lead acetate) (Fig. 4b) under similar experimental conditions. All three zinc deposits contained similar concentrations of lead (Table 1). At  $430 \text{ A m}^{-2}$  the effect of  $\text{PbSO}_4$  and  $\text{PbO}$  (Figs. 6c and f) was similar to that produced at  $870 \text{ A m}^{-2}$ . The crystallographic orientation was predominately (1 0 1), i.e. the platelets were intermediate but tending towards a perpendicular alignment to the Al cathode. Lead contamination of the zinc deposits was less than when lead acetate was added under similar conditions (Table 1). The poor solubility of  $\text{PbSO}_4$  or  $\text{PbO}$  added to the zinc electrolyte as compared to lead acetate probably accounts for the difference. Contamination of the deposits by

particulate  $\text{PbSO}_4$  or  $\text{PbO}$  does not appear to be important under the conditions employed in these tests.

(c) The effect of lead [as lead acetate, lead sulphate or lead oxide ( $\text{PbO}$ )], added to the addition-free electrolyte on the current efficiency (CE) of zinc deposition for one hour deposits obtained at  $807$  and  $430 \text{ A m}^{-2}$  is given in Table 3. The data are summarized in Fig. 7 as a series of plots of current efficiency versus the lead content of the zinc deposits.

The current efficiency for zinc deposition at  $430 \text{ A m}^{-2}$  and  $807 \text{ A m}^{-2}$  generally decreased with increasing lead content in the zinc deposits. Overall, the current efficiency was about 1% higher at  $807 \text{ A m}^{-2}$  as compared to  $430 \text{ A m}^{-2}$  for similar lead contents in the zinc deposits. Temperature changes between  $35\text{--}45^\circ \text{C}$  had no significant effect on the current efficiencies.

The deposit morphologies and orientations (Table 3) followed the general pattern summarized in Table 2. The results indicate that under conditions similar to those employed in these tests, increasing lead contamination will cause a slight decrease in current efficiency while causing the

