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The effects of metallic impurities and 2-butyne-1,4-diol on zinc electrowinning from chloride solutions

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Zinc electrowinning tests from acidic chloride solutions showed that metallic impurities can be classified in the following order of detrimental effect on current efficiency: Sb > Co, Ni > Cu. This effect increased with higher HCl concentrations. Analysis of the impurity content of the zinc deposits showed the regular codeposition of Cu and the anomalous codeposition of Ni and Co.

The use of 2-butyne-1,4-diol ($0.86\,g\,l^{-1}$) was proven to be beneficial in the presence of Sb and particularly Ni. Both current efficiency and zinc deposit morphology were improved. The additive acted by selectively slowing the codeposition of the impurities with zinc.

1. Introduction

Zinc production via the sulphate process has drawbacks. Complex sulphide ores [1–3] and secondary zinc sources [4–6] are not directly amenable to conventional sulphate technology. The energy consumption for electrolysis is rather high, $3.1\,kWh\,kg^{-1}$ being a typical industrial value [7], and represents 35% of the cost [8]. Zinc electrowinning from chloride solutions is thus currently being considered as an alternative technology to the sulphate process [9].

In chloride media, the effects of metallic impurities (such as Sb, Ni, Co and Cu) on current efficiency (CE) [10–12] were shown to be less deleterious than in sulphate solutions. Organic additives were also tested with a view to improvement of the CE and the zinc deposit morphology. The most promising were tetrabutyl ammonium chloride [11, 13], arabic gum [12] and glues [14, 15].

Metallic impurities are also a problem in the industrial sulphate process [16, 17] and, in order to control their level, costly purification steps are required. The effects of glue additions in the presence of Sb have been studied extensively [18]. The use of organic corrosion inhibitors for zinc electrowinning from sulphate solutions containing Ni was proposed by Mathieu and Piron [19]. They showed that 2-butyne-1,4-diol ($0.86\,g\,l^{-1}$) could improve the CE from 37 to 70% in the presence of $10\,mg\,l^{-1}$ Ni.

The objective of this work was to establish the effects of impurities in chloride electrolytes with compositions different from those previously studied and to investigate the influence of 2-butyne-1,4-diol in counteracting them.

2. Experimental details

The electrowinning tests were conducted using a Tacussel 10-20X potentiostat operated galvanostatically as described previously [19]. The cell was constructed from Plexiglas according to Fig. 1 and it had a volume of 0.7 l. Semi-continuous electrolyte feeding was used to maintain a zinc ion concentration of $30\,g\,l^{-1}$ during the 6 h tests. The temperature was maintained at 35° C by immersing the cell in a water bath. The aluminium cathode was partially covered with electroplating tape (Scotch 3M #484) and the dimensionally stable anodes were partially masked by a Plexiglas sheet. The exposed surface on each face of the cathode was $15\,cm^2$. The current density was $500\,A\,m^{-2}$ and the anode–cathode distance was 3.8 cm. Dynel cloth diaphragms were used to separate the anode from the cathode compartment. The chlorine gas produced at the anodes was neutralized in concentrated NaOH solution. Air sparging was employed to promote mass transfer at the cathode.

The electrolytes were prepared from double-distilled water and reagent grade chemicals. Pb was removed from $ZnCl_2$ by cementation with zinc dust. Antimony potassium tartrate, $NiCl_2$, $CoCl_2$ and $CuCl_2$ were added from stock solutions. 2-Butyne-1,4-diol was added just before commencing the tests.

The CE was obtained by weighing deposits. These were washed with double-distilled water and methanol prior to drying. Samples were cut from each deposit and were analysed by atomic absorption spectrophotometry to determine their impurity content.

