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Zinc electrowinning from aqueous chloride electrolyte[*]

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Smooth, compact, dendrite-free zinc deposits can be electrowon from acid zinc chloride electrolyte using a diaphragm cell featuring catholyte agitation by air sparging. A correlation exists between the degree of zinc deposition polarization and the zinc deposit structure and orientation that can be used to evaluate the effectiveness of addition agents and, ultimately, to control deposit quality. The effect of impurities on the current efficiency for zinc deposition and on the morphology and orientation of 24 h zinc deposits is discussed.

1. Introduction

One objective of CANMET's Minerals Research Programme is to develop and evaluate energy efficient and environmentally acceptable extraction/refining processes which are capable of giving high yields of metals from complex sulphide ores. Detailed studies on the fine grained pyritic zinc–lead–copper–silver sulphide ore found in New Brunswick have been carried out and have demonstrated that > 90% recovery of the total metal values in the ore can be achieved practically only when a relatively low grade bulk concentrate is produced. However, this bulk concentrate is not amenable to conventional metal extraction processes. Two of the process options currently being developed for extracting valuable components from this concentrate are ferric chloride leaching [1] and anhydrous chlorination/oxidation at elevated temperatures [2].

A major problem associated with developing these chloride routes is the difficulty in obtaining smooth, compact, dendrite-free metal deposits from the resulting chloride solutions during the electrolysis operation. Recent work from this laboratory has been successful in developing conditions for electrowinning smooth, compact, dendrite-free, 24 h zinc deposits from chloride electrolyte [3]. This paper describes various aspects of zinc electrowinning from chloride electrolyte including: operating conditions, evaluation of addition agents using polarization techniques, the effect of impurities, individually and combined, on zinc deposition polarization and current efficiency and on the zinc deposit quality.

2. Experimental procedure

2.1. *Electrolysis cell*

Details of the cell design and construction are shown in Figs. 1 and 2. The cell was constructed from polycarbonate and consisted of three compartments: two anode compartments which were separated from a central cathode compartment by Dynel cloth diaphragms. The anode compartments were sealed to the atmosphere, and the chlorine gas and spent anolyte were withdrawn via glass tubes inserted through the anode seals (Fig. 2). The cathode compartment was open to the atmosphere so that the cathode could be easily removed from the cell to strip the zinc deposit. Vigorous agitation of the electrolyte over the cathode surface was achieved by sparging moist air from the bottom of the cell. Cathodes were cut from 0.4 cm commercial aluminium. An area of 25.3 cm^2 was masked off on each side of the cathode using electroplating tape (total surface area 50.6 cm^2). The tape also covered the sides of the cathode to minimize edge build-up and to facilitate stripping

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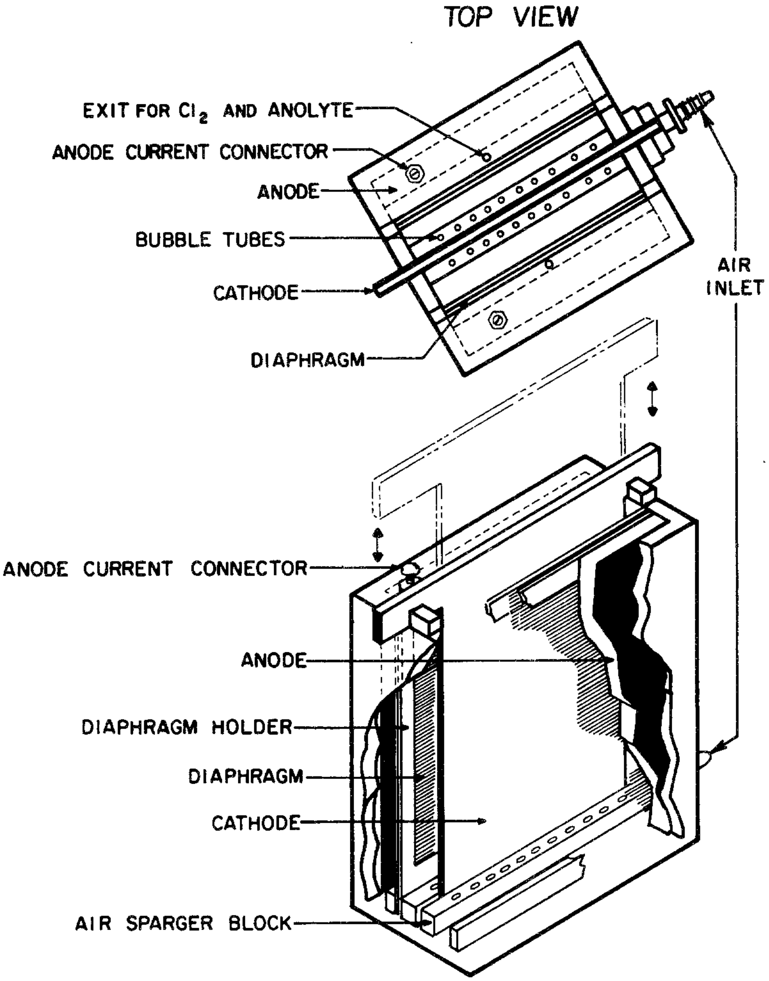


Fig. 1. Detail of the electrolysis cell.

of the zinc deposit. The dimensionally stable anodes (DSA) were 0.1 cm thick. These anodes extended through a slot in the anode seal and electrical contacts were bolted to the exposed tops of the anodes. Current to the cell was provided by a dc rectifier (6/30 A; 25 V). The cumulative ampere–hours (total coulombs) were recorded using an ampere–time meter.

2.2. *Electrolyte composition*

The electrolyte was prepared from reagent grade zinc chloride ($ZnCl_2$) and had the average analysis shown in Table 1. Each impurity is present at a concentration significantly less than 1 mg dm^{-3} and since good quality zinc deposits could be electrowon from this solution, purification was not required. Various addition agents and metallic cations were added to the electrolyte in order to assess their effect on the zinc deposit structure and quality. The impurities copper, cobalt, cadmium, nickel and lead were added to the electrolyte as aliquots from stock solutions prepared from their respective chloride salts. Antimony additions were made as a potassium antimony tartrate solution and germanium was added as a stock solution prepared from its oxide. The desired concentration of organic additives (Pearl glue, Separan NP10, Percol 140 and various tetraalkylammonium chlorides) in the electrolyte was obtained by adding the appropriate amount of their respective stock solutions.

