JOURNAL OF APPLIED ELECTROCHEMISTRY **18** (1988) 32–37

Effect of sodium and potassium sulphates on zinc electrowinning

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Received 23 December; revised 2 March 1987

In order to evaluate the intrinsic effect of high concentrations of sodium and potassium sulphates in zinc electrowinning solutions, measurements of coulombic efficiency were carried out under mass transfer-controlled conditions in synthetic solutions of very high purity. A solution composition of 1 mol dm^{-3} $ZnSO_4$ + 1.5 mol dm^{-3} H_2SO_4 was employed with and without additions of 0.5 mol dm^{-3} Na_2SO_4 and/or 0.25 mol dm^{-3} K_2SO_4. With temperature and current density similar to plant practice (37° C, 650 A m^{-2}) and electrode rotation rates of 10 and 45 s^{-1}, the coulombic efficiency for three successive batch tests ($\sim$ 200 mg zinc) increased by an average of $\sim$ 1.2% (from an average of 96.0%) for additions of 0.5 mol dm^{-3} Na_2SO_4 + 0.25 mol dm^{-3} K_2SO_4. The results were evaluated in terms of available theories, solution purity and predicted changes in solution composition (zinc and hydrogen ion activities) and physical properties following additions of Na_2SO_4/K_2SO_4. It was concluded that in the plant situation the increase in coulombic efficiency would probably be offset by an increase in cell voltage of about 2%, the net effect on power efficiency being a decrease of about 1%. The zinc deposit morphology and preferred orientation were also studied. The addition of sodium and/or potassium sulphate to the solution resulted in rougher, darker zinc deposits, a slight grain refining effect, and a change from random to predominantly basal (0 0 2), (0 0 4) crystal orientation (at 45 s^{-1}).

1. Introduction

The Broken Hill Associated Smelters Pty Ltd (BHAS) electrolytic zinc plant at Port Pirie, South Australia, treats a feed material of zinc oxide fume recovered from lead blast furnace slag [1]. This fume typically contains 0.1 wt % sodium and 0.14 wt % potassium. Since the start-up of the plant in 1967, the sodium and potassium concentrations in the electrowinning solution have risen to steady state levels of $\sim$23 g l^{-1} sodium (i.e. $\sim$0.5 mol dm^{-3} Na_2SO_4) and $\sim$20 g l^{-1} potassium (i.e. $\sim$0.25 mol dm^{-3} K_2SO_4). At these levels the new inputs of sodium and potassium in the fume are balanced by the deportment of entrained soluble sodium and potassium salts in the washed, leached residue stream. By contrast, a conventional plant handling zinc concentrates and employing deliberate solution bleed and/or jarosite residue disposal technology (precipitation of sodium, potassium jarosites for iron control), might typically have a solution containing < 0.5 g l^{-1} sodium and potassium [2].

It is generally believed [3–6] that the alkali and alkaline earth metals are not detrimental in the electrowinning of zinc, at least with regard to coulombic efficiency (QE) and deposit morphology. However, in early work, Turomshina and Stender [7] reported that additions of 1 and 50 g l^{-1} Na^+ to a pure zinc electrowinning solution (60 g l^{-1} zinc, 100 g l^{-1} H_2SO_4) caused decreases in QE of $\sim$ 5 and 15%, respectively, at 400 A m^{-2} and 30° C. They concluded that sodium was discharged jointly with zinc ions forming intermetallic compounds which acted as microanodes in short-circuited elements on the cathode surface. More recently, Saloma and Holtan Jr. [8] studied the effect of additions of 0.1–1.0 g l^{-1} Na^+ to 1 mol dm^{-3} $ZnSO_4$ on zinc morphology and deposition. They found that zinc deposits were darker and more porous following Na^+ addition and that the zinc electrode potential shifted in the positive direction. They concluded that the ions (Na^+, Ca^{2+}, Mg^{2+}) acted by an adsorption mechanism to suppress the inhibiting action of hydrogen on zinc deposition, which was reported by Titova and Vagramyan [9].

