Effects of certain impurities on zinc electrowinning in high-purity synthetic solutions

A. R. AULT

Research Department, Electrolytic Zinc Company of Australasia Ltd, Risdon Works, GPO Box 377D, Hobart, Tasmania 7001, Australia

E. J. FRAZER*

CSIRO Institute of Minerals Energy and Construction, Division of Mineral Products, PO Box 124, Port Melbourne, Victoria 3207, Australia

The individual effects of lead, copper, nickel, cobalt and antimony on zinc electrowinning were evaluated by measurements in high-purity synthetic solutions, free from additives. The coulombic efficiency (QE) of zinc electrodeposition was determined over 2 h under mass transfer-controlled conditions at a temperature of 35°C and a current density of $400\,A\,m^{-2}$ in a solution of $0.8\,M$ $ZnSO_4$ + $1.07\,M\,H_2SO_4$. Antimony had a very detrimental effect on QE causing decreases of ~ 5 and 50% at 4 and $14\,\mu g\,l^{-1}$, respectively. Antimony also exerted a strong grain-refining effect and changed the deposit orientation from random to (112) to (004) with increasing concentration. Lead had a small beneficial effect on QE at the electrode rotation rate employed ($20\,s^{-1}$). It also exerted a grain-refining effect and changed the deposit orientation from random to (102), (103), (104), to strong basal (004), (002) with increasing concentration. Copper, nickel and cobalt had minor effects on QE, with reductions at $5\,mg\,l^{-1}$ of 0.8, 0.3 and 0.3%, respectively. The effects of copper on morphology and orientation were very concentration dependent, but with a general trend towards grain-refining and random orientation. Nickel promoted coarse-grained deposits and changed the orientation from random to (114), (102) to (204), (102) with increasing concentration. Cobalt had the least effect on the morphology of the deposit, although it gradually increased the basal plane orientation with increasing concentration.

1. Introduction

The zinc electrowinning process is particularly sensitive to many solution impurities, the general effects of which have been surveyed in early literature dealing with plant practice [1-4]. Over the past decades there have also been numerous laboratory studies dealing with the effects of ranges of impurities in zinc electrowinning [5-15]. While most electrolytic zinc plants follow the same general procedures, the optimal operating conditions at each plant have usually been arrived at by experience and depend on the type of zinc ore treated and its impurity content. When changes in the process stream or the introduction of new control procedures are contemplated, it is then, in particular, that detailed knowledge on the effects of the various solution impurities is necessary.

The present investigation is limited to five commonly occurring solution impurities, viz. lead, copper, nickel, cobalt and antimony. Some preliminary results for nickel and copper have already been reported [16]. While a substantial amount of literature on the effects of the above impurities already exists, much of the information is inconsistent or unable to be compared because of differences in electrodeposition conditions and/or solution composition and purity. The approach taken here is based on the identification of the intrinsic effects of impurities on coulombic efficiency (QE) and zinc deposit morphology by studies in high-purity synthetic solutions which have been carefully characterized [17, 18]. While the practical situation is much more complex because of the number of impurities/additives involved simultaneously, this work is intended to form the baseline for studies of combinations of impurities and the identification of synergistic effects. It should also be a useful aid in the recognition of the most injurious impurities and in making preliminary decisions regarding necessary solution purification procedures.

2. Experimental details

2.1. Determination of coulombic efficiency

The glass electrochemical cell and the fabrication of the $\sim 2\,cm^2$ aluminium rotating disc electrodes (to fit a Tacussel Type EDI rotator) have been described previously [16, 19]. The solution in the working com-

* Author to whom correspondence should be addressed.

partment ($\sim$ 120 ml) was deoxygenated by nitrogen sparging before electrolysis because dissolved oxygen caused a decrease in QE [19]. Zinc deposits were produced at a temperature of 35° C and a current density of 400 A m^{-2}, consistent with typical plant practice; the electrode rotation rate was fixed at 20 rev s^{-1}. The QE for zinc electrodeposition was determined using Faraday's Law from the weight of zinc deposited after 2 h (equivalent to $\sim$ 200 mg Zn); the zinc deposit was stripped and weighed separately as described previously [17]. The constant-current source was a PAR 173 Potentiostat/Galvanostat equipped with a PAR 179 Digital Coulometer (accuracy 0.1%). The QE could be determined very precisely, with a standard deviation of better than 0.2% [18].