2.3. *Experimental procedure*

2.3.1. 24 h deposits. The cell electrolyte was maintained at 35° C, using a thermistor controller and small immersion heater located in the cathode

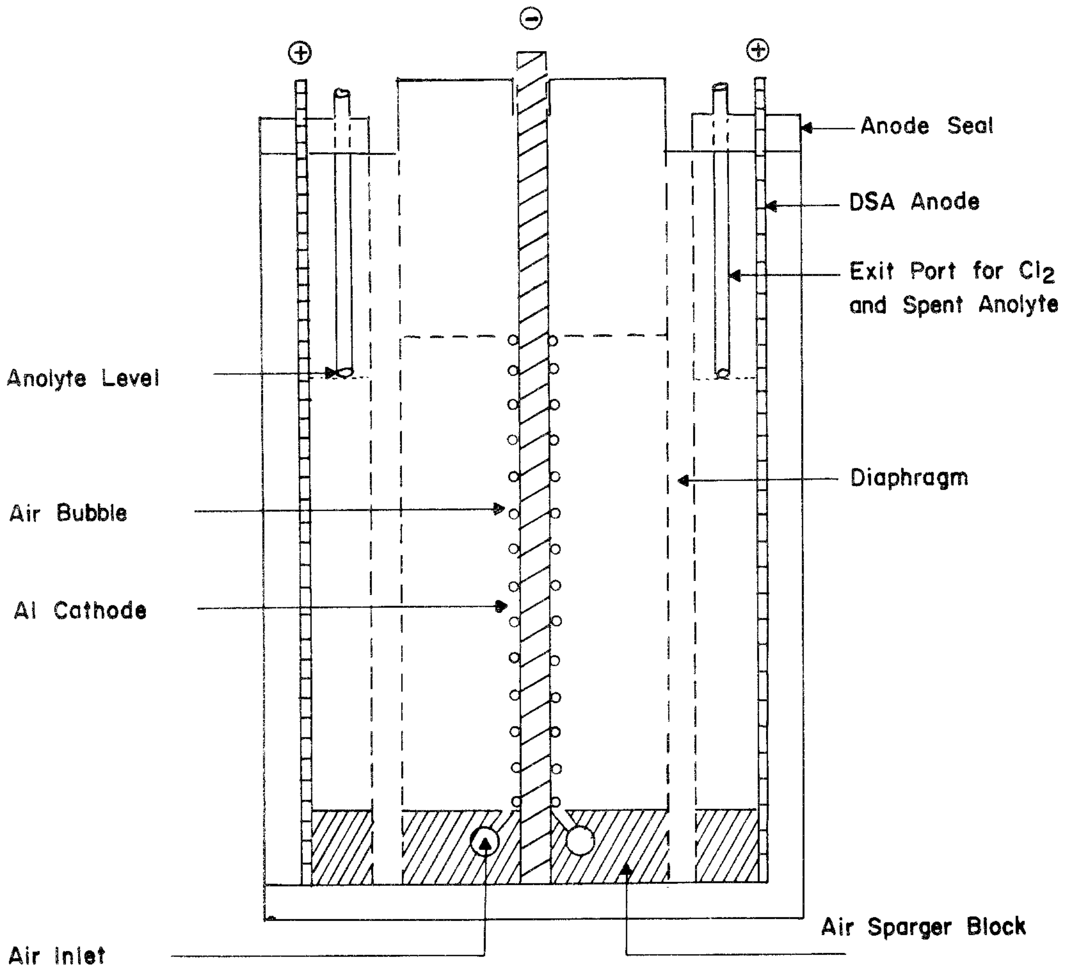


Fig. 2. Cross-sectional drawing of the electrolysis cell.

compartment of the cell. Feed solution was supplied to the cathode compartment at a rate of 2.2 $cm^3 min^{-1}$ using a tubing pump. This feed rate was sufficient to maintain the Zn concentration in the cell at 15 $g dm^{-3}$ over the duration of the electrolysis. Both the cell and the feed electrolytes contained the appropriate level of addition agent.

A constant head of solution was maintained in the cathode compartment by withdrawing solution and Cl_2 from the anode compartments from below the cathode level. Moist air was continuously sparged over the cathode faces at a rate of ≈ 5 $dm^3 min^{-1}$, via the air sparger block at the base of the cathode.

Prior to use for the first time, the exposed faces of the aluminium cathode were hand-polished, using 600 grit polishing paper. At the end of the electrolysis period, the cathode was pulled from the cell, and the zinc deposit was rinsed, stripped, dried and weighed. The surface of the stripped cathode was also water rinsed and dried;

Table 1. Average analysis of the $ZnCl_2$ electrolyte. Electrolyte contains 15 $g dm^{-3}$ Zn, 0.12 $mol dm^{-3}$ HCl

Element	*Concentration* ($mg dm^{-3}$)
As	< 0.3
Cd	0.2
Co	< 0.03
Cu	0.03
Fe	< 0.02
Ni	< 0.03
Pb	< 0.1
Sb	< 0.03

no additional surface treatment was necessary before it was used in subsequent tests. Samples of anolyte and catholyte were analysed for Zn, free acid and total Cl after each test.

Sections of the deposits electrowon at 323 A m^{-2} (30 ASF) 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. Deposit cross sections were examined by optical microscopy (OM) techniques. Deposits were analysed for their impurity content using the following procedure.

Small pieces were cut at random from the selected deposits. The pieces were accurately weighed and dissolved in hot 60% nitric acid. The resulting solution was cooled and diluted with water to a total volume of 100 cm^3. The solution was then analysed by atomic absorption (AA) spectrophotometry for zinc and the particular impurity of interest. The percentage of the metallic impurity in the zinc was calculated from the AA data.

The current efficiency (CE) was calculated from the weight of the zinc deposit and the number of coulombs passed. The energy requirement (ER) was calculated in terms of kWh kg^{-1}, using the average cell voltage recorded during each test and the weight of the zinc deposits.

2.3.2. Polarization studies. Cyclic voltammetry experiments were conducted to determine the polarization characteristics of zinc deposition in the presence of addition agents and impurities. The tests were done on 300 cm^3 acid zinc solutions (15 dm^{-3} Zn, 0.12 mol dm^{-3} HCl) held at 35° C. The additives and/or impurities were introduced into the electrolyte five minutes prior to the start of the tests. The aluminium cathode was polished with 600 grit paper and washed with acetone and distilled water prior to every test. Platinum foil was used as the anode and a saturated calomel electrode (SCE) for the reference electrode. The potential was cycled between -0.8 and -1.2 V versus SCE at a potential sweep rate of 1 mV s^{-1}. The cyclic voltammograms were recorded as i versus E plots on an x–y recorder.

Table 2. Standard electrolysis conditions

Parameter	*Value*
Cell electrolyte	15 g dm^{-3} Zn, 0.12 mol dm^{-3} HCl 15 mg dm^{-3} TBACl
Feed electrolyte	30 g dm^{-3} Zn, 0.12 mol dm^{-3} HCl 15 mg dm^{-3} TBACl
Current density	323 A m^{-2} (30 ASF)
Temperature	35° C
Feed rate	2.2 cm^3 min^{-1}
Air sparging rate	4750 cm^3 min^{-1}
Aluminium cathode	0.005 m^2
Anodes	DSA
Time	24 h

3. Results and discussion

3.1. *Standard electrolysis conditions*

Standard electrolysis conditions were established that consistently produced smooth, compact, dendrite-free 24 h zinc deposits. These standard conditions are summarized in Table 2 and a typical 24 h zinc deposit is shown in Fig. 3a. The zinc deposit is smooth with bevelled edges showing no signs of dendritic growth. A cross section of the deposit is shown in the photomicrograph (x 70), Fig. 3b, which indicates the deposit to be compact and relatively even. The typical morphology of zinc deposits obtained for the experimental conditions given in Table 2 is shown in the SEM photomicrograph, Fig. 3c. The refined grain size is caused by the presence of 15 mg dm^{-3} TBACl in the electrolyte. This deposit morphology is very similar to that obtained previously [4] for 1 h zinc deposits. The preferred orientation, relative to the ASTM standard for zinc powder, was [1 0 1], [1 1 0]. Similar deposit structures were also obtained under these conditions (Table 2) for deposition times > 48 h, Fig. 4. However, the 75 h deposit is characterized by a rough surface and pronounced edge growth.

