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On the effects of antimony and glue on zinc electrocrystallization behaviour

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An investigation has been made to determine the effects that additions of glue and antimony have on the electrowinning of zinc from acid sulphate solutions. In particular, the zinc crystal growth and cathode current efficiencies were studied in an attempt to establish a correlation between morphology and the nature of the additives. Operating conditions of 55 A ft^{-2} * and 35°C were used for most of the experiments with electrolyte concentrations of approximately 55 g l^{-1} zinc and $150 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$. Additional runs were made at 40, 75 and 100 A ft^{-2} at 30, 40 and 50°C in order to verify certain trends. Primarily by means of scanning electron microscopy (SEM) techniques, it was possible to categorize deposit morphologies according to the type and concentration of the additives. The general effect of antimony was to refine the grain size and cause the basal plane platelets to lie parallel to the substrate. Glue also caused some refinement, but caused the platelets to become aligned perpendicular to the substrate. Level deposits were obtained in the latter case, which would effectively prevent dendritic growths. A relationship between the relative amounts of glue and antimony in solution and the current efficiency was also obtained.

1. Introduction

Two of the principal problems encountered in electrowinning zinc from acid sulphate electrolytes are (1) maintaining high cathode current efficiencies and (2) producing level deposits. The effects of impurities on current efficiency are well appreciated and have been the subject of numerous experimental studies [1-3]. In most instances, however, the mechanisms by which certain concentrations of impurities become active or detrimental to current efficiency have not been identified. Determining these mechanisms is often complicated by what seems to be synergistic effects which occur when more than one impurity species is present in solution.

With regard to cathode deposit behaviour, a general statement can be made to the effect that: ions of those metals with standard potentials more negative than zinc, such as Al, Mg, Ca, and Na have

little effect; ions of metals which are marginally more positive than zinc, such as Cd, and Pb, tend to deposit at the cathode, decreasing its purity; ions of those metals which are much more positive than zinc and which are characterized by a high melting point and low hydrogen over-potential such as Pt, Ag, Au, Fe, Co, Ni, Cu decrease current efficiency. A more complex situation occurs with metals like Sb, As, Ge, Se and Te. Since they can form hydrides, the formation of which could serve as the cathodic reaction for localized corrosion, it is possible for the zinc to redissolve even while cathodically polarized. It is more difficult to generalize about the action of organic impurities, but experience has shown that although a few additives such as gum arabic and animal glue can be beneficial, most organics are harmful to zinc deposition.

Despite knowledge of these effects, zinc smelters often make intentional additions of impurities in order to control the deposition

* $1 \text{ A ft}^{-2} = 10.76 \text{ A m}^{-2} = 1.076 \text{ mA cm}^{-2}$.

process. At the Cominco Ltd. zinc plant at Trail, B.C., for example, 15–30 mg l⁻¹ of animal glue and 0.04–0.08 mg l⁻¹ of antimony are added to the electrolyte to obtain an empirically determined maximum metal recovery. The present practice is to purify the solution as much as possible and then add antimony and glue in controlled amounts rather than to try to purify consistently to a specific concentration of antimony.

The effects of impurities on deposit morphology, smoothness, and the tendency for zinc to adhere to aluminum starting sheets have received considerably less attention than their effects on current efficiency. However, those aspects of electrodeposition become very important when attempting to extend the deposition time from one day to two or three days. The lack of a suitable method of characterizing the rather rough deposits by microscope has hindered these studies in the past, but with the development of the scanning electron microscope (SEM), these studies are now relatively easy.

In the present study, the effects of antimony and glue additions on zinc crystal growth and on current efficiency were determined. The principal objective was to determine if microscopy techniques could be used to establish a correlation between morphology of the deposits and the nature of the zinc electrolyte additives. If so, it should be possible to detect when improper additions had been made to the electrolysis cells, by visual examination of the deposits.