3. Results

3.1. *Choice of electrolyte compositions*

Tests were first conducted to verify the effects of HCl and NaCl on the energy consumption in zinc electrowinning. The results are presented in Figs 2 and 3. The lowest specific energy consumption (around

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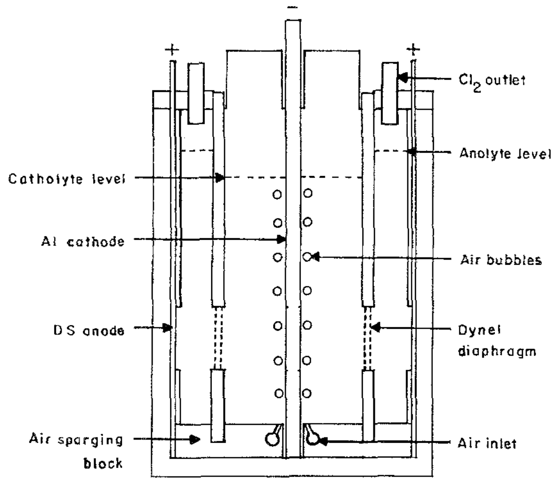

Fig. 1. Electrowinning cell.

2.6 kWh kg^{-1} zinc) was obtained with the electrolyte compositions B and C of Table 1. These electrolytes were thus selected for the studies on impurities and additives. Bath A (Table 1) was used for preliminary tests and for study of the effects of HCl and NaCl on the behaviour of impurities.

3.2. *Effects of impurities on current efficiency*

In bath A, CE was close to 94% in pure solution and it was practically unaffected by the presence of Ni, Co and Cu (Table 2). Sb had a detrimental effect, decreasing the CE to 75.8% at 0.2 mg l^{-1}.

However, this effect of Ni was due, in part, to the low concentration of HCl (4.4 g l^{-1}). As the acid concentration was increased, the CE dropped in the presence of Ni (Figs 4 and 5). In bath B, CE was 92.7% in pure solution and 56.0% with 15 mg l^{-1} Ni. The CE also dropped in the presence of Co (53.4% at 15 mg l^{-1}), Cu (85.5% at 15 mg l^{-1}) and Sb (8.3% at 0.2 mg l^{-1}).

In the bath C, the CE was 91.6% in pure solution. As shown in Fig. 5, the addition of NaCl produced a detrimental effect in the presence of Ni. A decrease in CE was also observed with Co, but only slightly with Cu (Table 2). The effect of Sb was not increased (76.8% at 0.2 mg l^{-1}) by the presence of NaCl.

3.3. *Impurity content of zinc*

Analysis of the impurity content of zinc revealed that Ni codeposited less than Cu (Fig. 6) when the rate of air sparging was 5.3 l min^{-1}. The amount of Ni was dependent on the composition of the electrolyte as shown in Fig. 7 (air sparging rate of 4.0 l min^{-1}). An increase in total Cl− concentration (bath C) resulted in an increase in Ni content of the deposits. This was also verified in the case of Co, although it codeposited less than Ni (Table 2). No such effects were observed in the case of Cu and Sb.

Table 1. Electrolyte composition

Concentration (*g l^{-1}*)	Bath A	Bath B	Bath C
Zinc	30	30	30
Acid and salt	HCl: 4.4	HCl: 27.4	HCl: 4.4 NaCl: 203

3.4. *Combination of impurities*

It has been reported both in chloride [11] and sulphate media [20, 21] that combined impurities are more detrimental than individual impurities. In bath A, Table 3 shows that the combination of Cu + Ni is more detrimental to CE only at the highest concentration. Analysis of the impurity content of the zinc deposits showed, however, an effect of Cu on Ni codeposition, the Ni content increasing in the presence of Cu. Ni had no effect on Cu codeposition, considering the possible small variations of air sparging rate. In bath C, Cu also increased the Ni content of the deposit. Similar results were obtained in the case of the combination Cu + Co (Table 2).

3.5. *Effect of 2-butyne-1,4-diol and impurities on current efficiency*

Fig. 8 shows that 2-butyne-1,4-diol was very beneficial in increasing CE in the presence of Ni. In bath C, the CE was increased by 5% to 10% compared with the results in the pure solution. In bath B, the improvement of CE with the addition of 2-butyne-1,4-diol was even more impressive and the CE was increased from 17% to 87% in the presence of 20 mg l^{-1} Ni. Fig. 9 shows that 2-butyne-1,4-diol was less beneficial in the presence of Sb, although it still improved the CE at Sb concentrations smaller than 1 mg l^{-1}.