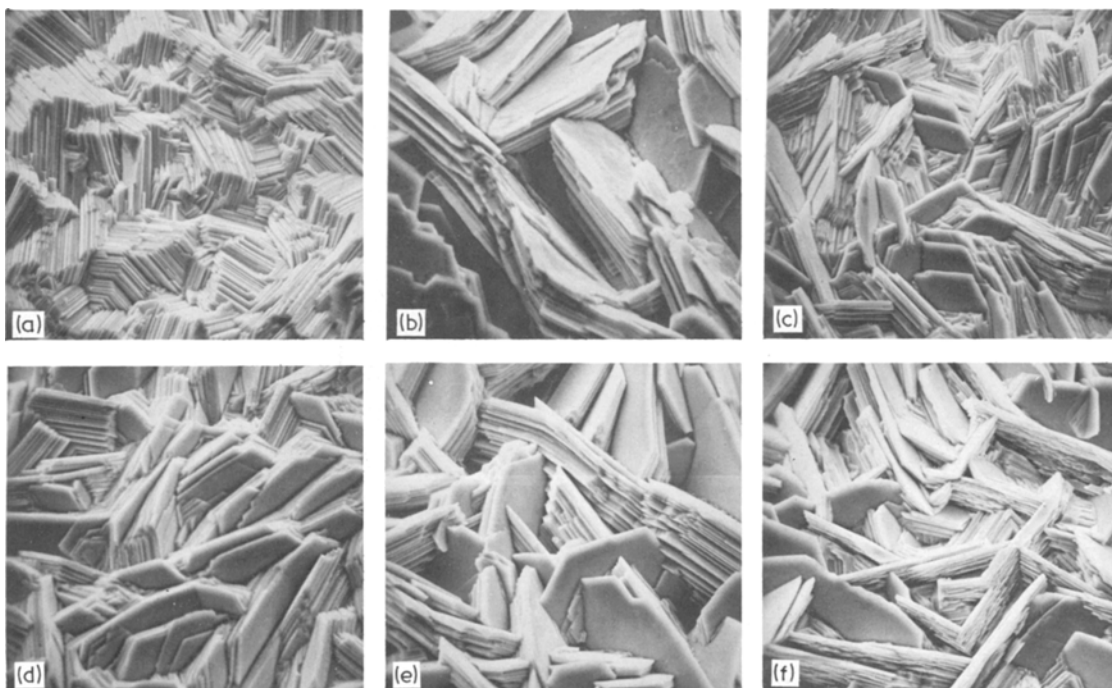


Fig. 6. SEM photomicrographs ( $\times 770$ ) showing the effect of  $\text{PbSO}_4$  and  $\text{PbO}$  on the morphology of zinc deposits obtained from addition-free electrolyte at (a), (b), (d), (e)  $807$  and (c), (f)  $430 \text{ A m}^{-2}$ . (a)  $3 \text{ mg l}^{-1}$   $\text{PbSO}_4$ ; (b)  $9 \text{ mg l}^{-1}$   $\text{PbSO}_4$ ; (c)  $9 \text{ mg l}^{-1}$   $\text{PbSO}_4$ ; (d)  $3 \text{ mg l}^{-1}$   $\text{PbO}$ ; (e)  $9 \text{ mg l}^{-1}$   $\text{PbO}$ ; (f)  $9 \text{ mg l}^{-1}$   $\text{PbO}$ .

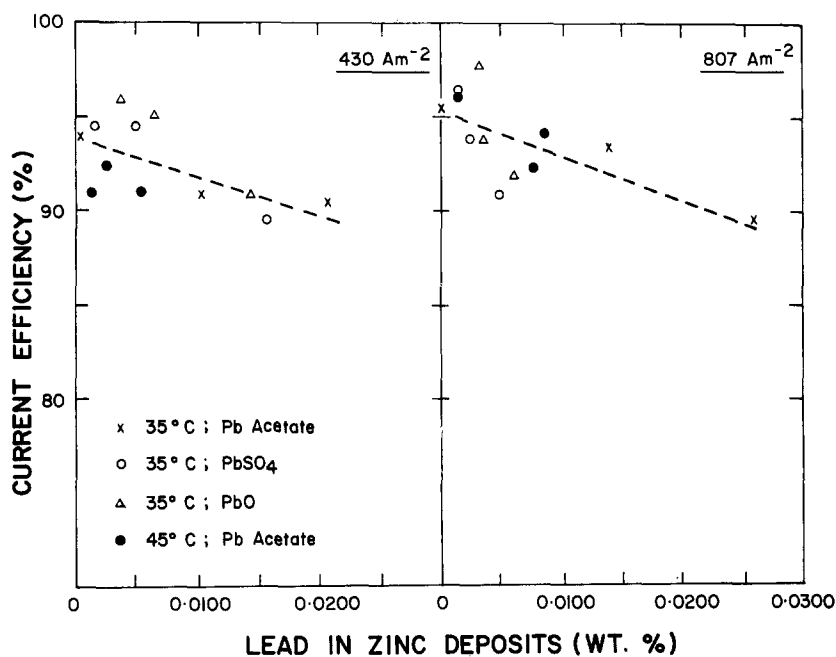


Fig. 7. Plots of current efficiency for zinc deposition from addition-free electrolyte as a function of the lead content of the zinc deposits; current density 430 and 807 A m<sup>-2</sup>.

Table 3. Zinc deposition current efficiency (CE), crystallographic orientation and lead content of zinc deposits as a function of temperature and current density obtained from addition-free electrolyte (electrolysis conditions: 55 g l<sup>-1</sup> Zn; 150 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; Pt anodes)