Some typical current efficiency (CE), and energy requirement (ER) values for zinc electrowinning from aqueous chloride electrolyte are summarized in Table 3. The average value for the energy requirement, 3.5 kWh kg^{-1}, obtained under these conditions (Table 2) is the same as that for commercial zinc electrowinning from acid sulphate electrolyte [5]. Semiquantitative spectrochemical analysis of sections of the deposits obtained from the conditions listed in Table 3 indicated 99.97% Zn.

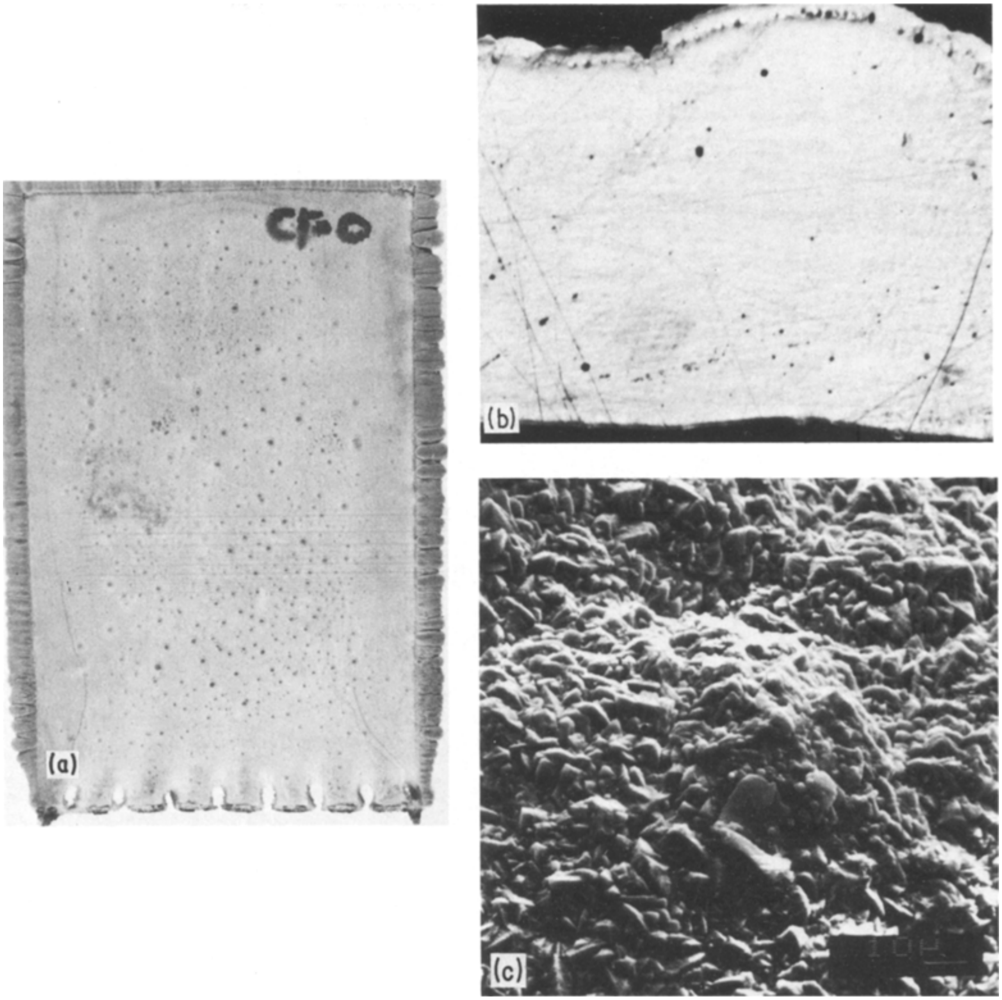


Fig. 3. Zinc deposit characteristics obtained under standard electrolysis conditions. (a) × 1; (b) × 56; (c) × 558.

3.2. *Zinc deposition polarization*

3.2.1. Addition-free. A typical cyclic voltammogram obtained for addition-free acid zinc chloride electrolyte is shown in Fig. 5. The cycle was initiated at − 0.8 V SCE and the potential was scanned to about − 1.1 V SCE at a rate of 1 mV s^{-1}. The voltammogram in Fig. 5 is divided into 5 regions for discussion purposes.

Region AB. The small current which flows in this region is attributed to hydrogen ion reduction on aluminium; this current increases with increasing hydrogen ion concentration in the electrolyte.

Region BC. At point B, the overpotential is sufficient to initiate zinc deposition and from B

Table 3. Current efficiency and energy requirement standard electrolysis conditions

Time (h)	*CE* (%)	*ER** (kWh kg^{-1})
24	99.4	3.7
24	96.3	3.2
24	96.7	3.3
48	92.5	3.0
75	93.0	3.6

* Approximate values, based on average cell voltages.

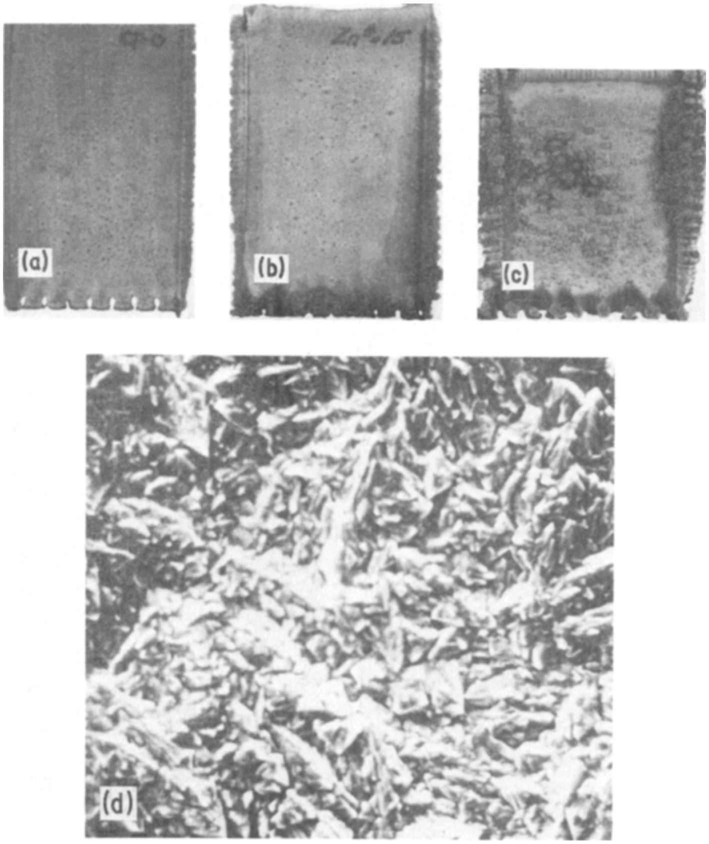


Fig. 4. Effect of deposition time on zinc deposit characteristics obtained under standard electrolysis conditions. (a) 24 h, (b) 48 h, (c) 75 h, (d) 48 h, × 650.

to C simultaneous reduction of zinc and hydrogen ions occurs. This co-deposition occurs on both the aluminium and freshly nucleated zinc, the latter predominating with increasing potential.