3.6. *Effect of 2-butyne-1,4-diol on impurity content of zinc*

Fig. 10 demonstrates that the 2-butyne-1,4-diol decreased the amount of Ni codeposited with zinc. The Sb content of zinc was also lowered by the

Table 2. Effects of impurities on current efficiency and contamination of zinc

Impurities in solution (mg l^{-1})	*Bath A and 5.3 l min^{-1} air sparging*		*Bath C and 4.0 l min^{-1} air sparging*	
	CE (%)	*Impurity content (p.p.m.)*	*CE (%)*	*Impurity content (p.p.m.)*
0	93.7	–	91.6	–
20 Cu	92.1	2440	88.8	1895
25 Ni	93.3	325	83.2	1170
25 Co	93.4	28	81.5	329
20 Cu +25 Ni	86.3	2765 Cu +804 Ni	80.4	2010 Cu +2305 Ni
20 Cu +25 Co	82.5 84.7	2400 Cu + 102 Co 2370 Cu + 75 Co	78.3	1715 Cu +733 Co

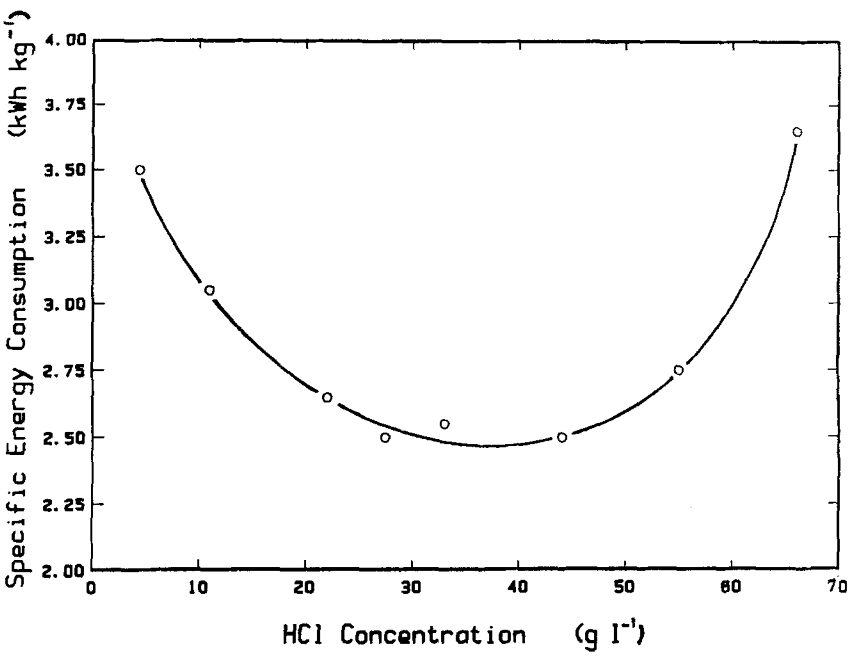

Fig. 2. Effect of HCl on specific energy consumption. 30 g l^{-1} Zn, 500 A m^{-2}, 35°C, 4.0 l min^{-1} air sparging and 6 h.