| Temperature (°C) | Current density (A m <sup>-2</sup> ) | Pb* added to electrolyte (mg l <sup>-1</sup> ) | Current efficiency (%) | Crystallographic orientation† | Cathode lead (%) |
|------------------|--------------------------------------|--|------------------------|-------------------------------|------------------|
| 35               | 807                                  | 0  | 95.4                   | (1 1 2)                       | 0.0005           |
| 35               | 807                                  | 3  | 93.2                   | (1 0 1)                       | 0.0140           |
| 35               | 807                                  | 6  | 89.5                   | (1 0 0) (1 1 0)               | 0.0260           |
| 35               | 430                                  | 0  | 93.8                   | (1 1 2)                       | 0.0003           |
| 35               | 430                                  | 3  | 90.8                   | (1 0 1)                       | 0.0105           |
| 35               | 430                                  | 6  | 90.4                   | (1 0 1)                       | 0.0205           |
| 35               | 807                                  | 3‡   | 96.5                   | (1 0 1) (1 1 2)               | 0.0023           |
| 35               | 807                                  | 6‡   | 93.9                   | (1 0 2) (1 1 0)               | 0.0027           |
| 35               | 807                                  | 9‡   | 90.7                   | (1 0 2) (1 0 1)               | 0.0056           |
| 35               | 430                                  | 3‡   | 94.5                   | (1 1 0) (1 1 2)               | 0.0021           |
| 35               | 430                                  | 6‡   | 94.5                   | (1 1 0) (1 1 2)               | 0.0051           |
| 35               | 430                                  | 9‡   | 89.5                   | (1 0 1) (1 1 2)               | 0.0055           |
| 35               | 807                                  | 3§   | 97.6                   | (1 0 1)                       | 0.0032           |
| 35               | 807                                  | 6§   | 93.7                   | (1 0 2) (1 0 5)               | 0.0035           |
| 35               | 807                                  | 9§   | 91.7                   | (1 0 1)                       | 0.0063           |
| 35               | 430                                  | 3§   | 95.8                   | (1 0 1)                       | 0.0040           |
| 35               | 430                                  | 6§   | 95.0                   | (1 0 1)                       | 0.0060           |
| 35               | 430                                  | 9§   | 90.8                   | (1 0 1) (1 1 2)               | 0.0149           |
| 45               | 807                                  | 0  | 96.0                   | (1 0 1)                       | 0.0021           |
| 45               | 807                                  | 3  | 94.2                   | (1 0 1)                       | 0.0083           |
| 45               | 807                                  | 6  | 92.9                   | (1 0 1)                       | 0.0077           |
| 45               | 430                                  | 0  | 91.0                   | (1 1 2)                       | 0.0011           |
| 45               | 430                                  | 3  | 92.3                   | (1 0 1)                       | 0.0023           |
| 45               | 430                                  | 6  | 91.0                   | (1 0 1)                       | 0.0055           |

\* Pb added as lead acetate.

† Relative to ASTM standard for zinc powder.

‡ Pb added as lead sulphate.

§ Pb added as lead oxide (PbO).

orientation to shift from intermediate to perpendicular. This effect is similar to that observed with glue additions [1], where increasing glue levels in zinc electrolyte shift the orientation from intermediate to perpendicular and cause a slight decrease in the current efficiency. It should be noted that these observed decreases in current efficiency with increasing lead contamination of electrodeposited zinc become noticeable only at lead levels which are much higher than those normally encountered in a zinc electrowinning plant.

**3.2.2. 'Excess antimony' electrolyte.** The addition of lead as a lead acetate solution to acid zinc sulphate electrolyte also had an effect on the morphology and orientation of zinc deposits obtained from excess antimony electrolyte (i.e. containing added antimony but no glue) (Table 4). The effect of excess antimony on the morphology and orientation of the preferred zinc deposit structure was described in a previous publication [4]. The effect of Pb additions on the morphology of zinc deposits obtained at  $807 \text{ A m}^{-2}$  from excess antimony electrolyte is shown in Fig. 8 in a series of SEM photomicrographs. For the electrolyte containing  $0.04 \text{ mg l}^{-1}$  antimony, the addition of 3 and  $9 \text{ mg l}^{-1}$  Pb (see Figs. 8b and c, respectively) changed the orientation from (1 1 4) (1 0 3) to a more vertical orientation, i.e. (1 0 2) (1 0 3). The morphology

changed from small platelets with serrated edges to small platelets with rounded edges.

For the electrolyte containing  $0.08 \text{ mg l}^{-1}$  antimony, the addition of 3 and  $9 \text{ mg l}^{-1}$  Pb (see Figs. 8e and f, respectively) had only a slight effect on the orientation [(1 0 3) (0 0 2) to (1 1 4) (1 0 3)]. The platelets became more defined with increasing lead, with the edges changing from serrated to rounded.

The crystallographic orientations and lead contents of zinc deposits obtained from excess antimony electrolyte containing various additions of Pb are summarized in Table 4. In general Pb-Sb combinations tend to yield zinc deposits which are composed of rounded platelets having a predominant basal orientation. The lead content of the zinc deposits increased with increasing Pb in solution, with decreasing Sb in solution and with decreasing current density.