2. Experimental

2.1. Electrolysis

The laboratory electrowinning cell is shown schematically in Fig. 1. Conventional electrode materials were used as indicated, with the anodes narrower than the cathode to prevent rough edge growths. A propeller stirrer was used in the cell to add to the mixing induced by electrode gassing. The neutral electrolyte, which was taken from the Trail sulphide leaching plant after final purification, had the following analysis: Zn 155 g l⁻¹, Mn 1.5 g l⁻¹, Fe 0.01 g l⁻¹, Cd 0.3 mg l⁻¹, Sb 0.02 mg l⁻¹, Co 0.4 mg l⁻¹, Ge 0.01 mg l⁻¹, Ni < 0.05 mg l⁻¹, Cl 102 mg l⁻¹. Operating conditions of 55 A ft⁻² and 35°C were used for most

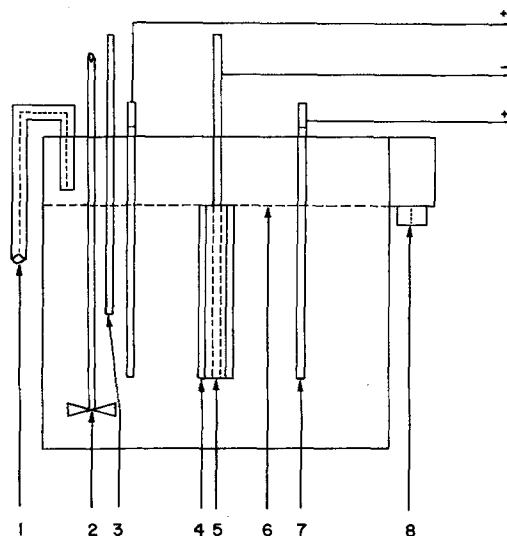


Fig. 1. Laboratory electrowinning cell. (1) Solution feeder; (2) agitator; (3) thermistor probe; (4) plastic edge strip; (5) aluminum cathode; (6) solution level; (7) conditioned Ag-Pb anode; (8) cell overflow.

of the experiments. Additional tests were conducted at 40, 75 and 100 A ft⁻² and at 30, 40 and 50°C to verify certain trends. The principal variables studied were the concentrations of antimony, added as potassium antimony tartrate, between 0 and 0.08 mg l⁻¹ and of glue, added as a water solution, between 0 and 100 mg l⁻¹ of electrolyte. Deposit duration varied between 1 and 30 h.

Cell solutions were prepared by adding H₂SO₄, water and the desired impurities to neutral electrolyte to give concentrations of 55 g l⁻¹ zinc and 150 g l⁻¹ H₂SO₄. Neutral electrolyte with the proper impurity additions was fed to the cell to maintain these concentrations of zinc and acid. Aluminum cathodes were initially prepared by wire brushing followed by a water wash, but because the grooves seem to affect deposit roughness, brushing was replaced by polishing with 600A wet emery paper. It was found that careful cell operation to avoid cell contamination was essential to obtain consistent results.

2.2. Deposit examinations

Sections of the deposits were examined by X-ray diffraction (XRD), scanning electron microscope (SEM) and optical microscope (OM) for crystal orientation and morphology. Little preparation



Fig. 2. Deposit from addition-free solution. (a) Macro view $\times 0.75$; (b) S.E.M. view of surface; (c) cross section, $\times 25$.

was required for the first two methods while for the last, the cross sections were mounted in lucite or epoxy and polished. Etching involved three immersions in nitric acid with repolishing on $0.05 \mu\text{m}$ alumina between each dip, to remove the cold worked layers and finally a dip in Palmerton's reagent (200 g CrO_3 , $15 \text{ g Na}_2\text{SO}_4$ and 1 liter of H_2O) to reveal the grain structure.

3. Results

From this investigation, it was possible to categorize deposit morphologies according to whether there was no addition, a balanced combination of glue and antimony, or a preponderance of one or the other of these two components. These four distinct morphology patterns are shown in Figs. 2–5 and are described below.