2.2. Solution preparation

The solution composition chosen was 0.8 M ZnSO$_4$ + 1.07 M H$_2$SO$_4$, representative of that used in low-acid ($\sim$ 100 g l^{-1}) zinc electrowinning processes. The solutions were prepared by dissolving 99.9999% zinc (Koch-Light) in sulphuric acid solution (BDH Aristar); zinc dissolution was catalysed by contacting the zinc with a platinum grid [17]. The resultant slightly acidic zinc sulphate solution was further acidified with sulphuric acid (BDH Aristar) and made up to volume with deionized water (MILLI-Q, Millipore Corporation). The above preparation method results in an extremely pure solution with virtually no trace impurities detectable by either anodic stripping voltammetry or inductively coupled plasma [17]. The various trace impurities were introduced into the catholyte by pipetting appropriate volumes of concentrated aqueous stock solutions prepared from PbCl$_2$, CuSO$_4 \cdot$ 5H$_2$O, NiSO$_4 \cdot$ 7H$_2$O, CoSO$_4 \cdot$ 6H$_2$O and K(SbO)C$_4$H$_4$O$_6 \cdot$ 0.5H$_2$O.

2.3. Examination of deposits

Morphological examination of the zinc deposits involved visual inspection and optical microscopy using a Wild type 376788 low-power ($\times$ 50) binocular microscope. The preferred orientation of the deposits was evaluated by X-ray diffraction (XRD) using a Philips type PW1010 unit. The relative intensities of the various crystal planes were calculated using the ASTM index values for zinc powder, with the (101) plane as the standard [20].

3. Results and discussion

3.1. Effects of lead

MacKinnon et al. [21] conducted the most recent investigation of the influence of lead in an industrial zinc electrowinning solution of similar bulk composition (55 g l^{-1} Zn + 150 g l^{-1} H$_2$SO$_4$) to that used here. They found that the effect of lead (6 mg l^{-1}, 35° C) on QE was current-density dependent, producing an increase of 0.7% at $\sim$ 400 A m^{-2} and a reduction

of 1.5% at $\sim$ 800 A m^{-2}. Increasing amounts of lead in the zinc deposits progressively changed the preferred orientation from (112) to (101) to (100) to finally a poorly crystalline (002) structure. The lead content of the zinc deposits was dependent on the solution concentration of the lead, the form in which the lead was added, the current density and the presence of antimony or glue. Fukubayashi et al. [5] added high concentrations (g l^{-1}) of PbO$_2$, PbSO$_4$ or PbO$_2$/PbCO$_3$ to a 65 g l^{-1} Zn + 200 g l^{-1} H$_2$SO$_4$ synthetic solution and produced 2 h deposits at 40° C and 820 A m^{-2}. They reported increases in QE in the 0.8–3.2% range for PbO$_2$ and PbO$_2$/PbCO$_3$ additions and a decrease of 0.8% for PbSO$_4$; the preferred orientations of the deposits ranged from mixed to (002). Other workers [6, 11, 13] have reported increases [11, 13] and decreases [6] in QE of similar magnitudes in synthetic and commercial solutions. The interaction of lead with other impurities may also be important in determining QE [22, 23]; this particular area will be discussed in a subsequent communication dealing in more detail with the electrochemical behaviour of lead in zinc electrowinning [24].

The present results on the effects of lead in high-purity solutions are presented in Fig. 1 and Table 1. The QE increased slowly with increasing lead concentration, with a disproportionately larger effect at $\leqslant$ 2 mg l^{-1}. Such changes in QE are of a similar magnitude to some of those reported by MacKinnon et al. [21] at 430 A m^{-2} and 35° C. The percentage of lead removed from solution during each electrolysis (see Table 1), and therefore presumed to have co-deposited with the zinc, was almost constant at $\sim$ 70% consistent with its electrodeposition being diffusion controlled.

When producing special-high-grade zinc, strontium carbonate is normally added to plant solutions to help control the lead concentration; values of $<$ 1 mg l^{-1} are typical. The increase in QE observed in this work at 1 mg l^{-1} was only 0.3%. However, when making high-grade zinc, pure lead anodes are used and strontium carbonate is not added to the solution; lead levels are usually in the range 2–4 mg l^{-1} and a higher QE is observed. In a subsequent communication [24], it will be shown that even at such levels lead, on its own, is not expected to exert a major influence on QE in practice; this followed from data indicating that mass transfer rates in plant cells are much lower than in the present laboratory cell. The effect observed in the plant could be due to the interaction of lead with other impurities/additives or perhaps related to the longer deposition times. It has already been reported [21] that the amount of lead co-deposited with the zinc depends on the presence of glue and antimony.