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0021-891X/88 $03.00 + .12

The present work was conducted with the aim of evaluating the intrinsic effect of high concentrations of Na_2SO_4 and K_2SO_4 in zinc electrowinning solutions. It was necessary, therefore, to employ synthetic solutions of high purity in order to avoid interferences (particularly on QE measurements) from impurities and/or addition agents normally present in plant solutions.

2. Experimental details

2.1. *Determination of coulombic efficiency*

The measurements were carried out under mass transfer-controlled conditions in a glass electrochemical cell specially designed to minimize contamination of the catholyte by anode products [10]. The cathode consisted of an aluminium disc ($\sim 2\,cm^2$) fabricated to fit the threaded shaft of a Tacussel type EDI electrode rotator. Each disc was encapsulated in epoxy resin with only the working surface exposed to the solution. The surface of the electrode was lightly ground with P1200 silicon carbide paper, quickly rinsed with water in an ultrasonic bath and dried before each run [11]. The QE for zinc electrodeposition was determined from the weight of zinc deposited at constant current after the passage of $\sim 300\,C\,cm^{-2}$ (equivalent to ~ 200 mg zinc); the zinc deposit was normally stripped and weighed separately [10, 11]. The constant current source was a PAR 173 Potentiostat/Galvanostat equipped with a PAR 179 Digital Coulometer (accuracy of 0.1%). The QE could be estimated very precisely, with a standard deviation of better than 0.2% [11, 12].

2.2. *Choice of electrodeposition conditions*

Zinc deposits were produced at a temperature of 37° C and a current density of $650\,A\,m^{-2}$. These conditions were chosen after a consideration of BHAS plant operating [1] and laboratory testing conditions. The deposition time (~ 75 min) was chosen to give a total charge passed of $\sim 300\,C\,cm^{-2}$, consistent with previous investigations [11]. Since no reliable plant mass transfer data were available to estimate an equivalent electrode rotation rate (revolutions per second), the QE was determined at two arbitrary values, namely 45 and $10\,s^{-1}$. The former figure was chosen since it can be shown, using a response surface model [12], that the QE (at 37° C and $650\,A\,m^{-2}$) in a high-purity zinc electrowinning solution is least dependent on electrode rotation rate at $\sim 45\,s^{-1}$.

2.3. *Solution preparation*

The basic solution composition employed was $1\,mol\,dm^{-3}\,ZnSO_4 + 1.5\,mol\,dm^{-3}\,H_2SO_4$, similar to the BHAS plant solutions [1]. No organic or inorganic reagents (other than Na_2SO_4/K_2SO_4) were deliberately added to the solutions. A sample of 500 ml of slightly acidic $2\,mol\,dm^{-3}\,ZnSO_4$, i.e. sufficient to make up 1 litre of the final solution, was prepared by dissolution of zinc rod (Koch-Light, 99.9999%) in sulphuric acid (BDH Aristar), while in contact with a platinum grid [11]. Since there may be some variation in the impurity composition of individual zinc rods [11], this method ensures a constant starting composition (i.e. before Na_2SO_4/K_2SO_4 addition) with respect to both total zinc/acid and impurity levels.

The appropriate amount of Na_2SO_4 and/or K_2SO_4 (BDH Aristar) was added to a 250 ml volumetric flask and partially dissolved in ~ 75 ml of deionized water (MILLI-Q System). Following this, 125 ml of the $2\,mol\,dm^{-3}\,ZnSO_4$ solution were then added and the remaining Na_2SO_4 and/or K_2SO_4 dissolved. Finally, the appropriate amount of H_2SO_4 was added and the solution made up to the mark with water. When dissolving Na_2SO_4 and K_2SO_4 in the same solution it was necessary to slightly warm the mixture and treat it in an ultrasonic bath to achieve complete dissolution; this solution may well be approaching saturation in metal sulphates at room temperature [13].