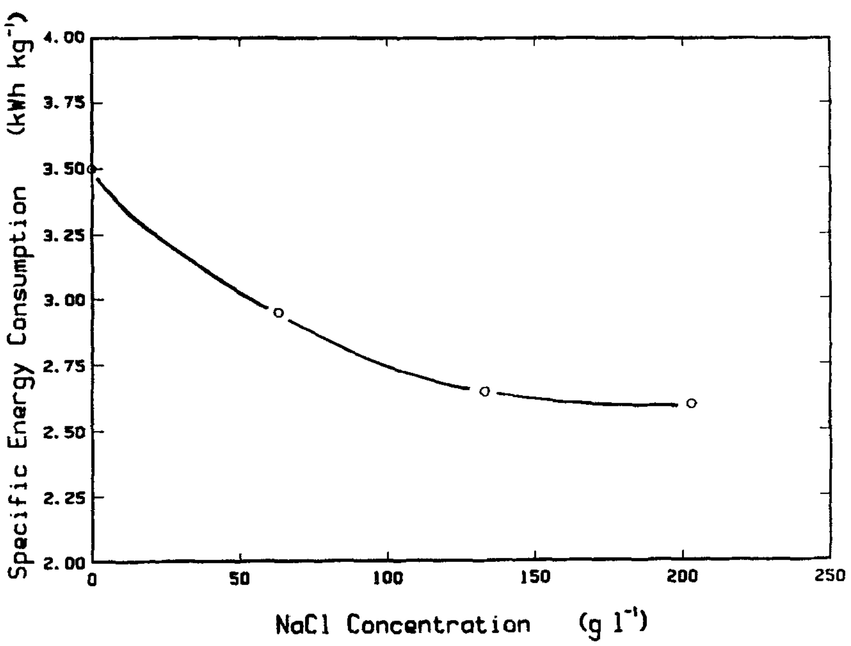

Fig. 3. Effect of NaCl on specific energy consumption. 30 g l^{-1} Zn + 4.4 g l^{-1} HCl, 500 A m^{-2}, 35°C, 4.0 l min^{-1} air sparging and 6 h.

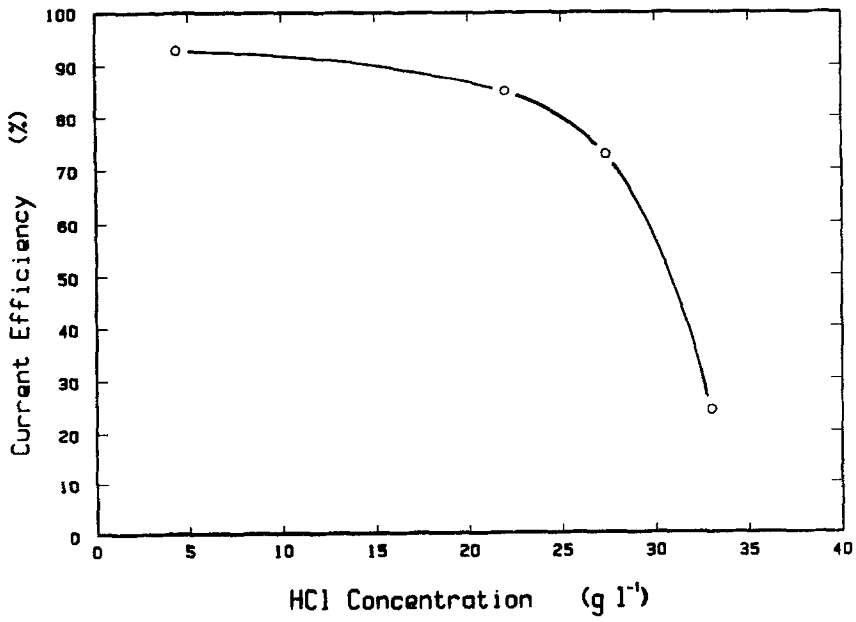

Fig. 4. Effect of HCl on current efficiency in the presence of 10 mg l^{-1} Ni.