3.1. Addition-free solutions

The most prominent feature was the leaflike appearance of the cross section and the hexagonal platelets in the SEM photograph. These platelets were characteristic of the basal plane of the hcp zinc unit cell; they had a diameter of about $100 \mu\text{m}$ and were oriented between 30 and 70° to the substrate as shown in Fig. 2b. The general orientation was slightly preferred (1 0 1), (1 0 2), (1 0 3) with a notable lack of (0 0 2) and (1 0 0).

On these deposits, some nodules or clusters of platelets would grow further out into the solution than others as is evident on the deposit photograph in Fig. 2a. There was never a tendency to form dendrites or to short out, even for 30 h deposits at 100 A ft^{-2} , but some nodules were

about one-eighth of an inch wide in relief. The deposits were firm, but ductile enough to allow the $3 \times 5 \text{ in}^*$ cathodes to be bent with fracturing. Current efficiencies were consistently between 91 and 94%.

3.2. Glue addition

Low glue concentration-produced deposits were generally similar to those shown in Fig. 2 except that the platelet size had decreased to a diameter of about $25 \mu\text{m}$. Thus, the first noticeable effect of glue was platelet refinement. Increasing the glue content to 50 mg l^{-1} caused a rotation of the platelet angle from about 45 to 90° to the substrate so that only the (1 1 0) type orientation was present. This type of orientation yielded the 'finlike' growths evident in Figs. 3b and c.

The morphologies were a function of time in some instances, depending on the original glue concentration. Indications were that at lower glue content ($< 20 \text{ mg l}^{-1}$), the effect of glue diminished with deposition time so that the orientation which had been (1 1 0) after 2–4 h became more random by 16 h. At the higher glue contents ($> 30 \text{ mg l}^{-1}$), this (1 1 0) orientation was still predominant after 16 h.

20 h current efficiencies decreased linearly with glue content from 94% at 5 mg l^{-1} to 84% at 50 mg l^{-1} . This decrease seemed to be due to freely evolving hydrogen concurrent with zinc deposition rather than to zinc local cell corrosion, as is evident from the platelets in Fig. 3b where the edges are sharply defined rather than rounded.

* $1 \text{ in} = 2.54 \text{ cm}$.



Fig. 3. Deposit from solution with 50 mg l^{-1} glue addition: (a) Macro view, $\times 0.75$; (b) S.E.M. view of surface; (c) cross section, $\times 25$.

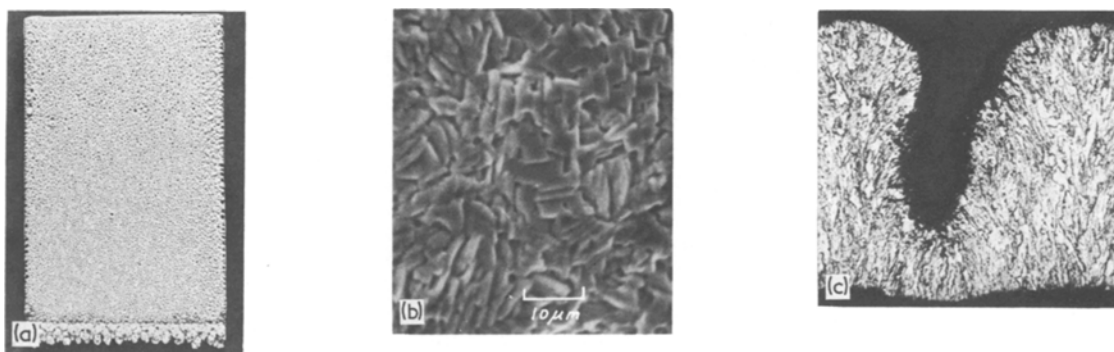


Fig. 4. Deposit from solution with 0.04 mg l^{-1} antimony addition: (a) Macro view, $\times 0.75$; (b) S.E.M. view of surface; (c) cross section, $\times 25$.