Four separate solutions were prepared:

(A) $1\,mol\,dm^{-3}\,ZnSO_4 +$
$1.5\,mol\,dm^{-3}\,H_2SO_4$

(B) $1\,mol\,dm^{-3}\,ZnSO_4 +$
$1.5\,mol\,dm^{-3}\,H_2SO_4 +$
$0.5\,mol\,dm^{-3}\,Na_2SO_4$

(C) $1\,mol\,dm^{-3}\,ZnSO_4 +$
$1.5\,mol\,dm^{-3}\,H_2SO_4 +$
$0.25\,mol\,dm^{-3}\,K_2SO_4$

(D) $1\,mol\,dm^{-3}\,ZnSO_4 +$
$1.5\,mol\,dm^{-3}\,H_2SO_4 +$
$0.5\,mol\,dm^{-3}\,Na_2SO_4 +$
$0.25\,mol\,dm^{-3}\,K_2SO_4$

3. Results and discussion

3.1. *Impurities in electrolyte additions*

It is generally accepted [3–6] that the QE of zinc electrowinning is determined to a large extent by trace impurities present in the solution at p.p.m. and p.p.b. levels. Therefore, when making large additions of salts to a nominally high-purity solution it is essential that only the purest reagents are used and that the resultant solution is analysed. It is quite possible that a particular reagent is within specification for total metal impurities (e.g. $\leqslant 10$ p.p.m.), yet still contains sufficient quantities of a particular cation to be extremely deleterious in zinc electrowinning. For example, a zinc solution prepared with added Na_2SO_4 and K_2SO_4 (Spex, 99.999%) produced abnormally low QEs, apparently because it contained 0.04 p.p.m. antimony [14]. Assuming that all the antimony was introduced with the added Na_2SO_4/K_2SO_4, this is still only equivalent to ~ 0.4 p.p.m. in these reagents (i.e. well within specification).

The solutions used in the deposition tests reported here were prepared using BDH Aristar Na_2SO_4 and K_2SO_4. The strict purity specifications for these

Table 1. Maximum limits of impurities in BDH Aristar Na_2SO_4 and K_2SO_4 [15]

Impurity	*Max. limit Na_2SO_4 (p.p.m.)*	*Max. limit K_2SO_4 (p.p.m.)*
Chloride (Cl)	2	2
Nitrate (NO_3)	1	1
Phosphate (PO_4)	0.5	0.1
Aluminium (Al)	0.05	0.2
Ammonium (NH_4)	2	2
Arsenic (As)	0.05	0.05
Barium (Ba)	5	2
Cadmium (Cd)	0.01	0.02
Caesium (Cs)	5	–
Calcium (Ca)	0.1	0.5
Cobalt (Co)	0.01	0.02
Copper (Cu)	0.01	0.02
Iron (Fe)	0.01	0.05
Lead (Pb)	0.01	0.02
Lithium (Li)	0.1	0.5
Magnesium (Mg)	0.05	0.1
Manganese (Mn)	0.01	0.02
Mercury (Hg)	0.01	0.05
Nickel (Ni)	0.01	0.02
Potassium (K)	5	–
Rubidium (Rb)	1	–
Sodium (Na)	–	10
Strontium (Sr)	0.1	0.1
Thallium (Tl)	0.01	0.02
Zinc (Zn)	0.01	0.02

salts are shown in Table 1 [15]. From the maximum limits of impurities quoted it was expected that the maximum increase in the concentration of typical impurities of concern (e.g. arsenic, cobalt) caused by Na_2SO_4/K_2SO_4 additions to solution A would be < 10 p.p.b. The solutions themselves were also analysed for several trace impurities and the results are shown in Table 2. The addition of Na_2SO_4 and/or K_2SO_4 to solution A had no detectable effect on cobalt and antimony levels. While there appears to have been a small increase in nickel and arsenic levels, the concentration of the latter impurity in solution D is slightly higher than might have been expected from the corresponding arsenic levels in solutions A, B and C.

3.2. *Effect of sodium and potassium sulphates on coulombic efficiency*

A sample of each solution (~ 120 ml) was deoxygenated by nitrogen sparging and subjected to three successive QE determinations (denoted runs 1, 2, 3); the results are shown in Table 3. The electrolysis conditions employed were: runs 1, 2, 37° C, 650 A m^{-2}, electrode rotation rate = 45 s^{-1}; run 3, 37° C, 650 A m^{-2}, electrode rotation rate = 10 s^{-1}. Run 2 would be expected to be less subject to the influence of residual impurities by virtue of the partial pre-electrolysis effected during Run 1. Run 3 followed a further pre-electrolysis (i.e. run 2) and was conducted at a much lower electrode rotation rate to reduce the influence of any trace impurities whose deposition was controlled by mass transfer.