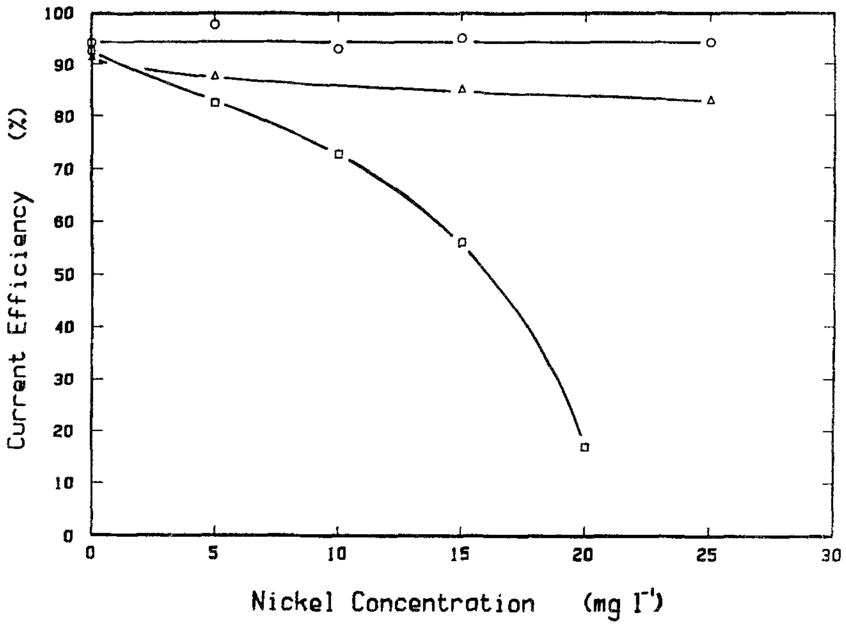

Fig. 5. Effect of Ni and bath composition on current efficiency. (○) Bath A; (□) Bath B; (△) Bath C.

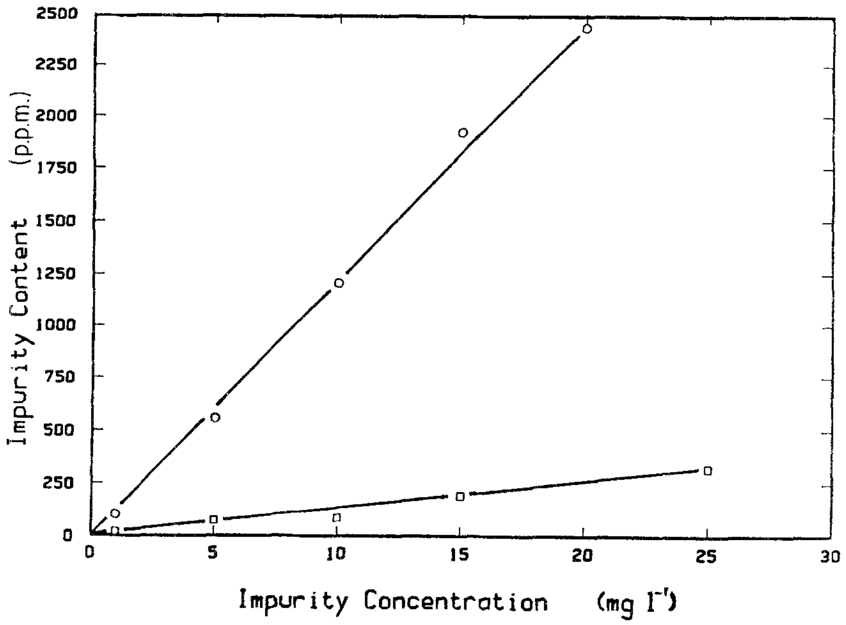

Fig. 6. Effect of Cu and Ni on contamination of zinc in bath A. 5.3 l min⁻¹ air sparging. (○) Copper; (□) nickel.