The results obtained, though limited in number, indicated that these deposits did not have a time dependent current efficiency.

Deposits from solutions with 30 mg l^{-1} or more of glue were quite brittle; as the (1 1 0) type orientation became dominant, attempts to flex the cathode by $20\text{--}30^\circ$ caused it to break along the bend line (Fig. 3a). Depressions or pits evidently due to adsorbed hydrogen bubbles were always present on 'glue type' deposits, as shown in Fig. 3a.

3.3. Antimony addition

In the Cominco tankroom antimony has been found useful in two ways. Problems with overly-tight bonding, or sticking, of zinc to aluminum starter sheets have been alleviated and current efficiency optimized by proper combination of antimony with glue. In order to gain an under-

standing of the role of antimony by itself, deposits were prepared with additions of $0\text{--}0.08 \text{ mg l}^{-1}$. The adherence problem could not be duplicated in the laboratory, possibly because the cathode size was so small, but a relationship between crystal structure and current efficiency was detected.

The deposit morphology was very similar for all antimony addition concentrations. The sharp angular nature of the crystals observed on the addition-free and glue solution cathodes was missing, as seen in Fig. 4b. The platelet edges appeared rounded, and there was a network of fine pits or pores at the crystalline boundaries. It appeared that this type of morphology was a result of re-resolution of the zinc; hence the more rounded appearance of the structure. Examination of the cross sections (Fig. 4c) showed that the tops of nodules continued to grow while the valleys between them dissolved toward the aluminum substrate. The resulting nodules became so weakly attached

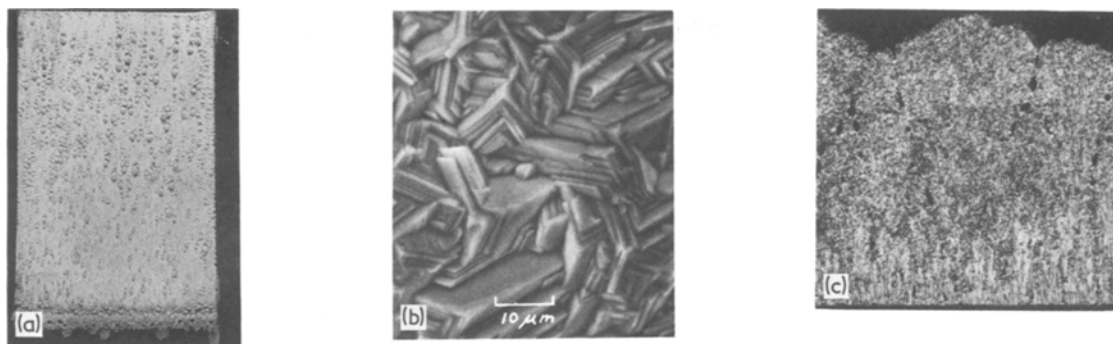


Fig. 5. Deposit from solution with addition of 0.04 mg l^{-1} antimony and 15 mg l^{-1} glue. (a) Macro view, $\times 0.75$; (b) S.E.M. view of surface; (c) cross section, $\times 25$.

that they would often fall off if the cathode was lightly tapped. It was observed that these valleys were generally associated with depressions on the aluminum surface, indicating an 'anti-levelling' characteristic of the antimony addition; such corrosion pitting is evident from Fig. 4a.

These were the most ductile deposits produced, often retaining a permanent set instead of fracturing at the bend line. XRD data from these deposits were erratic, possibly due to the rough outer surface; however, the back surfaces were strongly (0 0 2) oriented.

There were decreases in cathode current efficiency with increases of both deposit time and antimony content. For example, 2 h at 0.04 mg l^{-1} gave 87% compared to 70% for 0.08 mg l^{-1} ; 16 h at 0.08 mg l^{-1} gave 11.5%. In this entire program, it was noted that reproducible results could not be obtained for current efficiencies less than about 70%.