Table 2. Trace analyses of zinc electrowinning solutions (figures are in p.p.b.)

Solution	*Cobalt*	*Nickel*	*Arsenic*	*Antimony*
A	< 10	< 10	20	< 20
B	< 10	< 10	30	< 20
C	< 10	< 10	20	< 20
D	< 10	16	50	< 20

Table 3. The effect of sodium and potassium sulphates on coulombic efficiency (QE)

Solution	*Coulombic efficiency (%)*		
	Run 1	*Run 2*	*Run 3*
A	96.4	96.1	95.6
B	97.4(1.0)[a]	97.4(1.3)	97.1(1.5)
C	97.3(0.9)	97.2(1.1)	97.0(1.4)
D	97.2(0.8)	97.3(1.2)	97.2(1.6)

[a] The figure shown in brackets is the increase in QE over the corresponding run in solution A.

Under all experimental conditions used here, the addition of Na_2SO_4 and/or K_2SO_4 to solution A resulted in an increase in QE. The average increases for additions of 0.5 mol dm^{-3} Na_2SO_4, 0.25 mol dm^{-3} K_2SO_4 and 0.5 mol dm^{-3} Na_2SO_4 + 0.25 mol dm^{-3} K_2SO_4 were 1.3, 1.1 and 1.2%, respectively. In view of the consideration of electrolyte purity in Section 3.1, it must be assumed that these measurements were not significantly affected by residual impurities either associated with the Na_2SO_4/K_2SO_4 additions or already present in solution A, i.e. that the observed effects were due to the added salts alone. Such changes in QE are statistically significant since the standard deviation of the QE determination is expected to be ~ 0.2% [11, 12]. It also appears that the effects of the sodium and potassium sulphates are similar but not additive at these concentrations. It should be noted that the possible effect of increasing the *total* sulphate concentration (i.e. the total ionic strength) in going from say, solution A to D, has not been addressed here. However, the results of Wark [16, 17] suggest that any effect is probably small. He observed an average increase in QE of only 0.2% in going from 1.5 to 2.125 mol dm^{-3} total sulphate for solutions with $[ZnSO_4]/[H_2SO_4]$ (the zinc/acid ratio) in the range 0.5 to 1 (0.66 for solution A).

The present results are not consistent with those reported by Turomshina and Stender [7]. However, the large decreases in QE (5–15%) observed in that work appear to be the result of the introduction of deleterious impurities with the Na_2SO_4 additions. The increase in QE, i.e. change in the relative rates of the hydrogen and zinc deposition reactions, is difficult to explain on simple electrochemical grounds. The work of Saloma and Holtan Jr. [8] can be used to predict an increase in QE, but the underlying theory is not conclusively proven. These authors suggested that ions such as Na^+, Ca^{2+} and Mg^{2+} act by some adsorptive mechanism to suppress the inhibiting action of hydrogen on zinc deposition [9], i.e. such ions do not directly promote the discharge of zinc. However, there is now evidence that the zinc ion may well be inhibiting the hydrogen evolution reaction [18, 19], rather than the reverse.

3.2.1. Changes in solution composition. It is generally accepted that the QE for zinc electrodeposition is a function of solution composition (i.e. zinc sulphate and sulphuric acid concentrations). Wark [16, 17] has formalized a relationship between QE and the zinc/acid ratio ($[ZnSO_4]/[H_2SO_4]$) based on a series of laboratory experiments, namely

$$\mathrm{QE}/(100 - \mathrm{QE}) = K_1[\mathrm{ZnSO_4}]/[\mathrm{H_2SO_4}] \qquad (1)$$

where K_1 is a constant which was claimed to be almost independent of temperature, current density and deposition period within the probable limits of operation for a commercial plant. This relationship has been shown to apply over a wide range of composition in high-purity zinc electrowinning solutions [11]. The decrease in zinc concentration and the corresponding increase in acid concentration resulting from an electrodeposition run is of the order of 2–3%. Thus, using Equation 1 and assuming $K_1 = 40.2$ (solution A, QE = 96.4%), the corresponding decrease in zinc/acid ratio would be expected to result in a decrease in QE of only ~0.2%. For solutions B, C and D, the observed decreases in QE for successive runs were of this magnitude; however, the decreases in QE were somewhat larger than predicted in solution A (see Table 3).