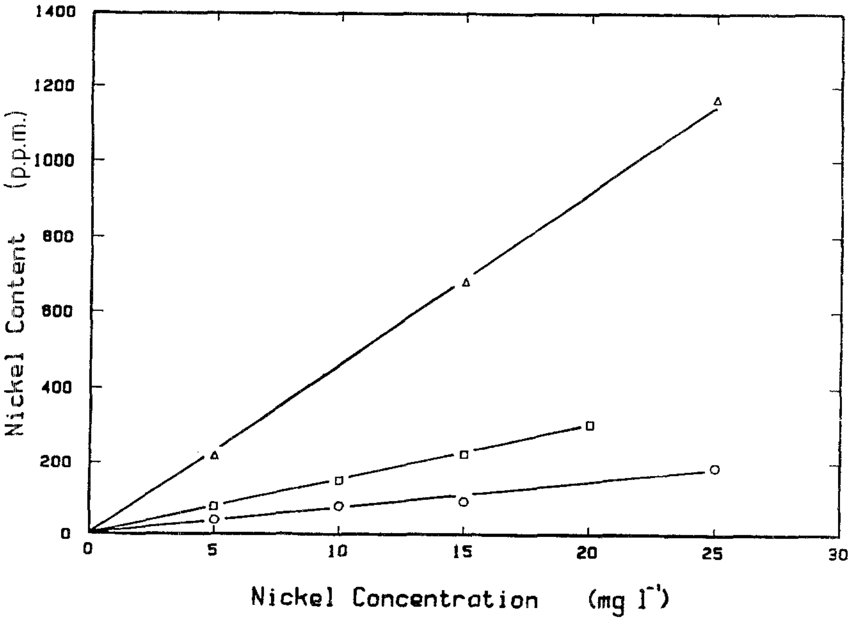

Fig. 7. Effect of Ni and bath composition on contamination of zinc. 4.0 l min⁻¹ air sparging. (○) Bath A; (□) Bath B; (△) Bath C.

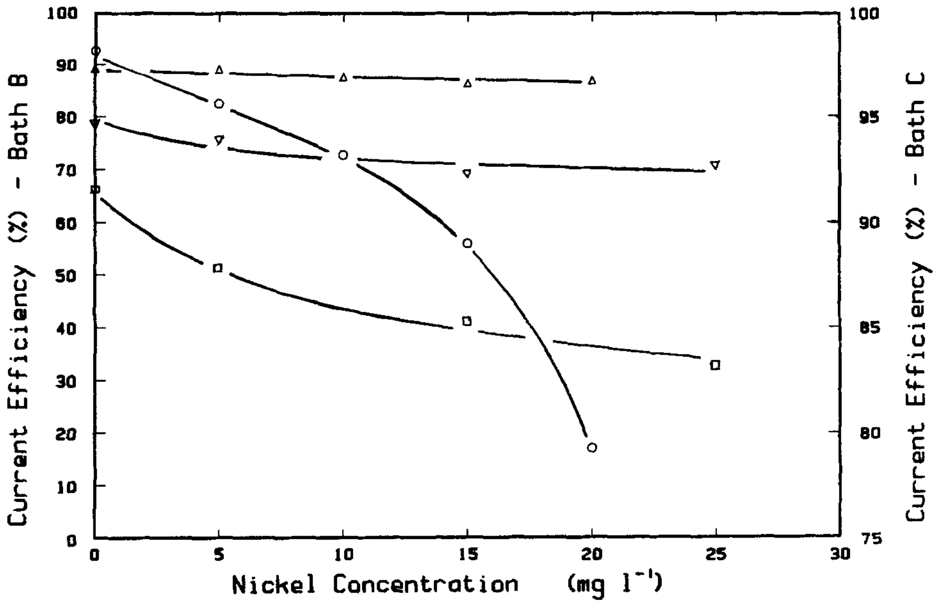

Fig. 8. Effect of Ni and 2-butyne-1,4-diol on current efficiency in baths B and C. Bath B (○) without 2-butyne-1,4-diol; (△) with 2-butyne-1,4-diol: Bath C (□) without 2-butyne-1,4-diol; (▽) with 2-butyne-1,4-diol.