3.4. Glue and antimony addition

When glue and antimony were both present in the solution, it became apparent that deposit growth control could be afforded by whichever was present in excess. For example, a 'glue-type' morphology was produced for additions of 50–100 mg l^{-1} glue even with as much as 0.08 mg l^{-1} antimony, whereas with 0.08 mg l^{-1} antimony and only 5 mg l^{-1} glue, the 'antimony type' structure prevailed. It was possible to develop optimum combinations to maximize current efficiency; the data presented in Fig. 6 summarize the trends. Additions of 0.04 mg l^{-1} Sb and 15 mg l^{-1} glue, or 0.08 mg l^{-1} Sb and 30 mg l^{-1} glue represented approximate optimum combinations.

The morphology for these optimum additions was similar to that for the addition-free deposits except for a refined platelet size (Figs. 5b and c). Deposit rigidity was also similar. Current efficiencies were generally about 90%, i.e. not as high as from the addition-free solutions.

4. Discussion

4.1. General

Glue additions of 20–40 mg l^{-1} have been observed to increase the cathode polarization at low current densities as much as 30 mV, depending on electrolyte temperature [4]. These additions also caused the platelet angle change noted above. A third characteristic is that high glue cathodes are more difficult to melt, and yield a froth-like cover on the molten metal which would indicate inclusion of a glue dissociation product in the cathodes. It appears that the glue component activates sites for increased hydrogen evolution but is continually plated over with zinc. Thus, the amount of cathodic hydrogen produced is proportional to the surface coverage of glue which in turn is a function of the concentration. Despite the increase in the hydrogen current, the glue would seem to decrease the effective surface area sufficiently to cause increased polarization.

The platelet edges become the most preferred sites to receive zinc and these then tend to grow directly outward into the solution, with the result that the deposit is macroscopically level since the edge planes all tend to grow at a uniform rate.

When antimony has been present in excess, it has been found to deposit with the zinc [5], and to significantly increase the rate of hydrogen

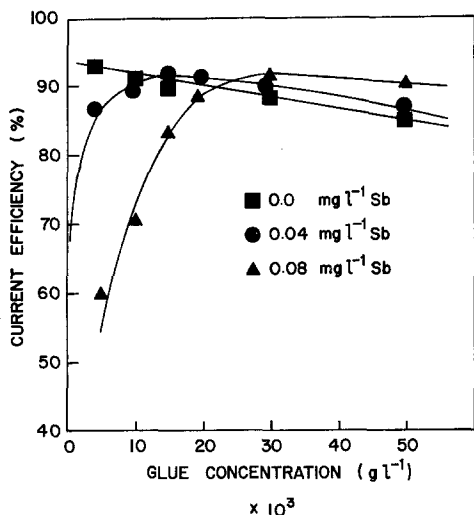


Fig. 6. Effect of glue addition on current efficiency for antimony containing solutions.

evolution. Fig. 4b shows the presence of basal plane platelets with rounded or corroded edges, possibly due to hydrogen evolution from (002) faces by a local cell corrosion mechanism with zinc dissolution from the edges as the anode reaction.

One of the assumptions made in this research was that the tartrate ion did not have a major influence on the behaviour of the antimony nor on the observed results. Although it is difficult to prove this absolutely, there are a number of factors which indicate that this is the case. First, when experiments are run with tartrate ion present, but without antimony, there were no observable detrimental effects on the current efficiency. However, the antimony could be added as the oxide and the poor current efficiencies were again noted. It therefore appears that the antimony concentration is the primary cause of the observed efficiency effects [5]. However, it must be recognized that the behavior of antimony in solution is most likely very complex. Therefore, possible interactions with other ions or chemical species in solution are always a definite possibility and their influence should not be underestimated.