Wadsley [20] has employed the CSIRO–SGTE Thermodata System [21] to calculate single ion activities in the $ZnSO_4/H_2SO_4/H_2O$ system. Examination of data for a solution of $0.8\,\mathrm{mol\,dm^{-3}}$ $ZnSO_4$ + 0.5–$2.5\,\mathrm{mol\,dm^{-3}}$ H_2SO_4 (i.e. similar to solution A) suggests that an analogous relationship to Equation 1 can be expressed in terms of activities, namely

$$\mathrm{QE}/(100 - \mathrm{QE}) = K_2(a_{\mathrm{Zn}^{2+}}/a_{\mathrm{H}^+}) + K_3 \qquad (2)$$

where $a_{\mathrm{Zn}^{2+}}$ and a_{H^+} now represent activities rather than concentrations, and K_2 and K_3 are constants. Similar activity calculations for the solutions used here suggest that for the addition of $0.5\,\mathrm{mol\,dm^{-3}}$ Na_2SO_4 + $0.25\,\mathrm{mol\,dm^{-3}}$ K_2SO_4 to solution A, the $a_{\mathrm{Zn}^{2+}}/a_{\mathrm{H}^+}$ ratio increases by ~6%. It is not possible to estimate the values of K_2 and K_3 in Equation 2 for solution A without the appropriate calibration curve for $1\,\mathrm{mol\,dm^{-3}}$ $ZnSO_4$ (+H_2SO_4) under the present experimental conditions. However, an estimate of the range of the expected change in QE in going from solution A to D can be made by choosing extreme values of K_3 and assuming that this constant is not strongly dependent on total ionic strength. Assuming $K_3 = -20 \pm 20$ (from available data for $0.8\,\mathrm{mol\,dm^{-3}}$ $ZnSO_4$), then K_2 will be in the range 460–1150; for the expected increase in $a_{\mathrm{Zn}^{2+}}/a_{\mathrm{H}^+}$, the QE will increase by 0.2–0.5%. While this predicted change in QE is in the *direction* observed experimentally, it is less than half the actual change in QE.

3.2.2. Changes in physical properties of solution. The addition of Na_2SO_4/K_2SO_4 will also have some effects on the physical properties of solution A, namely density, electrical conductivity and hydrogen solubility. The hydrogen solubility would be expected to be somewhat lower in a solution containing more dissolved salts [22]. However, it is difficult to assess what effect this might have on the hydrogen evolution reaction without detailed knowledge of the overall reaction mechanism. The density of solution A (at 20°C) increased by ~7% from 1.224 to $1.309\,\mathrm{g\,cm^{-3}}$ with the addition of $0.5\,\mathrm{mol\,dm^{-3}}$ Na_2SO_4 + $0.25\,\mathrm{mol\,dm^{-3}}$ K_2SO_4. Assuming that this increase in density is accompanied by an increase in viscosity, then the diffusion coefficients (and limiting currents) of residual impurity ions would be expected to be lower and this could also affect the QE.

In acidic sulphate solutions the electrical conductivity increases with the concentration of free acid, but decreases with an increase in concentration of salts such as $MgSO_4$ and $ZnSO_4$ [23]. Apparently, increasing the concentration of soluble sulphate salts decreases the activity of the hydrogen ions, which are the main charge carriers, via the sulphate–bisulphate equilibrium. Similarly, additions of Na_2SO_4 and K_2SO_4 to zinc sulphate solutions also decrease the electrical conductivity [24]. For the BHAS operation it is estimated that a reduction in the sodium and potassium levels by an order of magnitude would result in an increase in conductivity of $\sim 50\,\mathrm{mS\,cm^{-1}}$ (from $350\,\mathrm{mS\,cm^{-1}}$). This translates to a reduction in total cell voltage of ~2.1% (~70 mV in 3.4 V) and would effectively mean an increase in power efficiency of the same magnitude (at a fixed current density).