Without added lead, a random crystal orientation was obtained with the (102), (104), (103), (114), (203) planes having relative intensities slightly greater than the major (101) plane (see Table 1). While the (102), (103), (104) planes dominated at 1 mg l^{-1} added lead, the basal planes (004), (002) assumed dominance over the range 2–5 mg l^{-1}. Coinciding with this change in
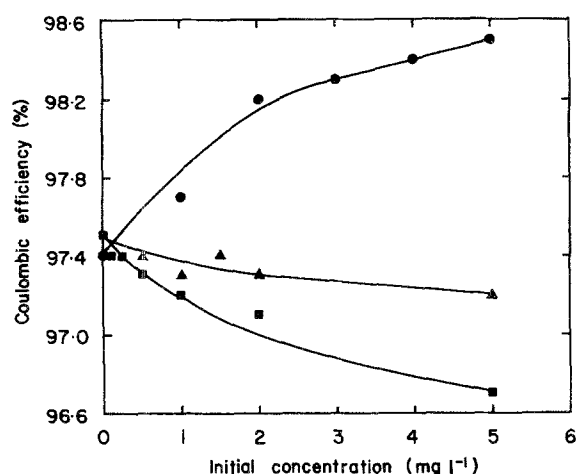
Fig. 1. Coulombic efficiency for zinc electrodeposition as a function of initial lead, copper and nickel concentration in a solution of 0.8 M $ZnSO_4$ + 1.07 M H_2SO_4 (35° C, 400 A m^{-2}, 2 h, 2 cm^2 Al cathode rotating at 20 s^{-1}): ●, lead; ■, copper; ▲, nickel.

crystal orientation, there was a major reduction in the size of the zinc crystals (grain-refining) and a much more cratered and honeycombed surface was observed; the colour changed from a reflective silver to a dark dull grey. It is interesting to note that there was also a marked change in the slope of the QE vs lead concentration curve (Fig. 1) at ~2 mg l^{-1}.

3.2. Effects of copper

Copper is generally considered to be a deleterious impurity in zinc electrowinning [1–4]. It is readily removed from the solution by conventional zinc dust purification provided the conditions are carefully controlled. However, it may be introduced if holes develop in the filter cloth during zinc dust filtering or by corrosion of bus-bars and hanger bars. It is known that trace copper is co-deposited with zinc [25, 26] reducing product quality. The effect of copper on QE has been investigated by a number of workers [5, 6, 10–14, 26] under a variety of conditions. Reports on the effect on QE of 5 mg l^{-1} Cu have ranged from −0.2 to −9% [5, 6, 12, 13, 26], depending on the electrolysis conditions, solution purity and method of QE measurement. The most recent study of the effects of copper in an industrial zinc electrowinning solution was conducted by MacKinnon [26]. QEs were measured at current densities in the range ~200–450 A m^{-2} from solutions containing up to 50 mg l^{-1} Cu; at 35° C, 430 A m^{-2} and 5 mg l^{-1} Cu, the QE

decreased by only 0.6%. MacKinnon [26] found that the copper content of the zinc deposit increased with increasing copper concentration (in the solution) and decreasing current density; the grain size of the deposit was also reduced in the presence of copper. At high current densities and low copper concentrations, the preferred orientation remained unchanged at (112); at lower current densities and higher copper concentrations, the orientation changed to predominantly (002).

The results of the present study on the effects of copper in high-purity solutions are given in Fig. 1 and Table 2. The QE decreased monotonically from ~97.5 to ~96.7% at 5 mg l^{-1} Cu; this change in QE is consistent with the results reported by MacKinnon [26]. The percentage of copper removed from solution during each electrolysis, and therefore presumed to have co-deposited with the zinc, was in the range 55–80%. (Williams [25] has shown that the electrodeposition of copper from zinc sulphate solutions (250 g l^{-1}, pH 4.2) was diffusion controlled.) Copper levels in the plant are typically < 0.2 mg l^{-1} [20]; the decrease in QE observed here at 0.25 mg l^{-1} was only 0.1%. Since the mass transfer rate in the plant is presumed to be much less than in the laboratory (see Section 3.1), then the effect of copper (alone) on QE is not expected to be significant in practice. Obviously, the occurrence of large concentrations of copper in the solution via corrosion reactions or ineffective purification control should still be avoided if only to maintain product purity. Again, the role of other impurities cannot be neglected, with recent work pointing to the interaction of copper with antimony and glue [26].

The crystal orientation (see Table 2) in going from 0 to 0.25 mg l^{-1} initial copper, changed from random to (114), (102). Also, in this range copper appeared to increase crystal size and make the surface rougher. Between 1 and 2 mg l^{-1} Cu some grain-refining was observed; further grain-refining occurred at 5 mg l^{-1} Cu. Crystal orientation changes were also observed with a random structure in which the planes (101), (102), (103), (114), (211), (203), (204), (112) all showed similar intensities.