Region CD. At point C the scan direction is reversed and, from C to D, zinc and hydrogen ions continue to be discharged on both zinc and aluminium surfaces. Point D is the crossover potential from cathodic to anodic current. The difference between point D and point B, the decomposition potential, is a measure of the zinc deposition overvoltage.

Region DE. As the potential becomes less negative zinc dissolution increases and the rate reaches a maximum at point E.

Region EF. As the anodic zinc reaction proceeds, the surface is eventually depleted of zinc causing a decrease in current; at point F, the anodic current is zero and the surface is depleted of zinc.

3.2.2. The effect of addition agents. The effect of various addition agents including Pearl glue, Separan NP10, Percol 140, tetraethylammonium chloride (TEACl), tetrapropylammonium chloride (TPrACl), tetrabutylammonium chloride (TBACl) and tetrapentylammonium chloride (TPACl), on the zinc deposition polarization curve was also determined using the cyclic voltammetry technique. The effect of 15 mg dm^{-3} TBACl on zinc deposition polarization is shown in Fig. 6; only the ABC cathodic portion of the voltammograms is shown. The presence of TBACl in the electrolyte results in a significant increase in the zinc decomposition potential (≈ 80 mV) and hence an increase in zinc deposition polarization. Similar curves were

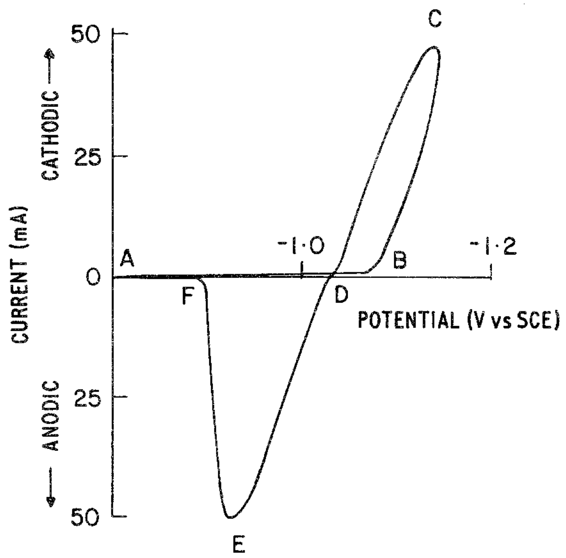


Fig. 5. Voltammogram for an electrolyte containing 15 g dm^{-3} Zn and 0.12 mol dm^{-3} HCl. Scan rate, 1 mV s^{-1}.

obtained for the other addition agents and their relative effect on zinc deposition polarization is as follows:

$$\text{Addition-free} \approx \text{TEACl} \approx \text{TPrACl} < \text{Percol 140} < \\ < \text{TBACl} < \text{TPACl} < \text{Separan NP10} < \text{glue}.$$

Additives which produce the largest increase in polarization generally result in zinc deposits having the finest grain size and a [1 1 0] preferred orientation. In a previous study [6] it was found that TBACl and low concentrations of TPACl (10 mg dm^{-3}) gave the smoothest, most compact, fine-grained deposits on a 24 h basis. Although Separan NP10 and glue were stronger polarizers they were not as effective as TBACl in smoothing the deposits. It is possible that these additives hydrolyse in the electrolyte over a period of time and hence their effectiveness may be reduced. Thomas and Fray [7] have shown that the polarization effect of proteinous additives such as glue decreases with solutions that have been aged or boiled prior to electrolysis. Percol, which is less polarizing than TBACl, did not refine the grain size or change the deposit orientation [6]. It was also shown previously [6] that additives which increased the zinc deposition polarization resulted in an increase in CE and changed the deposit orientation from [1 1 2], [1 1 4] to [1 1 0].

Thomas and Fray [7] studied the effect of additives on zinc electrowinning from zinc chloride electrolyte at high current densities, i.e., > 2000 A m^{-2}. Of the additives studied, the only one in common with the present work was Pearl glue, which they also found to have the strongest polarizing effect on zinc deposition. They also observed that the additive which has the greatest polarizing effect produced the highest current efficiency. At the higher current densities employed by Thomas and Fray [7] they observed that 1 h zinc deposits electrowon from an electrolyte containing 40 mg dm^{-3} Pearl glue had a preferred [1 0 2] [1 0 3] orientation, compared to a preferred [0 0 2] in the absence of additives. At the lower current densities used in the present work, the addition of 30 mg dm^{-3} Pearl glue to the electrolyte changed the preferred orientation of the 24 h zinc deposit from [1 1 2], [1 1 4] to [1 0 0] [1 1 0].

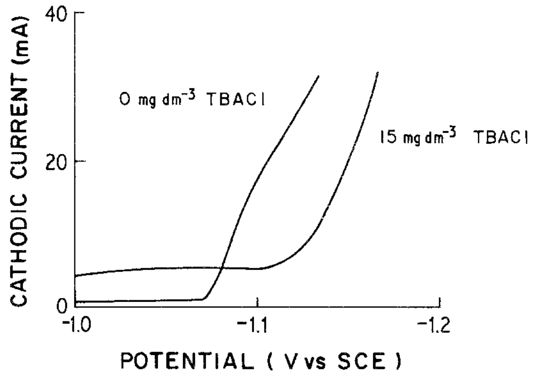


Fig. 6. Effect of TBACl on cathodic polarization curve for zinc deposition. 15 g dm^{-3} Zn + 0.12 mol dm^{-3} HCl. Scan rate, 1 mV s^{-1}.

3.2.3. Effect of impurities. The effect of 10 mg dm^{-3} Cu, Co, Cd and Ni, 5 mg dm^{-3} Pb, 1 mg dm^{-3} Ge and 0.2 mg dm^{-3} Sb on zinc deposition polarization was determined using the cyclic voltammetry technique. Figure 7 shows the effect of these impurities on cathodic polarization curves for zinc deposition from an electrolyte containing 15 g dm^{-3} Zn and 0.12 mol dm^{-3} HCl. Compared to the impurity-free solution (heavy black line, Fig. 7) both Cu and Sb depolarized the zinc deposition reaction whereas Ni, Co, Ge, Cd and Pb increased zinc polarization. Thus, in terms of increasing polarization the impurities may be ranked as follows:

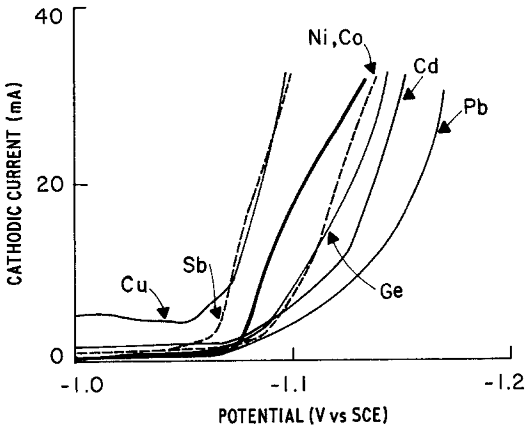


Fig. 7. Effect of impurities on zinc deposition polarization curves obtained from an addition-free electrolyte. 15 g dm^{-3} Zn + 0.12 mol dm^{-3} HCl. Scan rate, 1 mV s^{-1}.