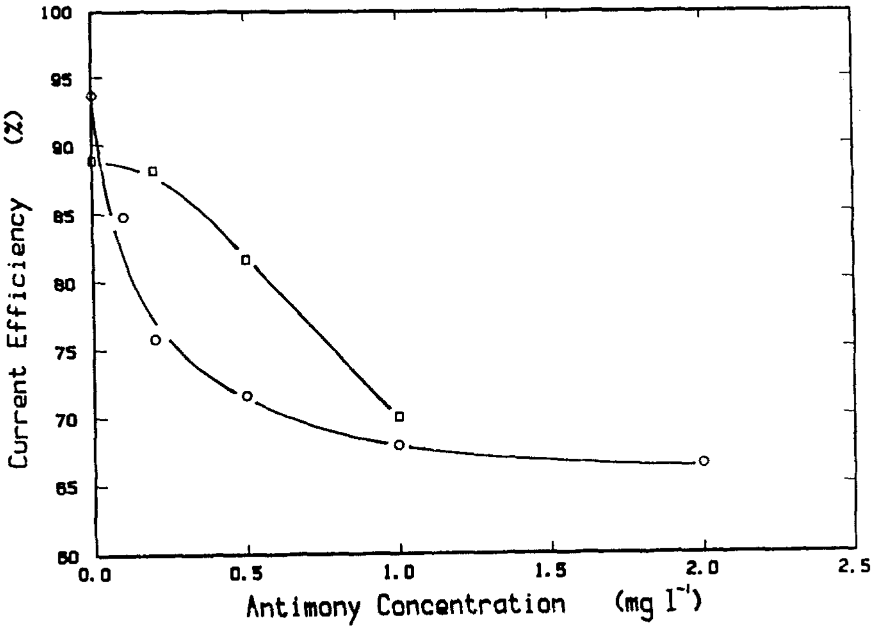

Fig. 9. Effect of Sb and 2-butyne-1,4-diol on current efficiency in bath A. (○) Without 2-butyne-1,4-diol; (□) with 2-butyne-1,4-diol.

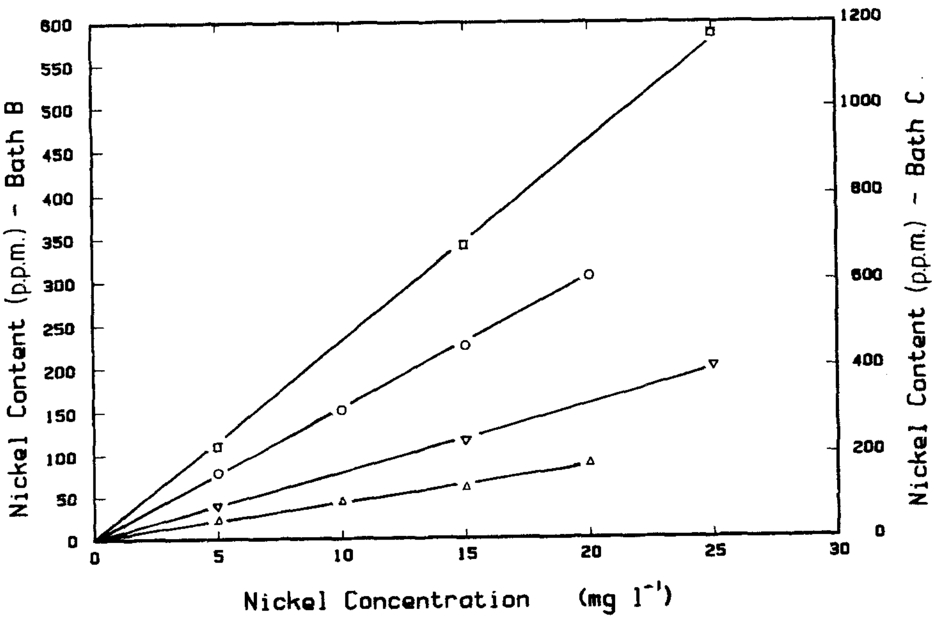

Fig. 10. Effect of Ni and 2-butyne-1,4-diol on contamination of zinc in baths B and C. 4.0 l min^{-1} air sparging. Bath B (○) without 2-butyne-1,4-diol; (△) with 2-butyne-1,4-diol; Bath C (□) without 2-butyne-1,4-diol; (▽) with 2-butyne-1,4-diol.