3.3. Effects of nickel

The effects of nickel on QE, zinc morphology and preferred orientation have been studied by a number of workers [5, 6, 10–14, 27, 28]. There is no agreement

Table 1. Variation of coulombic efficiency and preferred orientation of deposit with addition of lead

Initial Pb (mg l^{-1})	Final Pb (mg l^{-1})	Pb removed (%)	Change in QE (%)	Preferred orientation
Nil	< 0.01	–	–	Random
1.0	0.25	75	0.3	(102), (103), (104)
2.0	0.6	70	0.8	(004), (002)
3.0	0.9	70	0.9	(004), (002)
4.0	1.4	65	1.0	(004), (002)
5.0	1.7	66	1.1	(004), (002)

Table 2. Variation of coulombic efficiency and preferred orientation of deposit with addition of copper

Initial Cu $(mg\,l^{-1})$	Final Cu $(mg\,l^{-1})$	Cu removed (%)	Change in QE (%)	Preferred orientation
Nil	< 0.01	–	–	Random
0.10	0.02	80	−0.1	(114), (102)
0.25	0.08	68	−0.1	(114), (102)
0.50	0.18	64	−0.2	Random
1.0	0.40	60	−0.3	Random
2.0	0.90	55	−0.4	Random
5.0	1.30	74	−0.8	Random

about the magnitude of its effect on QE [5, 6, 10–14, 27], with estimates ranging from zero [12] to a decrease of 13.8% [5] at $5\,mg\,l^{-1}$, depending on the electrolysis conditions, solution purity and method of QE measurement. The wide range of results may be due partly to reported induction-time effects which are apparently strongly dependent on temperature and sulphuric acid concentration [9, 10, 28]. The extent to which nickel co-deposits with zinc is doubtful, although Wang *et al.* [29], using voltammetry, have observed a nickel-activated hydrogen evolution peak which they considered might be useful for monitoring nickel concentration in solution. Both Fratesi *et al.* [28] and Maja *et al.* [10] claimed that the deposition of nickel is not mass transfer controlled, even at very low nickel concentrations. In recent work, MacKinnon *et al.* [27] showed that the effect of nickel on QE was very concentration dependent with a drop of $\sim 2\%$ at $5\,mg\,l^{-1}$, $\sim 70\%$ at $10\,mg\,l^{-1}$ and zero net zinc deposition at $20\,mg\,l^{-1}$; these tests were conducted over 1 h at $430\,A\,m^{-2}$ and $35°\,C$ in a commercial zinc electrowinning solution $(55\,g\,l^{-1}\ Zn + 150\,g\,l^{-1}\ H_2SO_4)$. They also found that while the addition of nickel $(10\,mg\,l^{-1})$ had no significant effect on deposit morphology or preferred orientation, there was a grain-refining effect.

The results of the present study on the effects of nickel in high-purity solutions are given in Fig. 1 and Table 3. The QE declined very slowly with increasing nickel concentration, with most of the decrease occurring in the $0{-}1\,mg\,l^{-1}$ range; the decrease in QE at $5\,mg\,l^{-1}$ Ni was only $\sim 0.3\%$. The analytical method was not sufficiently precise, especially at low concentrations, to detect any changes in the nickel concentration of the solution following electrolysis. However, pilot-scale deposition tests conducted at the Electrolytic

Table 3. Variation of coulombic efficiency and preferred orientation of deposit with addition of nickel

Initial Ni $(mg\,l^{-1})$	Change in QE (%)	Preferred orientation
Nil	–	Random
0.25	−0.1	(114), (102)
0.50	−0.1	(114), (102)
1.0	−0.2	(114), (102)
1.5	−0.1	(211), (105)
2.0	−0.2	(114), (102)
5.0	−0.3	(204), (102)

Zinc Company of Australasia Limited (EZ) over 24–48 h in the presence of antimony and glue have shown that some nickel is electrodeposited with the zinc. On the present results, it is not possible to predict any significant effect of nickel (alone) on QE in practice, particularly with typical plant levels of $\sim 0.2\,mg\,l^{-1}$ Ni [20]. Also, this study suggests that any induction-time effect occurs at longer deposition times (i.e. > 2 h) or is associated with the presence of other impurities; certainly, the interaction of nickel with antimony and glue has already been reported [22, 27].

The crystal orientation (see Table 3) changed from a relatively random pattern with (102), (104), (114), (204) as major planes (i.e. greater than (101)), to an orientation dominated by the (114), (102), (204), (203) planes (in that order), when the nickel concentration was in the range $0.25{-}2.0\,mg\,l^{-1}$. At $5\,mg\,l^{-1}$ Ni the (114) plane was replaced by the (204) plane. The zinc crystals also became coarser as the nickel level was increased, with a very coarse-grained, reflective, cratered deposit obtained at $5\,mg\,l^{-1}$ Ni; this effect was evident even at $0.25\,mg\,l^{-1}$ Ni.