**3.2.3. 'Excess glue' electrolyte.** The addition of lead acetate to acid zinc sulphate electrolyte also modified the morphology and orientation of zinc deposits obtained from *excess glue* electrolyte (i.e. containing added glue but no added antimony). The morphology changes as a result of lead addition to excess glue electrolyte are indicated in Fig. 9 for deposits obtained at  $807 \text{ A m}^{-2}$  from electrolytes containing 1, 3 and  $9 \text{ mg l}^{-1}$  Pb and 7.5 and  $50 \text{ mg l}^{-1}$  glue concentrations. The

Table 4. Crystallographic orientation and lead content of zinc deposits obtained from 'excess antimony' electrolyte (electrolysis conditions:  $55 \text{ g l}^{-1}$  Zn;  $150 \text{ g l}^{-1}$   $\text{H}_2\text{SO}_4$ ;  $35^\circ \text{ C}$ ; Pt anodes)

| Corresponding figures in text | Current density ( $\text{A m}^{-2}$ ) | Additives ( $\text{mg l}^{-1}$ ) |      |      | Crystallographic orientation* | Cathode lead (%) |
|-------------------------------|---------------------------------------|----------------------------------|------|------|-------------------------------|------------------|
|                               |                                       | Pb                               | Glue | Sb   |                               |                  |
| 8a                            | 807                                   | 0                                | 0    | 0.04 | (1 1 2) (1 1 4)               | 0.0003           |
| 8b                            | 807                                   | 3                                | 0    | 0.04 | (1 0 3) (1 1 4)               | 0.0069           |
| 8c                            | 807                                   | 9                                | 0    | 0.04 | (1 0 2) (1 0 3)               | 0.0393           |
| —                             | 430                                   | 0                                | 0    | 0.04 | (1 1 2) (1 0 1)               | —                |
| —                             | 430                                   | 3                                | 0    | 0.04 | (0 0 2) (1 0 0)               | 0.0310           |
| —                             | 430                                   | 9                                | 0    | 0.04 | (0 0 2) (1 0 1)               | 0.0385           |
| 8d                            | 807                                   | 0                                | 0    | 0.08 | (1 0 3) (1 0 2)               | 0.0005           |
| 8e                            | 807                                   | 3                                | 0    | 0.08 | (1 1 4) (1 0 3)               | 0.0043           |
| 8f                            | 807                                   | 9                                | 0    | 0.08 | (1 1 4) (1 0 3)               | 0.0120           |
| —                             | 430                                   | 0                                | 0    | 0.08 | (1 0 3) (1 0 2)               | —                |
| —                             | 807                                   | 3                                | 0    | 0.10 | (1 1 2)                       | 0.0034           |
| —                             | 807                                   | 9                                | 0    | 0.10 | (1 1 2) (1 1 4)               | 0.0176           |
| —                             | 430                                   | 3                                | 7.5  | 0.10 | (1 1 0) (1 0 1)               | 0.0115           |

\* Relative to ASTM standard for zinc powder.