$$\text{Sb.} \approx \text{Cu} < \text{addition-free} < \text{Co} < \text{Ni} <$$
$$< \text{Ge} < \text{Cd} < \text{Pb}.$$

The effect of the same concentration of these impurities on zinc deposition polarization in the presence of 15 mg dm^{-3} TBACl is shown in Fig. 8. The heavy black curve in Fig. 8 is that for a solution containing no added impurity, only 15 mg dm^{-3} TBACl. The presence of TBACl off-set the depolarization effects of Sb and Cu as the polarization curves for these impurities were similar to that for the additive-free solution, heavy dashed curve. The polarization caused by Ni, Co and Ge was increased in the presence of TBACl whereas that caused by Cd and Pb was slightly reduced.

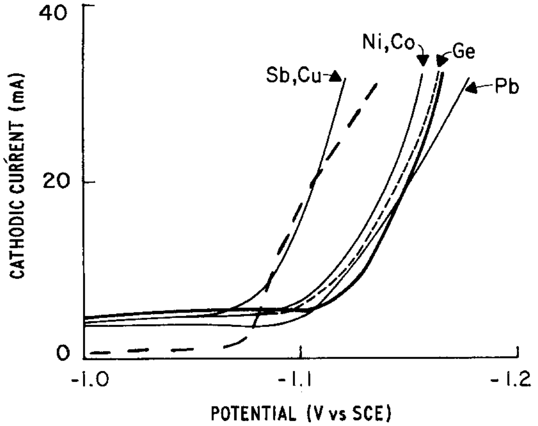


Fig. 8. Effect of impurities on zinc deposition polarization curves obtained from an electrolyte containing 15 mg dm^{-3} TBACl. 15 g dm^{-3} Zn + 0.12 mol dm^{-3} HCl. Scan rate, 1 mV s^{-1}.

Thus, in the presence of TBACl, the order of impurities in increasing zinc deposition polarization is as follows:

$$\text{Addition-free} < \text{Sb} < \text{Cu} < \text{Co} < \text{Ni} <$$
$$< \text{Ge} < \text{Cd} < \text{Pb}.$$

3.3. *Effect of impurities on 24 h zinc deposits*

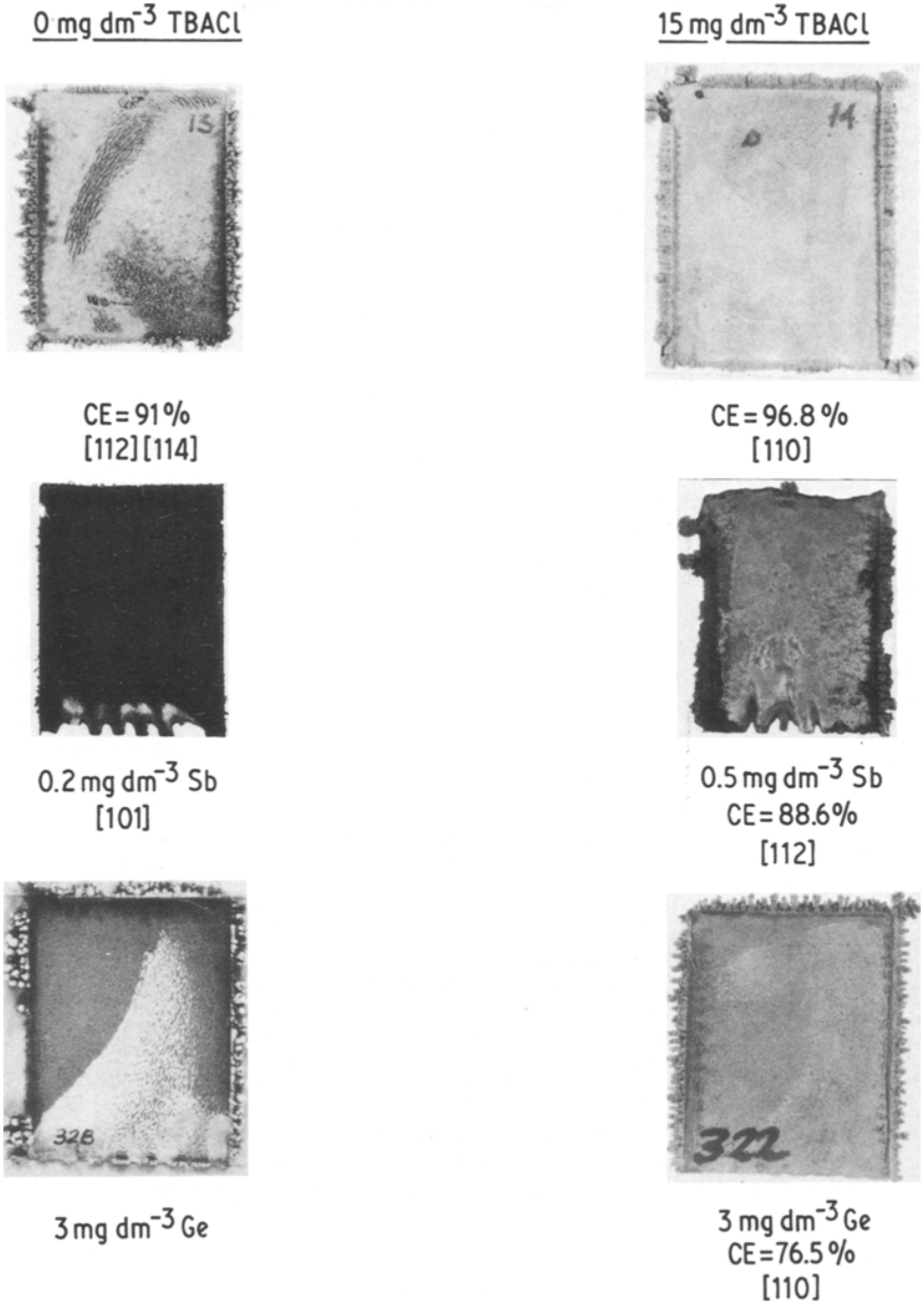
The effect of Sb, Cu, Ge, Co, Ni, Cd, Pb and Fe on the 24 h zinc deposits electrowon from acid zinc chloride electrolyte in both the presence and absence of TBACl is shown in Figs. 9–11. In all cases the deposits electrowon from the electrolyte containing TBACl were superior to those electrowon from the 'addition-free' electrolyte.

Antimony had the most detrimental effect on the 24 h zinc deposits, Fig. 9. In the absence of TBACl, the deposit electrowon from an electrolyte containing 0.2 mg dm^{-3} Sb consisted of a black powder. With TBACl present in the electrolyte, black powder formed only along the edges of the deposit when the Sb concentration reached 0.5 mg dm^{-3}; however, the remainder of the deposit surface was rough and nodular.