3.3. *Effect of sodium and potassium sulphates on zinc morphology and preferred orientation*

Photographs of the zinc deposits from runs A_1 to D_3 are shown in Fig. 1. Samples E_1 and E_2 are included for comparison purposes; they were produced under similar experimental conditions on a slightly larger cathode from plant solutions, without and with standard addition agents, respectively. Obviously the macromorphology of the samples produced from the high-purity solution bears no resemblance to that of E_1 and E_2. However, the samples produced from solutions containing either Na_2SO_4 or K_2SO_4 or Na_2SO_4 + K_2SO_4 are very similar. They are somewhat rougher, darker and more uniform than those produced from solution A (A_1 to A_3), although the difference is less noticeable at the lower electrode rotation rate (compare A_3 with B_3, C_3, D_3). While the addition of Na_2SO_4 and/or K_2SO_4 to solution A appeared to have a slight grain refining effect, all the deposits produced from the high-purity solutions had much larger grains than those produced from plant

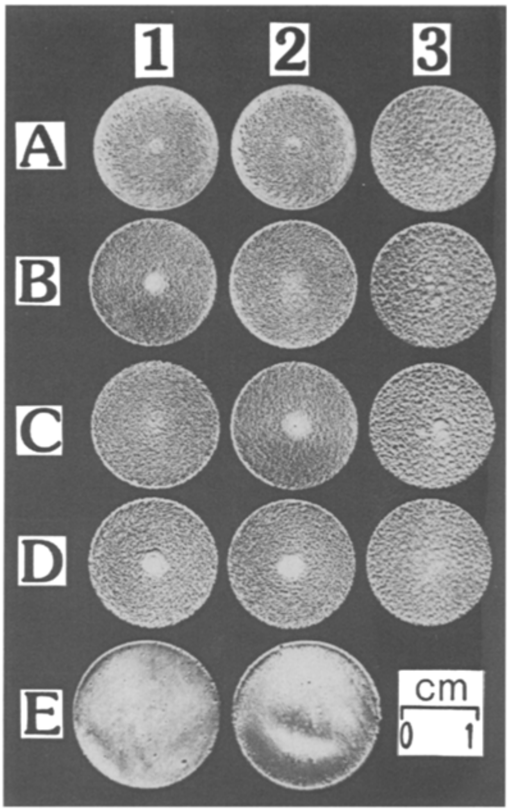

Fig. 1. Macromorphology of zinc electrodeposits produced from high-purity and plant electrowinning solutions. A_1, A_2, A_3 (solution A, runs 1–3); B_1, B_2, B_3 (solution B, runs 1–3); C_1, C_2, C_3 (solution C, runs 1–3); D_1, D_2, D_3 (solution D, runs 1–3); E_1 (plant solution without addition agents); E_2 (plant solution with addition agents).

solutions; also, the grain size tended to increase somewhat from run to run, e.g. $B_3 > B_2 > B_1$.

The preferred orientation of the deposits was evaluated by X-ray diffraction as before [25]. The relative intensity of the various crystal planes was calculated using the ASTM index values for zinc powder with the (1 0 1) plane as the standard; the results are presented in Table 4. During the first few moments of zinc deposition the deposit normally has a preferred basal plane orientation [26], i.e. crystal growth is preferred on the hexagonal, high-density basal crystal planes such as (0 0 2) and (0 0 4). This orientation can be lost and other orientations evolve as the deposit grows. The present results show that additions of potassium or sodium sulphate promote and perpetuate the initial basal plane orientation throughout the whole test period. This trend is accentuated in successive tests on each solution, where growth switches from crystal planes such as (1 0 0), at right angles to the basal plane, to crystal planes such as (1 0 5), (1 0 4), (1 1 4), which lie closer to the angle of the basal plane. There is no similarity between the preferred orientation of deposits produced from synthetic solutions containing Na_2SO_4/K_2SO_4 (B_1–B_3/C_1–C_3/D_1–D_3) and those produced from plant solutions (E_1, E_2). This suggests that the large quantity of sodium and potassium sulphates in the plant electrowinning solution is not determining the preferred orientation of the plant deposit.