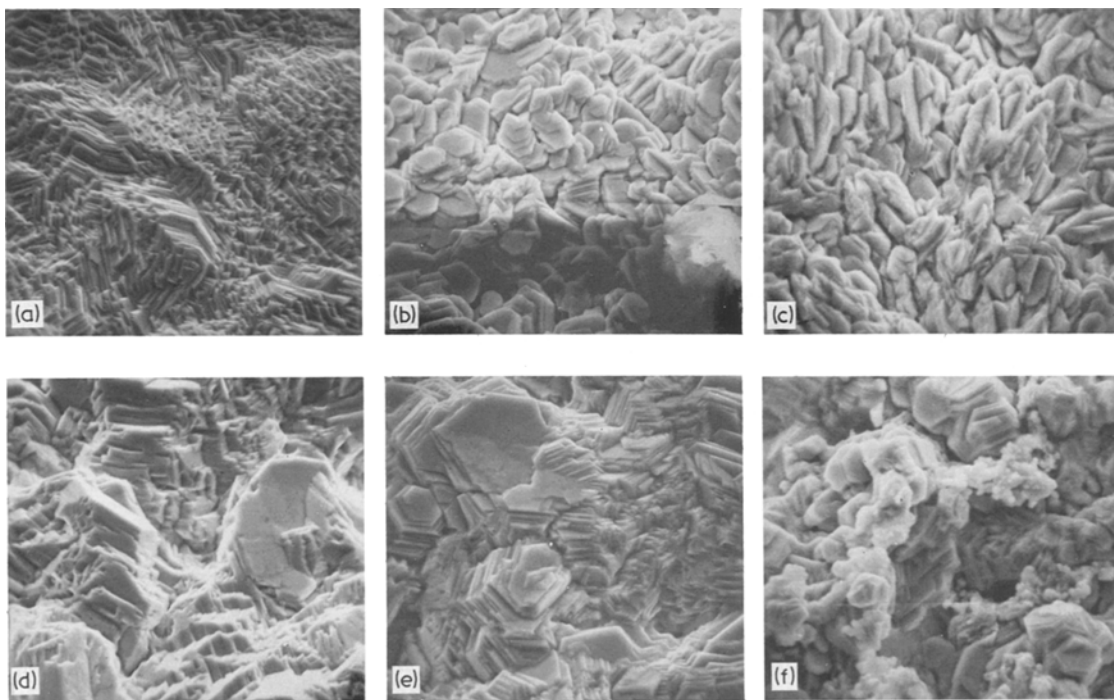


Fig. 8. SEM photomicrographs ( $\times 770$ ) showing the effect of lead on the morphology of zinc deposits obtained from excess antimony electrolyte at  $807 \text{ A m}^{-2}$ . (a)  $0 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.04 \text{ mg l}^{-1} \text{ Sb}$ ; (b)  $3 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.04 \text{ mg l}^{-1} \text{ Sb}$ ; (c)  $9 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.04 \text{ mg l}^{-1} \text{ Sb}$ ; (d)  $0 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.08 \text{ mg l}^{-1} \text{ Sb}$ ; (e)  $3 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.08 \text{ mg l}^{-1} \text{ Sb}$ ; (f)  $9 \text{ mg l}^{-1} \text{ Pb}$ ,  $0.08 \text{ mg l}^{-1} \text{ Sb}$ .

effect of excess glue on the zinc deposit morphology was described previously [4]. With glue in the electrolyte the resulting deposits had smooth surfaces and the deposit grain size generally decreased with an increase in the amount of glue addition (Figs. 9a and e). The preferred orientation was (1 0 1). At low glue concentrations ( $7.5 \text{ mg l}^{-1}$ ), the orientation changed from (1 0 1) to a vertical (1 0 0) (1 0 1) orientation with increasing lead concentration (Figs. 9b–d). At high glue concentrations ( $50 \text{ mg l}^{-1}$ ) the orientation remained at (1 0 1) with increasing lead concentration (Figs. 9f–h). The morphology changed in both cases to a larger grain size with increasing lead concentration.

The crystallographic orientations and lead contents of zinc deposits obtained at  $807$  and  $430 \text{ A m}^{-2}$  from excess glue electrolyte containing various amounts of added Pb are summarized in Table 5. The lead content of the zinc deposits increased with increasing Pb in solution, with decreasing glue in solution and with decreasing current density.

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

The polarization behaviour associated with zinc deposition from acid sulphate electrolyte is sensitive to impurities such as antimony and to organics such as animal glue in solution [2–4]. In the present study, changes in the activation overpotential associated with zinc deposition onto aluminium cathodes that were caused by lead impurities in the zinc electrolyte were measured by cyclic voltammetry (see Section 2.4) and related to morphological and orientation changes in the zinc deposit.

The addition of lead as lead acetate solution to acid zinc electrolyte increased the activation overpotential for zinc deposition from addition-free electrolyte, from excess glue electrolyte and from excess antimony electrolyte. The effect of lead additions on the activation overpotential are listed in Table 6 and illustrated in Fig. 10. Lead additions as lead acetate had no appreciable effect on the activation overpotential in the balanced electrolyte.