3.4. Effects of cobalt

The effects of cobalt and its mode of action in zinc electrowinning have been the subject of numerous studies over the years [5, 6, 10–13, 27, 30–36]. The spread of results for the effect of cobalt on QE [5, 6, 10–13, 30–34] is similar to that for nickel (see Section 3.3) with reported decreases at $5\,mg\,l^{-1}$ ranging from zero [27, 33] to $\sim 14\%$ [30], depending on the electrolysis conditions, solution purity and method of QE measurement. The mechanism of action of cobalt is apparently quite involved with reports of induction-time effects [10, 31], complex voltammetry [34–36] and interactions with antimony [22, 27, 34, 37], germanium [4], arsenic [32] and copper [22]. Bellobono [33] reported a diffusion-controlled deposition mechanism. The most recent work on cobalt has been conducted by Fosnacht and O'Keefe [32] and MacKinnon *et al.* [27], both groups reporting gradual decreases in QE with cobalt concentration (2–4% at $10\,mg\,l^{-1}$ Co); the former authors also reported a strong negative interaction between cobalt and acid, producing large losses in QE at $> 6\,mg\,l^{-1}$ Co and $\sim 150\,g\,l^{-1}\ H_2SO_4$. MacKinnon *et al.* [27] found that up to $20\,mg\,l^{-1}$ Co in solution had no significant effect on either deposit morphology or preferred orientation.
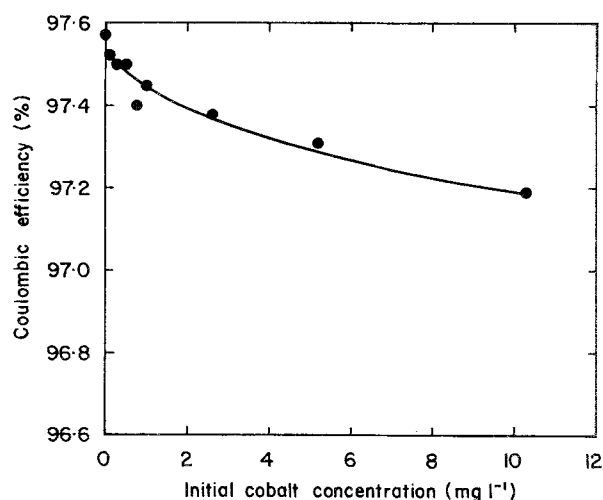
Fig. 2. Coulombic efficiency for zinc electrodeposition as a function of initial cobalt concentration in a solution of 0.8 M ZnSO$_4$ + 1.07 M H$_2$SO$_4$ (35° C, 400 A m^{-2}, 2 h, 2 cm^2 Al cathode rotating at 20 s^{-1}).

The present results on the effects of cobalt in high-purity solutions are summarized in Fig. 2 and Table 4. Like nickel, the QE declined very slowly with increasing cobalt concentration; the QE decreased by only ~ 0.3% at 5 mg l^{-1} and ~ 0.4% at 10 mg l^{-1}, results very similar to those reported by MacKinnon et al. [27]. Again, the analytical method was not sufficiently precise to detect any changes in the cobalt concentration of the solution following electrolysis; apparently little or no cobalt was co-deposited with the zinc, in agreement with previous studies [30, 33]. While most zinc electrowinning solutions contain very low cobalt levels (e.g. < 0.2 mg l^{-1}), some plants operate at much higher levels (e.g. ~ 8 mg l^{-1} in the feed solution [38]), due to the source of zinc ore and/or the cost of its removal. Even in the latter case, based on the present results, the effect of cobalt (alone) on QE would not be expected to be significant. Again, this study suggests that any induction-time effect occurs at deposition times greater than 2 h or is associated with the presence of other impurities; the laboratory evidence for such phenomena is substantial [4, 9, 10, 22, 27, 31, 32, 34–37]. The effect of cobalt might also be complicated by possible changes in

Table 4. Variation of coulombic efficiency and preferred orientation of deposit with addition of cobalt

Initial Co (mg l^{-1})	Change in QE (%)	Preferred orientation
Nil	–	Random
0.10	−0.1	(114), (103)
0.26	−0.1	(114), (204)
0.52	−0.1	(114), (102)
0.77	−0.2	(114), (204)
1.0	−0.1	(204), (112)
2.4	−0.2	(101), (204)
5.2	−0.3	(114), (102)
7.7	−0.3	(204), (101)
10.3	−0.4	(004), (103)

oxidation state [31], particularly in an undivided cell and where permanganate ion might be present.

Cobalt had only a minor effect on the physical appearance of the zinc deposits, generally making the deposit surface rougher, more reflective, and slightly increasing platelet size. It also modified the crystal orientation (see Table 4), increasing the strength of the (114), (204) and (102) planes at low concentrations, and gradually increasing the basal plane orientation (002), (004) at higher levels. The (004) plane dominated at 10 mg l^{-1} Co.