In the absence of TBACl, 3 mg dm^{-3} Ge produced a rough deposit surface with a large resolution area and increased edge growth; the deposit could not be stripped from the Al blank. With TBACl, the deposit electrowon from an electrolyte containing 3 mg dm^{-3} Ge was readily stripped, had a smooth surface but the deposit edges tended to be dendritic; the CE was only 76.5%, Fig. 9.

In the absence of TBACl, the deposits electrowon from electrolytes containing 5 mg dm^{-3} Cu, 30 mg dm^{-3} Co and 10 mg dm^{-3} Ni were rough and exhibited dendritic edge growth, Fig. 10. The addition of TBACl eliminated dendritic growth and in the case of Co, the deposit surface was smooth. For Cu and Ni, the deposit surfaces showed some nodular growth and the CE was > 93%. Copper, which depolarized zinc deposition, was more detrimental to deposit quality than either Ni or Co, both of which polarized zinc deposition.

Iron levels in the electrolyte as high as 200 mg dm^{-3} were reached before the deposit became rough, black and dendritic, Fig. 11. The addition of TBACl vastly improved this deposit by smooth-


0 mg dm^{-3} TBACl

15 mg dm^{-3} TBACl

CE = 91%
[112] [114]

CE = 96.8%
[110]

0.2 mg dm^{-3} Sb
[101]

0.5 mg dm^{-3} Sb
CE = 88.6%
[112]

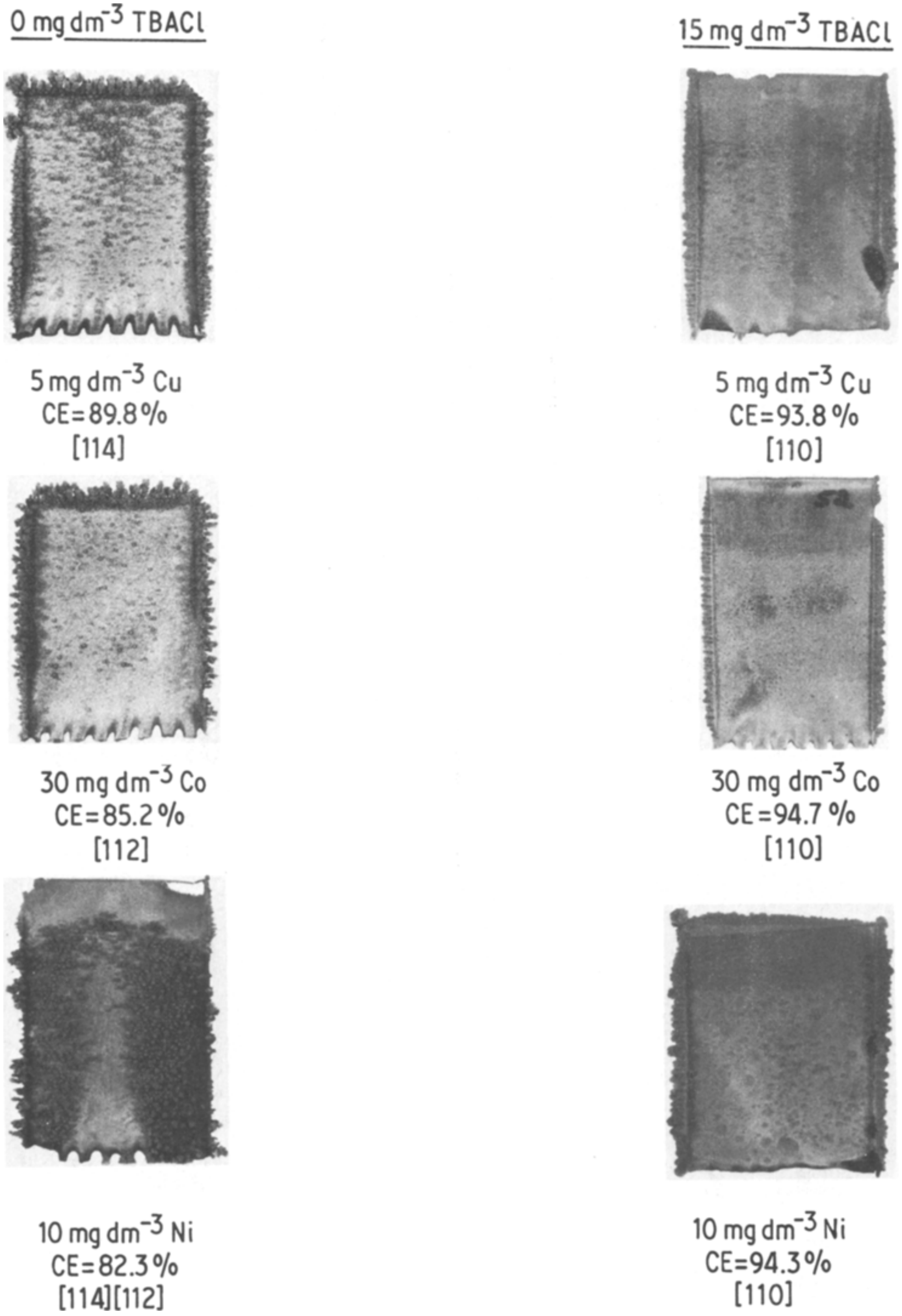
3 mg dm^{-3} Ge

3 mg dm^{-3} Ge
CE = 76.5%
[110]

Fig. 9. Photographs (X 0.5) showing the effects of antimony and germanium on zinc deposit quality in the presence and absence of 15 mg dm^{-3} TBACl.

ing the surface, eliminating dendrite edge growth and increasing the CE from 77.3 to 89.6%. Low levels of Cd and Pb (5 mg dm^{-3}) resulted in rough, dendritic deposits, Fig. 11. The presence of TBACl improved both these deposits although the surface of the deposit electrowon from the Pb-containing electrolyte showed signs of re-solution.

The effect of certain impurities on zinc deposition current efficiency is summarized in Table 4. Over the concentration range 0–10 mg dm^{-3}, anti-



0 mg dm^{-3} TBACl

15 mg dm^{-3} TBACl

5 mg dm^{-3} Cu
CE=89.8%
[114]

5 mg dm^{-3} Cu
CE=93.8%
[110]

30 mg dm^{-3} Co
CE=85.2%
[112]

30 mg dm^{-3} Co
CE=94.7%
[110]

10 mg dm^{-3} Ni
CE=82.3%
[114][112]

10 mg dm^{-3} Ni
CE=94.3%
[110]

Fig. 10. Photographs (× 0.5) showing the effects of copper, cobalt and nickel on zinc deposit quality in the presence and absence of 15 mg dm^{-3} TBACl.

mony was most detrimental in lowering the CE followed by Ge and Cu. For other impurities such as Co, Ni, Cd, Fe and Pb in this concentration range, the CE was > 93%.