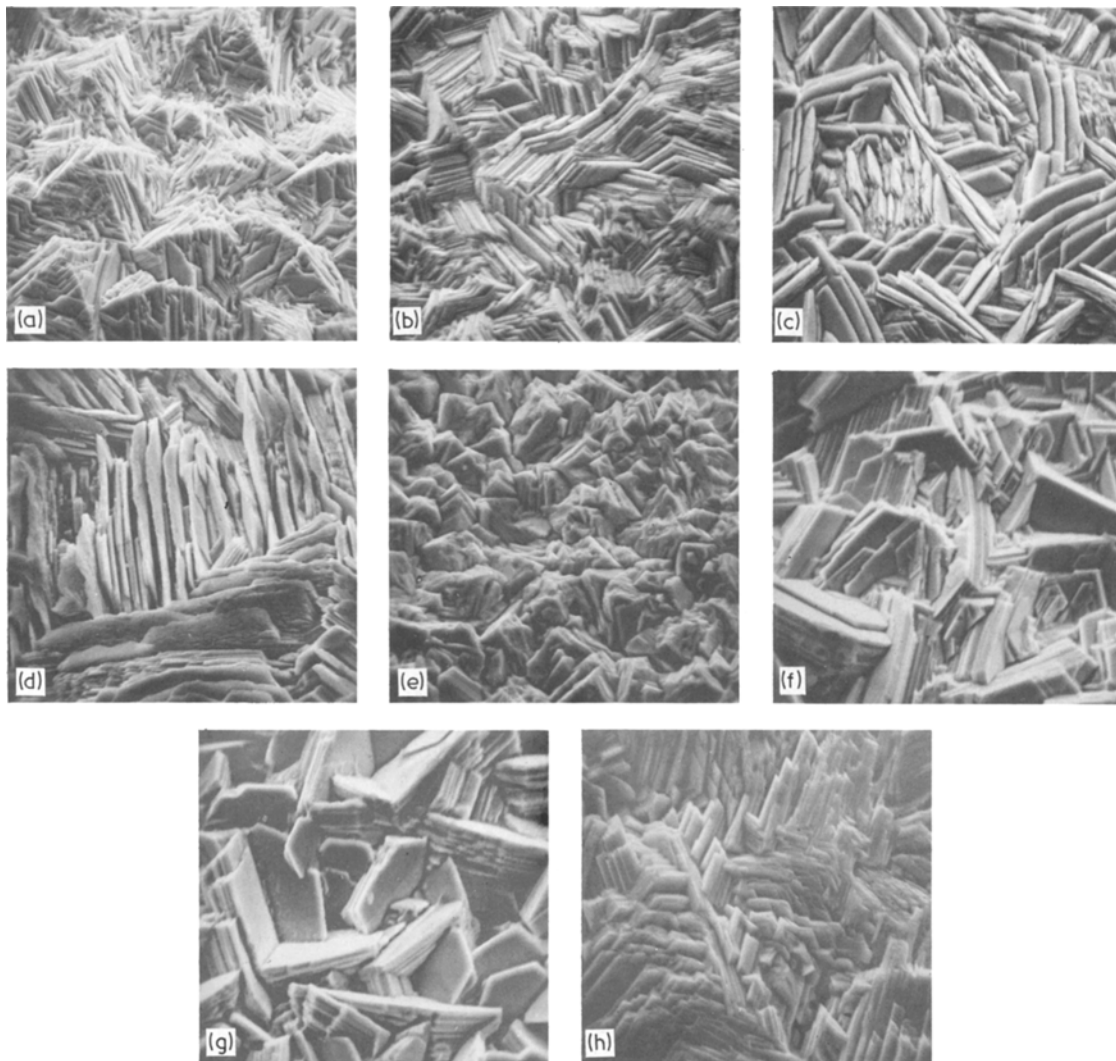


Fig. 9. SEM photomicrographs ( $\times 770$ ) showing the effect of lead on the morphology of zinc deposits obtained from excess glue electrolyte at  $807 \text{ A m}^{-2}$ . (a)  $0 \text{ mg l}^{-1} \text{ Pb}$ ,  $7.5 \text{ mg l}^{-1} \text{ glue}$ ; (b)  $1 \text{ mg l}^{-1} \text{ Pb}$ ,  $7.5 \text{ mg l}^{-1} \text{ glue}$ ; (c)  $3 \text{ mg l}^{-1} \text{ Pb}$ ,  $7.5 \text{ mg l}^{-1} \text{ glue}$ ; (d)  $9 \text{ mg l}^{-1} \text{ Pb}$ ,  $7.5 \text{ mg l}^{-1} \text{ glue}$ ; (e)  $0 \text{ mg l}^{-1} \text{ Pb}$ ,  $50 \text{ mg l}^{-1} \text{ glue}$ ; (f)  $1 \text{ mg l}^{-1} \text{ Pb}$ ,  $50 \text{ mg l}^{-1} \text{ glue}$ ; (g)  $3 \text{ mg l}^{-1} \text{ Pb}$ ,  $50 \text{ mg l}^{-1} \text{ glue}$ ; (h)  $9 \text{ mg l}^{-1} \text{ Pb}$ ,  $50 \text{ mg l}^{-1} \text{ glue}$ .

A comparison of the data given in Table 6 and the curves shown in Fig. 10 indicates that the order of increasing degree of Pb polarization with respect to electrolyte type is as follows:

$$\text{balanced} < \text{excess antimony} < \text{excess glue} \\ < \text{addition-free.}$$

This sequence is in good agreement with the observed Pb effects on the zinc deposit morph-

ology and orientation and the nature and relative concentrations of additives and impurities present in the acid zinc sulphate electrolyte.