3.5. Effects of antimony

There have been numerous laboratory studies on the effects of antimony in zinc electrowinning [5, 6, 11–14, 27, 30, 32, 34, 36, 39–42]. While antimony has long been recognized as one of the most toxic solution impurities with respect to QE [1–4], its apparently beneficial addition, particularly in combination with glue, to produce a 'balanced' or optimal solution [20, 32, 36, 39–42], suggests that its behaviour is complex. Indeed, the proper combination of antimony and glue which gives rise to a preferred morphology has also been shown to optimize QE under certain conditions [20, 39]. The available data on the effect of antimony on QE [5, 6, 11–14, 30, 32, 39, 40] show a similar scatter to the data for cobalt, nickel and copper, with reports of decreases at 10 µg l^{-1} ranging from ~ 2% [32] to ~ 34% [5]; several of these studies [6, 11, 12, 30] were conducted at antimony concentrations (e.g. 1 mg l^{-1}) far in excess of normal plant conditions (< 0.1 mg l^{-1} [20]), and hence are of less utility. Singh et al. [40] recently reported that the effects of antimony on voltammetry, product morphology and QE were dependent on the oxidation state, with Sb(III) being more potent than Sb(V); the relative amounts of Sb(III) and Sb(V) depend on the zinc ore, plant leaching and purification procedures and electrolysis conditions [43]. The evidence for the interaction of antimony with glue [20, 32, 36, 39–42] and cobalt [22, 27, 34, 37] is substantial; other trace impurities such as copper, iron and nickel [22, 27, 32] may also be involved. Much of the recent work on antimony deals with its effects on deposit morphology and preferred orientation in both commercial and synthetic solutions, particularly in the presence of glue [20, 39, 42].

The present results on the effects of antimony in high-purity solutions are summarized in Fig. 3 and Table 5. Antimony had a dramatic effect on QE with decreases of ~ 5, 24 and 52% for Sb(III) concentrations of 4, 10 and 14 µg l^{-1}, respectively. These drops in QE were generally larger than those reported previously [5, 32, 39, 40] for similar antimony concentrations in solutions where presumably glue was absent. With such small concentrations of antimony present in solution, it is difficult to assume other than the catalytic production of hydrogen. The solution analyses (see Table 5), although certainly not very precise at these levels, suggested that an average of ~ 30% of the antimony (ignoring the outlying result at 10 µg l^{-1})

Table 5. Variation of coulombic efficiency and preferred orientation of deposit with addition of antimony

Initial Sb $(\mu g\,l^{-1})$	Final Sb $(\mu g\,l^{-1})$	Sb removed (%)	Change in QE (%)	Preferred orientation
Nil	<4	–	–	Random
4	4	0	−5.2	(112), (212)
7	5	29	−10.0	(112), (211)
10	9	10	−23.6	(112), (101)
14	10	29	−52.4	(104), (101)
19	13	32	−62.3	(004), (103)

was removed from the solution during the electrolysis; the antimony was presumably co-deposited with the zinc [30], although other mechanisms, e.g. hydride formation, may have been operating [10]. Mass transfer was apparently not a significant factor here, since an electrodeposition at half the usual electrode rotation rate produced no significant change in QE. Since the range of concentrations employed here is similar to that occurring in practice, it can reasonably be assumed that in the plant the very deleterious effect of antimony on QE is essentially 'neutralized' by the glue normally added to the solution, e.g. see Singh *et al.* [40]. The glue/antimony 'balance' may well be one of the most important factors determining QE.

Antimony had a dramatic grain-refining effect on the zinc deposit, reducing platelet size even at $4\,\mu g\,l^{-1}$. Above $4\,\mu g\,l^{-1}$ the platelets did not appear to get much smaller, but corrosion became evident, with zinc dissolving away leaving rough crystallites (or nodules) behind. The basal planes (004), (002) gradually increased until they dominated at $19\,\mu g\,l^{-1}$ Sb; at lower antimony levels the (112) and (101) planes were more intense (see Table 5).