Certain impurities such as Cu, Pb and Cd co-deposited with the zinc. Fig. 12 shows a correlation between impurity concentration in the electrolyte and the impurity content of the zinc

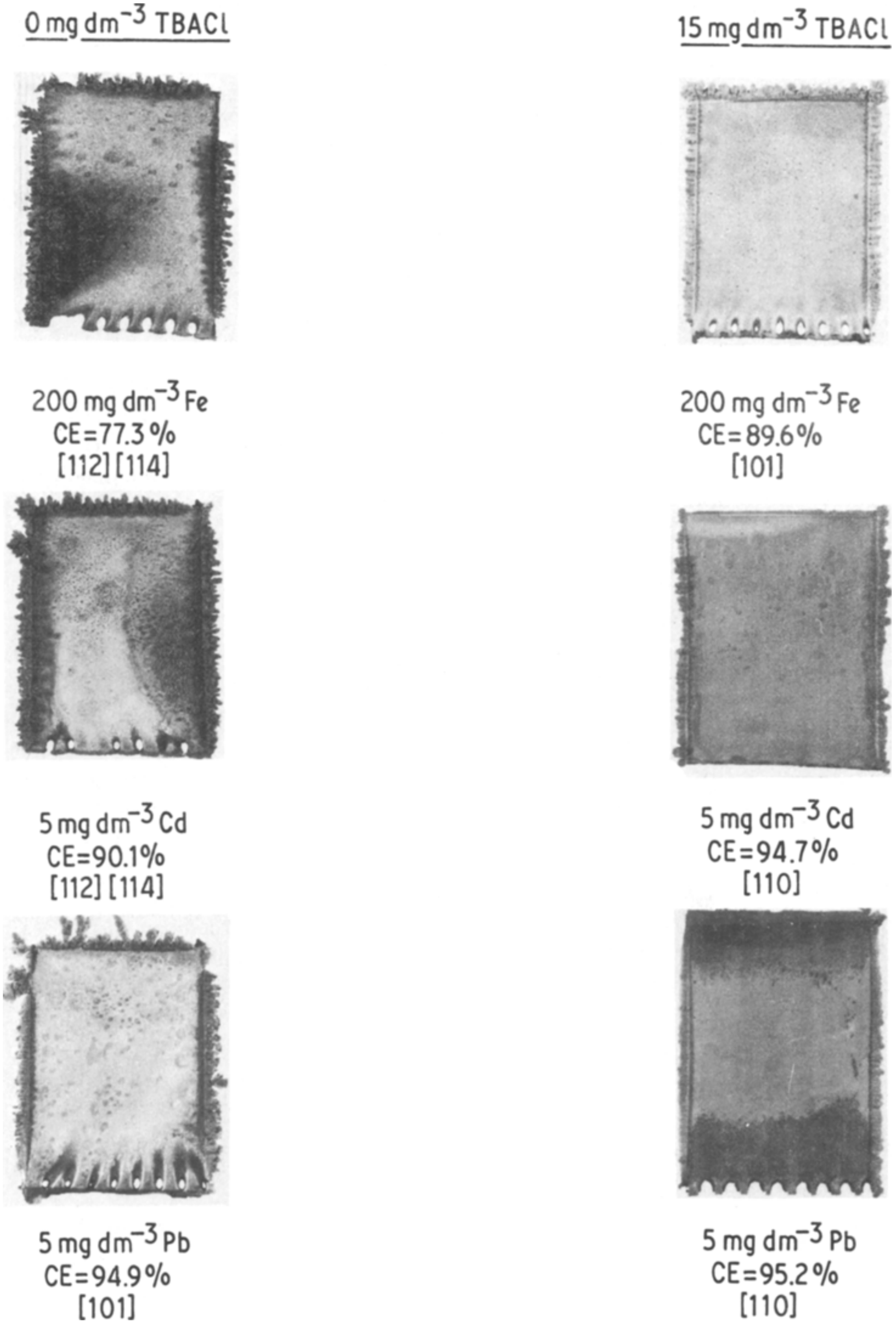


Fig. 11. Photographs (X 0.5) showing the effects of iron, cadmium and lead on the quality of zinc deposits in the presence and absence of 15 mg dm^{-3} TBACl.

deposits. As indicated in Fig. 12, for each mg dm^{-3} impurity in the electrolyte, the impurity content of the zinc deposits increased by $\approx 0.0045\%$. Nickel and cobalt did not co-deposit with zinc to any significant extent.

The effect of individual impurities on the 24 h

Table 4. Effect of certain impurities on the zinc deposition current efficiency. Conditions, 15 g dm^{-3} Zn, 0.12 mol dm^{-3} HCl, 15 mg dm^{-3} TBACl 24 h, 323 A m^{-2}, 35° C

Impurity (mg dm^{-3})	*Current efficiency (%)*		
	Sb	Ge	Cu
0	96.3	96.3	96.3
0.1	96.0	97.3	–
0.2	93.5	–	–
0.5	85.6	–	94.1
1.0	78.2	88.1	93.3
2.0	–	79.9	–
3.0	–	76.5	93.4
5.0	–	–	93.8
10.0	–	–	91.2

zinc deposits are summarized in Table 5. Both Sb and Ge decreased the CE and roughened the deposit whereas Cu lowered the CE and co-deposited with Zn. Lead roughened the deposit and also co-deposited with zinc; cadmium co-deposited with zinc whereas Co to 30 mg dm^{-3} had no significant effect on zinc deposition. Thus a relative ranking of impurities in order of their decreasing detrimental effect on zinc deposition is as follows:

$$\mathrm{Sb} > \mathrm{Ge} > \mathrm{Cu} > \mathrm{Pb} > \mathrm{Cd} > \mathrm{Ni} > \mathrm{Fe} > \mathrm{Co}.$$

A comparison of the results obtained from the polarization studies with those obtained from the 24 h deposits indicates that some correlation or trends exist. Both Sb and Cu which tend to depolarize zinc deposition also cause a significant decrease in CE and promote rough, dendritic deposits. Cadmium and lead which strongly polarize zinc deposition do not decrease the CE but co-deposit with zinc. Cobalt and nickel which cause intermediate polarization have the least effect on the zinc deposition both in terms of CE and deposit quality. Germanium, although it increases zinc deposition polarization, also decreases the CE.

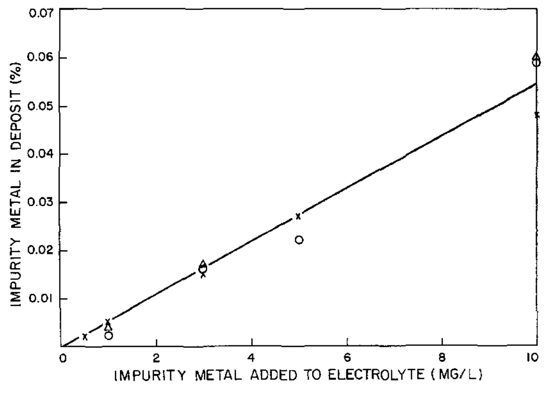


Fig. 12. Correlation between impurity concentration in the electrolyte and impurity content of the zinc deposits. 0.0045% = 1 mg dm^{-3}. X, Cu, ○, Pb, △, Cd.