The relationship between activation overpotential and crystallographic orientation is shown in Fig. 11. The high polarization observed for soluble Pb additions to addition-free electrolyte corresponded with vertically oriented  $(110)$   $(100)$  zinc deposits. Lead added to acid zinc electrolyte as a slurry of  $\text{PbSO}_4$  or  $\text{PbO}$  had almost no effect on the activation overpotential (Table 6), or on

Table 5. Crystallographic orientation and lead content of zinc deposits obtained from 'excess glue' electrolyte (electrolysis conditions:  $55 \text{ g l}^{-1} \text{ Zn}$ ;  $150 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$ ;  $35^\circ \text{ C}$ ; Pt anodes)

| Corresponding figure in text | Current density ( $\text{A m}^{-2}$ ) | Additives ( $\text{mg l}^{-1}$ ) |      |      | Crystallographic orientation* | Lead content (%) |
|------------------------------|---------------------------------------|----------------------------------|------|------|-------------------------------|------------------|
|                              |                                       | Pb                               | Sb   | Glue |                               |                  |
| 9a                           | 807                                   | 0                                | 0.00 | 7.5  | (1 0 1)                       | 0.0005           |
| 9b                           | 807                                   | 1                                | 0.00 | 7.5  | (1 1 2) (1 0 1)               | 0.0049           |
| 9c                           | 807                                   | 3                                | 0.00 | 7.5  | (1 0 1)                       | 0.0140           |
| 9d                           | 807                                   | 9                                | 0.00 | 7.5  | (1 0 0) (1 0 1)               | 0.0300           |
| —                            | 807                                   | 0                                | 0.00 | 15   | (1 0 1)                       | —                |
| —                            | 807                                   | 3                                | 0.00 | 15   | (1 1 2) (1 1 4)               | 0.0108           |
| —                            | 807                                   | 9                                | 0.00 | 15   | (1 0 2) (1 0 5)               | 0.0248           |
| —                            | 430                                   | 0                                | 0.00 | 15   | (1 0 1)                       | —                |
| —                            | 430                                   | 3                                | 0.00 | 15   | (1 0 1) (1 1 2)               | 0.0233           |
| —                            | 430                                   | 9                                | 0.00 | 15   | (1 0 1) (1 0 2)               | 0.0342           |
| —                            | 807                                   | 0                                | 0.00 | 30   | (1 0 1)                       | —                |
| —                            | 807                                   | 3                                | 0.00 | 30   | (1 1 2) (1 0 1)               | 0.0075           |
| —                            | 807                                   | 9                                | 0.00 | 30   | (1 1 2) (1 0 1)               | 0.0183           |
| —                            | 430                                   | 0                                | 0.00 | 30   | (1 0 1)                       | —                |
| —                            | 430                                   | 3                                | 0.00 | 30   | (1 1 2) (1 0 1)               | 0.0201           |
| —                            | 430                                   | 9                                | 0.00 | 30   | (1 0 1) (1 0 2)               | 0.0251           |
| 9e                           | 807                                   | 0                                | 0.00 | 50   | (1 0 1)                       | 0.0004           |
| 9f                           | 807                                   | 1                                | 0.00 | 50   | (1 0 1)                       | 0.0024           |
| 9g                           | 807                                   | 3                                | 0.00 | 50   | (1 0 1)                       | 0.0077           |
| 9h                           | 807                                   | 9                                | 0.00 | 50   | (1 0 1)                       | 0.0330           |
| —                            | 430                                   | 9                                | 0.00 | 50   | (1 0 1)                       | —                |
| —                            | 430                                   | 3                                | 0.02 | 45   | (1 0 1)                       | 0.0150           |

\* Relative to ASTM standard for zinc powder.

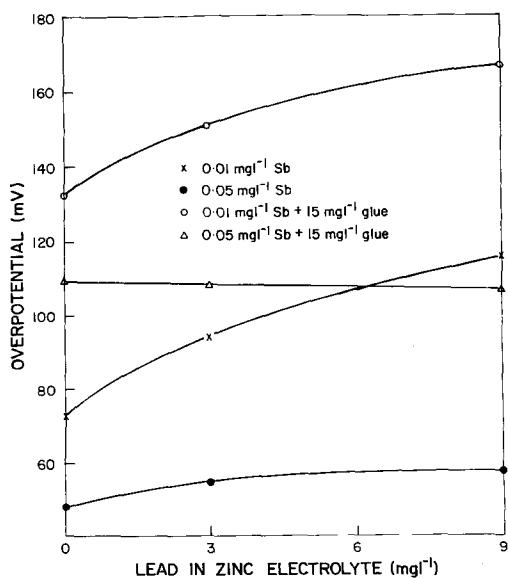


Fig. 10. Plots showing the effect of lead in zinc electrolyte on the overpotential of zinc electrodeposition.