4. Conclusions

The present study employed high-purity synthetic solutions in order to determine the intrinsic effects of some commonly occurring impurities on zinc electrowinning. The data were obtained under a specific set

Fig. 3. Coulombic efficiency for zinc electrodeposition as a function of initial antimony concentration in a solution of 0.8 M $ZnSO_4$ + 1.07 M H_2SO_4 (35° C, 400 A m^{-2}, 2 h, 2 cm^2 Al cathode rotating at 20 s^{-1}).

of electrolysis conditions which differed from the plant situation in various ways, including the following. (i) The deposition time (2 h) was chosen for convenience and to limit total experimental time. By contrast, plant deposition times are in the range 48–72 h, giving much more scope for long-term phenomena (e.g. induction-time effects) to make their presence felt. (ii) A rotating disc electrode was employed to control the hydrodynamic conditions in the laboratory cell; this is important when impurities whose deposition is mass transfer controlled are involved. Since the electrode rotation rate employed here presumably results in a much higher mass transfer rate than that pertaining in practice, the effects of impurities whose deposition is diffusion controlled would be expected to be enhanced. (iii) Interactive effects with other impurities were purposely minimized by the use of high-purity solutions; the present work sets up the necessary framework to study such effects. The literature evidence for interactive effects is extensive, although it is difficult to gauge their importance in practice, particularly in the presence of additives such as glue. Also, interactions between electrolysis variables themselves (e.g. temperature and current density [18]) and between electrolysis variables and impurities (e.g. acid level and cobalt [32]), cannot be overlooked. (iv) The possible effects of changes in oxidation states of the various impurities (e.g. cobalt, antimony) have not been addressed here, but may well be important in practice, particularly in undivided cells and in the presence of permanganate ion.

In the EZ Risdon plant, conditions producing high QEs and easily stripped zinc are usually characterized by the formation of fine-grained, non-porous, ductile deposits; the crystal orientation is either random or the (101) orientation predominates. By contrast, unsatisfactory conditions are usually associated with porous, brittle and coarse-grained deposits; in such cases the (110), (100), (211) and (112) crystal orientations predominate [20]. All of the impurities examined here exerted some influence on morphology and/or preferred orientation. Some had a grain-refining effect (antimony, copper, lead) and all (except copper) changed the crystal orientation away from the random orientation obtained in impurity-free solutions. However, the unfavourable orientations identified in plant deposits were not generally observed.

At the short deposition times employed in this study all the impurities (except antimony) had only minor effects on QE. The extremely detrimental effect of
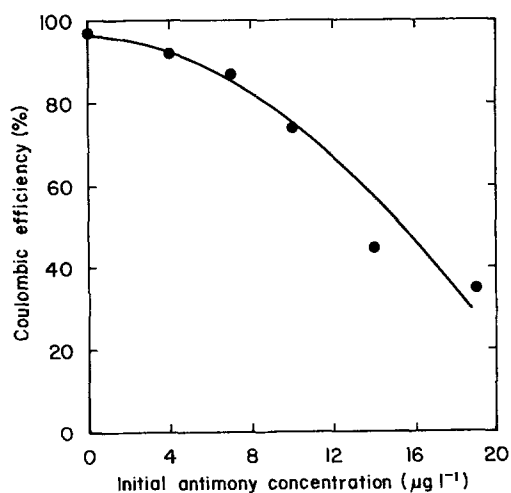
antimony on QE observed here in high-purity solutions points strongly to the importance of additives such as glue in the plant situation, where QEs of $\sim 90\%$ are usually obtained. Overall, the present study suggests that the reason for the widely varying and sometimes dramatic changes in QE reported previously for various impurities lies in their association with other impurities (i.e. synergistic effects) and/or in the existence of induction time effects (perhaps involving autocatalytic mechanisms) which make their presence felt at longer deposition times.

Acknowledgements

References

[1]   F. Laist, R. B. Caples and G. T. Wever, in 'Handbook of Nonferrous Metallurgy, Recovery of the Metals' (edited by D. M. Liddell), McGraw Hill, New York (1945) p. 379.

[2]   F. S. Weimer, G. T. Wever and R. J. Lapee, in 'Zinc, The Science and Technology of the Metal, its Alloys and Compounds' (edited by C. H. Mathewson), ACS Monograph Series, Reinhold, New York (1959) p. 174.

[3]   C. L. Mantell, 'Electrochemical Engineering', 4th edn, McGraw Hill, New York (1960) p. 210.

[4]   G. T. Wever, J. Metals 11 (1959) 130.

[5]   H. H. Fukubayashi, T. J. O'Keefe and W. C. Clinton, Bureau of Mines Report of Investigations 7966, US Dept. of the Interior, Washington (1974).

[6]   R. C. Kerby and T. R. Ingraham, Mines Branch Research Report R243, Dept. of Energy, Mines and Resources, Ottawa (1971).

[7]   G. C. Bratt, Electrochem. Tech. 2 (1964) 323.

[8]   G. C. Bratt, in 'The Aus. I.M.M. Conference, Tasmania, May, 1977', Australasian Institute of Mining and Metallurgy, Melbourne (1977) p. 277.

[9]   M. Maja and P. Spinelli, J. Electrochem. Soc. 118 (1971) 1538.