4. Conclusions

The presence of Na_2SO_4 and K_2SO_4 in a zinc electrowinning solution has both a positive (via QE) and negative (via electrical conductivity) influence on the net power efficiency. The addition of 0.5 mol dm^{-3} Na_2SO_4 and/or 0.25 mol dm^{-3} K_2SO_4 to a high-purity solution has a small positive effect of ~ 1.2% on the QE of zinc electrodeposition, under certain electrolysis conditions (37° C, 650 A m^{-2}). This would be equivalent to an increase of ~ 1.2% in power efficiency, at fixed cell voltage and total cell current. However, the presence of Na_2SO_4 and K_2SO_4 at such high levels also causes a drop in electrical conductivity and an estimated increase in plant cell voltage of ~ 2.1%, i.e. a ~ 2.1% decrease in power efficiency at fixed total cell current (and QE). Assuming that the intrinsic effect of Na_2SO_4/K_2SO_4 on QE determined here also pertains in the plant situation, then the *net* effect on power efficiency is probably a decrease of about 1%, i.e. slightly increased power costs. Based on the data contained in Table 3, one could presumably substantially reduce the Na_2SO_4/

Table 4. Preferred crystal orientation for zinc deposits produced from high-purity and plant electrowinning solutions

Solution/run	*Preferred crystal orientation*				
A_1	(1 0 3)[12]	(1 1 4)[11]	(1 1 2)[9]	(1 0 4)]7]	(2 0 4)[6]
A_2	(1 1 4)[7]	(1 0 3)[6]	(1 0 4)[5]	(2 0 4)[4]	(1 0 5)[3]
A_3	(0 0 4)[45]	(1 0 4)[33]	(1 0 3)[26]	(1 0 5)[25]	(1 1 4)[20]
B_1	(0 0 4)[31]	(0 0 2)[22]	(0 0 6)[11]	(1 0 0)[5]	(1 0 5)[5]
B_2	(0 0 4)[26]	(0 0 2)[15]	(0 0 6)[8]	(1 0 0)[3]	(1 0 5)[3]
B_3	(0 0 4)[29]	(0 0 2)[23]	(1 0 5)[9]	(1 0 4)[8]	(1 1 4)[3]
C_1	(0 0 4)[26]	(0 0 2)[22]	(1 0 0)[4]	(1 0 5)[3]	(1 0 4)[2]
C_2	(0 0 4)[23]	(0 0 2)[16]	(1 0 5)[4]	(1 0 0)[3]	(1 0 4)[3]
C_3	(0 0 4)[28]	(0 0 2)[23]	(1 0 4)[10]	(1 0 5)[8]	(1 0 3)[4]
D_1	(0 0 4)[30]	(0 0 2)[14]	(1 0 5)[3]	(1 0 0)[3]	(1 0 4)[2]
D_2	(0 0 4)[17]	(0 0 2)[11]	(1 0 5)[3]	(1 0 0)[2]	(1 0 4)[1]
D_3	(0 0 2)[37]	(0 0 4)[34]	(1 0 4)[18]	(1 0 5)[9]	(1 1 4)[3]
E_1	(1 0 2)[5]	(2 0 4)[3]	(2 0 3)[3]	(1 1 4)[1]	(1 0 1)[1]
E_2	(1 0 3)[12]	(1 1 4)[10]	(1 0 2)[7]	(2 0 4)[6]	(1 0 4)[4]

( ): Crystal plane.
[ ]: Relative intensity $(h\,k\,l) = [I/I_0(h\,k\,l)$ sample$]/[I/I_0(1\,0\,1)$ sample$] \times [I/I_0(1\,0\,1)$ ASTM$]/[I/I_0(h\,k\,l)$ ASTM$]$

K_2SO_4 levels in the BHAS electrowinning solutions without reducing QE. However, an accurate evaluation of any economic benefits to be gained by such action would require knowledge of the dependence of QE on the Na_2SO_4/ K_2SO_4 concentration and consideration of local power prices.