Table 6. Zinc deposition activation overpotentials as measured by cyclic voltammetry (electrolysis conditions:  $55 \text{ g l}^{-1} \text{ Zn}$ ;  $150 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$ ;  $25^\circ \text{ C}$ )

| Electrolyte type | Additives ( $\text{mg l}^{-1}$ ) |      |      | Overpotential (mV) |
|------------------|----------------------------------|------|------|--------------------|
|                  | Pb*                              | Sb   | Glue |                    |
| addition-free    | 0                                | 0.00 | 0    | 73                 |
|                  | 3                                | 0.00 | 0    | 97                 |
|                  | 9                                | 0.00 | 0    | 116                |
|                  | 9†                               | 0.00 | 0    | 81                 |
|                  | 9‡                               | 0.00 | 0    | 81                 |
|                  | 0§                               | 0.00 | 0    | 73                 |
| excess glue      | 0                                | 0.00 | 15   | 133                |
|                  | 3                                | 0.00 | 15   | 151                |
|                  | 9                                | 0.00 | 15   | 168                |
| excess antimony  | 0                                | 0.04 | 0    | 47                 |
|                  | 3                                | 0.04 | 0    | 56                 |
|                  | 9                                | 0.04 | 0    | 58                 |
| balanced         | 0                                | 0.04 | 15   | 107                |
|                  | 3                                | 0.04 | 15   | 105                |
|                  | 9                                | 0.04 | 15   | 104                |

\* Pb added as lead acetate.

† Pb added as lead sulphate.

‡ Pb added as lead oxide ( $\text{PbO}$ ).

§  $9 \text{ mg l}^{-1}$  acetic acid added.

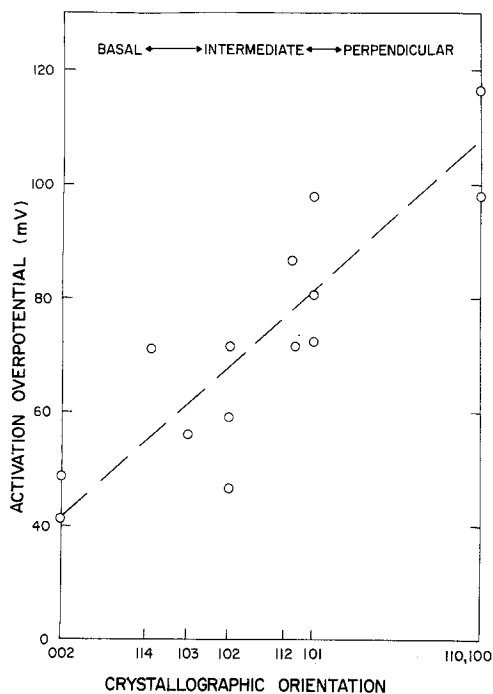


Fig. 11. Plot showing the correlation between zinc deposition overpotential and zinc deposit crystallographic orientation.

the crystallographic orientation (Table 1) and only a slight effect on the zinc deposit morphology (Fig. 6). The lack of effect of soluble Pb on the activation overpotential for the balanced electrolyte was similar to the minimal changes in morphology and crystallographic orientations observed for deposits obtained from this electrolyte.

Although both Pb and glue polarize the zinc deposition reaction, when they are both present in the electrolyte the glue seems to moderate the strong Pb polarization effect observed for the glue-free electrolyte. For solutions containing glue, increased lead in solution did not substantially change the crystallographic orientation from the preferred (1 0 1).

The addition of soluble Pb to the excess antimony electrolyte caused only a slight increase in the activation overpotential and also had no substantial effect on the deposit morphology and orientation. Antimony has a strong depolarizing effect on the zinc deposition reaction [2, 4] and the polarizing action of lead is not strong enough to counteract this effect.

#### 4. Conclusions

(a) 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 on the presence of other impurities such as antimony and glue.

(b) The amount of lead present in the zinc deposits was affected by the chemical form of the lead present in the electrolyte, by electrolysis conditions such as current density and temperature, and by the nature and concentration of impurities and additives in solution.

(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 lead up to 0.07% gave rise to greater overpotentials and more vertical deposit orientations. For lead concentrations greater than 0.07%, heavily pitted deposits with a basal orientation were obtained.

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