[10]   M. Maja, N. Penazzi, R. Fratesi and G. Roventi, J. Electrochem. Soc. 129 (1982) 2695.

[11]   U. F. Turomshina and V. V. Stender, J. Appl. Chem. USSR 28 (1955) 347.

[12]   A. G. Pecherskaya and V. V. Stender, J. Appl. Chem. USSR 23 (1950) 975.

[13]   A. D'este and R. Guerriero, Montevecchio 16 (1965) 1.

[14]   M. Kett, Hutn. Listy 16 (1961) 669.

[15]   S. Ohyama and S. Morioka, in 'Zinc '85, Proceedings of International Symposium on Extractive Metallurgy of Zinc' (edited by K. Tozawa), Mining and Metallurgical Institute of Japan (1985) p. 219.

[16]   T, Biegler, E. J. Frazer and T. Lwin, in 'Research and Development in Extractive Metallurgy — 1987', Australasian Institute of Mining and Metallurgy, Melbourne (1987) p. 203.

[17]   T. Biegler and E. J. Frazer, J. Appl. Electrochem. 16 (1986) 654.

[18]   E. J. Frazer and T. Lwin, J. Appl. Electrochem. 17 (1987) 453.

[19]   T. Biegler and D. A. Swift, Hydrometallurgy 6 (1981) 299.

[20]   P. A. Adcock, A. R. Ault and O. M. G. Newman, J. Appl. Electrochem. 15 (1985) 865.

[21]   D. J. MacKinnon, J. M. Brannen and R. C. Kerby, J. Appl. Electrochem. 9 (1979) 55.

[22]   U. F. Turomshina and V. V. Stender, J. Appl. Chem. USSR 28 (1955) 447.

[23]   D. J. MacKinnon, J. M. Brannen and R. M. Morrison, J. Appl. Electrochem. 12 (1982) 39.

[24]   E. J. Frazer, J. Electrochem. Soc. in press.

[25]   L. F. G. Williams, J. Electrochem. Soc. 126 (1979) 566.

[26]   D. J. MacKinnon, J. Appl. Electrochem. 15 (1985) 953.

[27]   D. J. MacKinnon, R. M. Morrison and J. M. Brannen, J. Appl. Electrochem. 16 (1986) 53.

[28]   R. Fratesi, G. Roventi, M. Maja and N. Penazzi, J. Appl. Electrochem. 10 (1980) 765.

[29]   Y.-M. Wang, T. J. O'Keefe and W. J. James, J. Electrochem. Soc. 127 (1980) 2589.

[30]   N. Matsuura and M. Kojima, Tokyo Univ., Coll. Gen. Ed., Sci. Pap. 11 (1952) 47.

[31]   I. W. Wark, in 'Proceedings of the First Australian Conference on Electrochemistry, Sydney and Hobart, 1963' (edited by J. A. Friend and F. Gutmann), Pergamon Press, London (1965) p. 889.

[32]   D. R. Fosnacht and T. J. O'Keefe, Met. Trans. B 14 (1983) 645.

[33]   I. R. Bellobono, Ind. Chim. Belge, Suppl. Chim. Civiliz. 32 (1967) 305.

[34]   O. Vennesland, H. Holtan and S. Solhjell, Acta Chem. Scand. 27 (1973) 846.

[35]   D. R. Fosnacht and T. J. O'Keefe, J. Appl. Electrochem. 10 (1980) 495.

[36]   T. J. O'Keefe and M. W. Mateer, in 'Physical Chemistry of Extractive Metallurgy' (edited by V. Kudryk and Y. K. Rao), Metallurgical Society of AIME, New York (1985) p. 165.

[37]   G. Steintveit and H. Holtan Jr, J. Electrochem. Soc. 107 (1960) 247.

[38]   C. J. Hamdorf and O. G. Woodward, in 'Mining and Metallurgical Practices in Australasia' (edited by J. T. Woodcock), Monograph Series No. 10, Australasian Institute of Mining and Metallurgy, Melbourne (1980) p. 254.

[39]   D. J. Robinson and T. J. O'Keefe, J. Appl. Electrochem. 6 (1976) 1.

[40]   R. Singh, T. J. O'Keefe, R. C. Kerby and K. Jibiki, in 'Zinc '85, Proceedings of International Symposium on Extractive Metallurgy of Zinc' (edited by K. Tozawa), Mining and Metallurgical Institute of Japan (1985) p. 235.

[41]   B. A. Lamping and T. J. O'Keefe, Met. Trans. B 7 (1976) 551.

[42]   D. J. MacKinnon and J. M. Brannen, J. Appl. Electrochem. 7 (1977) 451.

[43]   R. C. Kerby, Paper presented at 114th AIME Conference, New York, 24–28 February 1985 (Reference [3] quoted in [40]).