Calculations based on a modified form of Wark's rule [16, 17] suggest that the effect of the addition of Na_2SO_4 and K_2SO_4 on the $a_{Zn^{2+}}/a_{H^+}$ ratio of the solution could cause an increase in QE of 0.2–0.5%. However, the observed change in QE is larger ($\sim 1.2\%$) and hence some other mechanism is probably also operating. Sodium and/or potassium ions may directly or indirectly influence the zinc and/or hydrogen deposition reactions, e.g. by adsorption or by lowering hydrogen solubility in the solution. The observation that the magnitude of the change in QE was not significantly affected by either solution pre-electrolysis or change in mass transfer conditions suggests that residual impurities had little effect on the results; the trace analyses of the solutions tend to support this view. Finally, additions of sodium and potassium sulphates had a significant effect on zinc morphology/preferred orientation with rougher, darker deposits and a preferred basal plane orientation. However, the morphologies/orientations of these deposits were not similar to samples produced from plant solutions, where presumably trace impurities/addition agents are the determining factors.

Acknowledgements

Thanks are due to T. Biegler, M. D. Horne and R. Woods for comments on the manuscript, M. D. Horne for special experimental assistance, E. A. Kowal for photography and M. W. Wadsley for activity calculations using the CSIRO–SGTE Thermodata System. Thanks are also due to the managements of The Broken Hill Associated Smelters Pty Ltd and the Electrolytic Zinc Company of Australasia Ltd for permission to publish this paper.

References

[1] D. H. Hart, J. H. McNicol and J. D. Martin, in 'The Aus. IMM Conference, South Australia, June 1975', Australasian Institute of Mining and Metallurgy, Melbourne (1975) p. 211.
[2] 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.
[3] 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.
[4] 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.
[5] G. T. Wever, *J. Metals* **11** (1959) 130.
[6] C. L. Mantell, 'Electrochemical Engineering', 4th edn, McGraw-Hill, New York (1960) p. 218.
[7] U. F. Turomshina and V. V. Stender, *J. Appl. Chem. USSR* **28** (1955) 151.
[8] M. Saloma and H. Holtan, Jr., *Acta Chem. Scand.* **A28** (1974) 86.
[9] V. N. Titova and A. T. Vagramyan, *Sov. Electrochem.* **2** (1966) 1052.
[10] T. Biegler and D. A. Swift, *Hydrometallurgy* **6** (1981) 299.
[11] T. Biegler and E. J. Frazer, *J. Appl. Electrochem.* **16** (1986) 654.
[12] E. J. Frazer and T. Lwin, *ibid*, **17** (1987) 453.
[13] F. W. Linke, 'Solubilities of Inorganic and Metal-Organic Compounds', Vol. II, 4th edn, American Chemical Society, Washington, DC (1965) p. 320.
[14] D. R. Fosnacht and T. J. O'Keefe, *Met. Trans. B* **14** (1983) 645.
[15] 'Aristar: Very High Purity Chemicals', BDH Chemicals Ltd, Poole, UK.
[16] 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.
[17] *Idem*, *J. Appl. Electrochem.* **9** (1979) 721.
[18] D. R. Fosnacht and T. J. O'Keefe, *J. Appl. Electrochem.* **10** (1980) 495.
[19] T. Biegler, in 'Application of Polarization Measurements in the Control of Metal Deposition' (edited by I. H. Warren), Elsevier, Amsterdam (1984) p. 32.
[20] M. W. Wadsley, unpublished data.
[21] A. G. Turnbull and M. W. Wadsley, in 'Extractive Metallurgy Symposium (Melbourne Branch, 12–14 Nov. 1984, Melbourne, Vic., Australia)', Australasian Institute of Mining and Metallurgy, Melbourne (1984) p. 79.
[22] C. L. Young (ed.), 'Solubility Data Series, Vol. 5/6, Hydrogen and Deuterium', Pergamon Press, Oxford (1981).
[23] K. Tozawa, K. Sasaki and Y. Umetsu, in 'Hydrometallurgy: Research, Development and Plant Practice' (edited by K. Osseo-Asare and J. D. Miller), Metallurgical Society of AIME (1983) p. 375.
[24] A. G. Pecherskaya and V. V. Stender, *J. Appl. Chem. USSR* **23** (1950) 975.
[25] P. A. Adcock, A. R. Ault and O. M. G. Newman, *J. Appl. Electrochem.* **15** (1985) 865.
[26] A. R. Ault, unpublished data.