Table 5. Summary of impurity effects. Conditions, 15 g dm^{-3}, 0.12 mol dm^{-3} HCl, 15 mg dm^{-3} TBACl 35° C, 323 A m^{-2}, 24 h

Impurity effect	*Impurity*
Decrease CE	Sb, Ge, Cu, Fe
Roughen Deposit	Sb, Ge, Pb, Ni
Co-Deposit	Cu, Pb, Cd
None	Co

3.4. *Evaluation of the electrolyte*

In addition to providing useful information regarding the effect of impurities on zinc deposition, cyclic voltammograms may provide a means to characterize the zinc electrolyte prior to electrolysis. For certain impurities the voltammograms have characteristic features which may be useful for predicting which impurity is active in the electrolyte. Examples are shown in Fig. 13, where the cyclic voltammogram for an impurity-free solution, heavy black curve, is compared to those obtained from solutions containing nickel and germanium.

The interesting features of these curves appear during the back scan; i.e., after the potential has

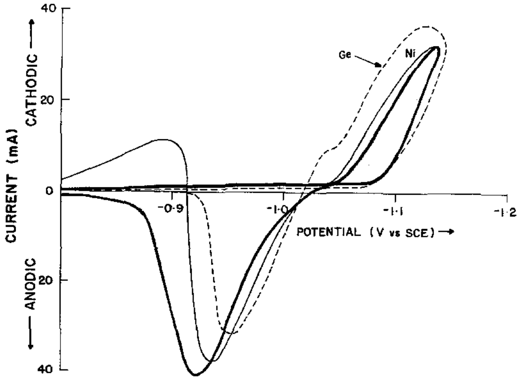


Fig. 13. Voltammograms for electrolytes containing no added impurity, 1 mg dm^{-3} germanium and 10 mg dm^{-3} nickel. 15 g dm^{-3} Zn + 0.12 mol dm^{-3} HCl. Scan rate, 1 mV s^{-1}.

10 mg dm^{-3} Co; 0.5 mg dm^{-3} Sb
CE=80.4%
[105]

10 mg dm^{-3} Co; 5 mg dm^{-3} Cu
CE=83.5%
[105]

10 mg dm^{-3} Co; 5 mg dm^{-3} Pb
CE=97.3%
[110]

10 mg dm^{-3} Co; 10 mg dm^{-3} Ni
CE=92.5%
[110]

10 mg dm^{-3} Co; 5 mg dm^{-3} Cu;
0.2 mg dm^{-3} Sb
CE=83.2%

10 mg dm^{-3} Co; 1 mg dm^{-3} Cu;
0.2 mg dm^{-3} Sb; 5 mg dm^{-3} Pb
CE=61.0%

Fig. 14. Photographs (× 0.5) showing the effects of various combinations of impurities on zinc deposit quality in the presence of 15 mg dm^{-3} TBACl.

been reversed. In the case of Ge, dashed curve, a shoulder appears prior to the crossover potential. At this point, vigorous hydrogen evolution occurs at the cathode. At higher acid concentration, e.g., 0.6 mol dm^{-3} HCl, the shoulder becomes a peak and the anodic portion of the curve is substantially reduced. This indicates that zinc re-solution has occurred prior to the crossover potential; i.e., when the current is still cathodic. In the case of nickel there is a substantial current for hydrogen ion reduction after the Zn has been anodically stripped from the cathode. Vigorous hydrogen evolution is observed at this point which indicates that some Ni must remain on the surface of the Al cathode. A similar effect was observed by Wang *et al.* [8] for a nickel-containing zinc sulphate electrolyte. Although further development is required, polarization techniques appear promising as an analytical tool to determine the quality of zinc chloride electrolyte prior to electrolysis.

3.5. *Effect of combined impurities*

The combined effects of various impurities on the zinc deposit quality and on the CE were also investigated using an electrolyte containing 15 g dm^{-3} Zn, 0.12 mol dm^{-3} HCl and 15 mg dm^{-3} TBACl. In one series of studies, the level of cobalt in the electrolyte was fixed at 10 mg dm^{-3} and various concentrations of antimony, copper, lead and nickel were added. The results are summarized in Fig. 14. The combined effects of the impurities, Co + Sb and Co + Cu on zinc deposition proved to be synergistic in that they were greater than the sum of the individual effects of Co, Sb and Cu. The CE was decreased, the deposits were rough and dendritic and the preferred orientation was changed from [1 1 0] to [1 0 5].

The combined presence of Co + Pb and Co + Ni had no significant effect on the deposit quality, orientation or CE; these quantities were comparable to those obtained for similar levels of single impurities. The presence of three or four impurities in the electrolyte; e.g., Co + Cu + Sb or Co + Cu + Sb + Pb, resulted in extremely rough, powdery zinc deposits.

The combined effect of Cu + Sb on the CE and deposit quality was more deleterious than that of

5 mg dm^{-3} Cu; 0.2 mg dm^{-3} Sb
CE = 86.0%
[110]

10 mg dm^{-3} Pb; 0.2 mg dm^{-3} Sb
CE = 97.3%
[110]

10 mg dm^{-3} Ni; 0.2 mg dm^{-3} Sb
CE = 81.7%

10 mg dm^{-3} Ni; 5 mg dm^{-3} Cu
CE = 85.2%

Fig. 15. Photographs (× 0.5) showing the effects of various combinations of impurities on zinc deposit quality in the presence of 15 mg dm^{-3} TBACl.

either impurity alone, Fig. 15. The combination of Sb + Pb actually increased the CE although the deposit was characterized by significant nodular growth along the edges. Nickel in combination with antimony and copper resulted in rough powdery deposits as indicated in Fig. 15.

4. Conclusions

Smooth, compact, dendrite-free 24 h zinc deposits were electrowon at > 96% current efficiency from zinc chloride electrolyte containing 15 g dm^{-3} Zn, 0.12 mol dm^{-3} HCl and 15 mg dm^{-3} TBACl using a diaphragm cell and catholyte agitation by air sparging.

Addition agents such as TBACl, Separan NP10, and glue which increased zinc deposition polarization produced fine-grained deposits having a preferred [1 1 0] orientation. TEACl and Percol 140 which caused only a slight or moderate polarization did not refine the zinc deposit grain size and resulted in a [1 1 2] preferred deposit orientation. Although TBACl was not as strongly polarizing as glue and Separan NP10, it was the most effective additive over a 24 h deposition period presumably because both glue and Separan hydrolyse during electrolysis.

Impurities such as Sb and Cu, which decreased zinc deposition polarization, had the most detrimental effect on the zinc deposits, resulting in decreased CE and rough, dendritic deposits. Cadmium and lead, which increased zinc deposition polarization, did not decrease the CE but did co-deposit with the zinc. Cobalt and nickel, which caused an intermediate degree of zinc deposition polarization, had the least effect on the quality of the zinc deposit and on the CE. The role of germanium appears to be more complex since it increased zinc deposition polarization but decreeased the CE.

The presence of TBACl in the electrolyte offset the effect of individual impurities to some extent and, in certain cases, e.g., Co, a high impurity concentration could be tolerated. A relative ranking of impurities in terms of their detrimental effect on zinc deposition is:

$$\mathrm{Sb} > \mathrm{Ge} > \mathrm{Cu} > \mathrm{Pb} > \mathrm{Cd} > \mathrm{Ni} > \mathrm{Fe} > \mathrm{Co}.$$

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