The mechanism of the interaction of antimony and glue, whether a solution or cathode surface phenomenon, could not be elucidated. At the optimum combination levels the presence of one modified the controlling effect of the other, but not to the extent that platelet refinement was

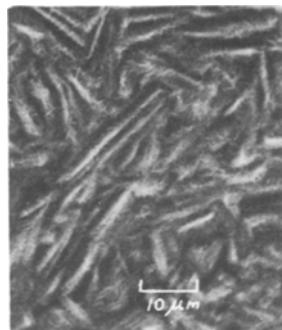


Fig. 7. Plant deposit from solution with excess glue; only platelet edges visible.

eliminated. The shape of the graph in Fig. 6 indicates that a wide variation of glue concentration can be tolerated with only a slight penalty in current efficiency. On the other hand, only a slight variation in antimony can be tolerated.

Each species migrates to the cathode to the same extent as if present individually; it is noteworthy, however, that when antimony is in excess, the local cell dissolution–re-deposition mechanism tends to concentrate it with increased deposit time. This concentration effect has also been reported for trace levels of nickel and silver in the electrolyte [6]. These impurities cause a drastic decrease in current efficiency with increase in deposit time.

The ductility results can be explained by realizing that the basal plane is the major slip plane for hexagonal close packed metals. As long as it is oriented at less than 60–70° to the substrate, slip and hence plastic deformation can occur. If this plane is oriented at 90° to the substrate, a bending moment represents a direct tensile stress on inter-basal plane adhesion and hence the limited ductility results. It is also possible that finely divided carbon or glue derivatives included in the deposit could function as hardening agents leading to brittleness.

4.2. Application to plant practice

4.2.1. *Growth models.* After determination of the microscopic properties, it becomes possible to recognize macroscopic characteristics of high and low current efficiency deposits. Since platelet angles are optimally inclined at 30–70° to the substrate it is essential that platelet colonies ‘balloon’

out from small nuclei, and some form of growth competition forces certain colonies to survive at the expense of less favourable ones. Thus, a good deposit would contain nodules of slightly varying size that would increase in diameter with increasing time. This growth is evident in Fig. 5c.

The use of a high glue solution produces small, uniform nodule size deposits with little variation in colony diameter with deposit time. The deposits are usually covered with pits formed by hydrogen bubbles clinging to the surface, and are brittle. A high antimony type deposit is ductile and exhibits a porous surface due to corrosion between the colonies or nodules of hexagonal platelets. In extreme cases nodules or 'peanuts' can be easily removed from the deposit surface.

4.2.2. Deposit control. Recently, one section of the Cominco plant was troubled by deposits which would separate from the aluminum except at the edges. The zinc would bow to the extent that a one inch gap existed between starter sheet and cathode zinc, leading eventually to short circuiting to the anodes. Examination of cathode samples showed only edge type growth as in Fig. 7, characteristic of a glue type deposit; they were also very brittle.

This information led to the discovery that the glue addition rate was approximately three times the normal value. Once the addition rate was corrected, deposit growth returned to its normal state. It would seem that an internal stress was developed between the initial coherent coating of zinc and subsequent layers, possibly due to incorporated glue, which caused a rupturing of the zinc-aluminum bond. This result of a high glue concentration was later confirmed when a three times normal addition of glue was intentionally added to

the cells, and the bowing condition developed once again.

5. Conclusions

- (1) There was a definite correlation between the cathode morphology and the additives in the electrolyte. Characteristic examples were presented for additive-free solutions, excessive glue or antimony solutions and for solutions with a balanced ratio of glue and antimony.
- (2) Current efficiency decreased moderately and in a linear fashion with increased glue content from 94% at 5 mg l^{-1} to 84% at 50 mg l^{-1} , but was drastically reduced with antimony addition.
- (3) Proper combinations of antimony and glue optimized the current efficiency, but yielded both a finer platelet size and slightly lower current efficiency than was obtained from addition free solutions.
- (4) Two mechanisms seemed to be involved in causing decreased current efficiency. On glue-type deposits, true cathodically-reduced hydrogen was evolved whereas on antimony type deposits local cell corrosion was operative.

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