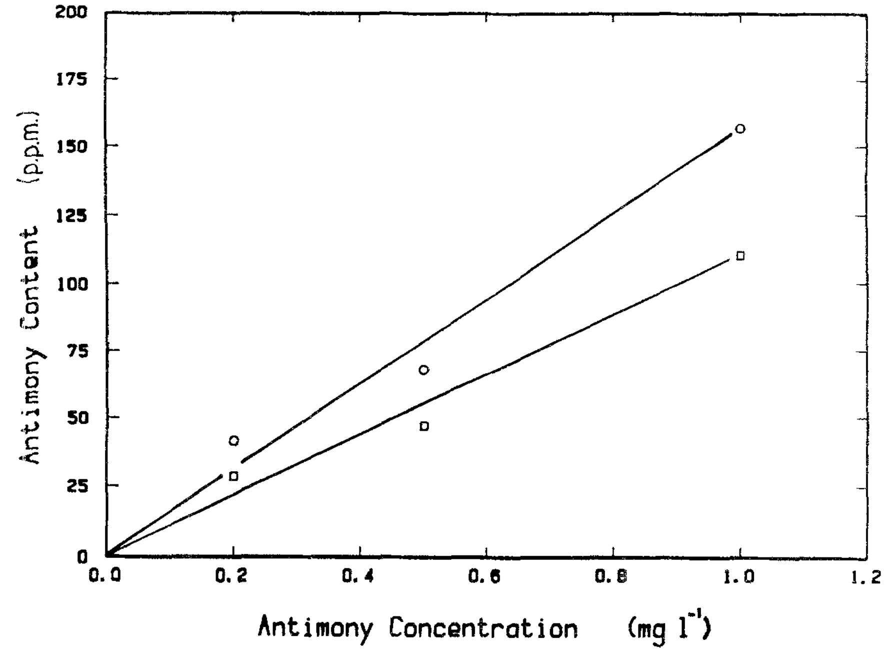

Fig. 11. Effect of Sb and 2-butyne-1,4-diol on contamination of zinc in bath A. 4.0 l min^{-1} air sparging. (○) Without 2-butyne-1,4-diol; (□) with 2-butyne-1,4-diol.

additive, but the effect is smaller than in the case of Ni (Fig. 11).

3.7. *Zinc deposit morphology*

Fig. 12 illustrates the effect of 2-butyne-1,4-diol on deposit morphology in pure solutions. The organic additive had a levelling action in the two baths. Fig. 13 shows the effects of Ni and 2-butyne-1,4-diol on zinc deposits. In bath B, Ni caused redissolution of zinc after 6 h, despite the cathodic polarization. 2-Butyne-1,4-diol could prevent that redissolution. In bath C, no redissolution was observed.

4. Discussion

4.1. *Effects of impurities*

The mechanism proposed for the effect of Ni implies that it codeposits with zinc and then acts as a site for H_2 evolution. It is also a site for local potential differences, the magnitude of which can be such that zinc redissolution is initiated [22, 23]. The zinc redissolution observed in bath B in the presence of Ni (Fig. 13a) conforms with this mechanism.

The drop in CE in the presence of impurities at higher HCl concentrations can be explained by the fact that the kinetics of H_2 evolution depend on the concentration of hydrogen ions. This interaction between impurities and acid strength has been reported in the sulphate media [21]. The increase of the detrimental effect of Ni with the addition of NaCl, at the same HCl concentration, results from the fact that the amount of Ni (the active site for H_2 evolution) which codeposits with zinc depends on the total Cl^- concentration. This strong dependence is surprising, however, if one considers that at the low level of Ni in the electrolyte (up to 25 mg l^{-1}) it should be reduced at a limiting current density.

The explanation for this dependence is also related to the fact that the Ni content of the zinc is low compared to Cu. This behaviour, which has also been reported in the sulphate media [24], is known as anomalous codeposition. It has been studied mostly in the field of alloy plating, such as Zn-Ni and Zn-Co [25–27]. Anomalous codeposition describes the inhibition of the deposition of a metal (like Ni) by a less noble metal (like Zn). This phenomenon has been shown to be affected by the concentration of Cl^-, in the case of Fe-Ni alloys [28]. The codeposition of Cu and Zn is classified as regular, and thus gives an indication of the total impurity content that can be

Table 3. Effects of Ni on current efficiency and contamination of zinc in bath A and with 5.3 l min^{-1} air sparging

Ni in solution (mg l^{-1})	*Cu in solution (mg l^{-1})*							
	0		*10*			*20*		
	CE (%)	*Ni content (p.p.m.)*	*CE (%)*	*Ni content (p.p.m.)*	*Cu content (p.p.m.)*	*CE (%)*	*Ni content (p.p.m.)*	*Cu content (p.p.m.)*
0	93.7	–	92.8	–	1210	92.1	–	2440
15	94.6	194	93.6	390	1100	91.1	508	2490
25	93.3	325	93.3	507	1000	86.3	804	2765

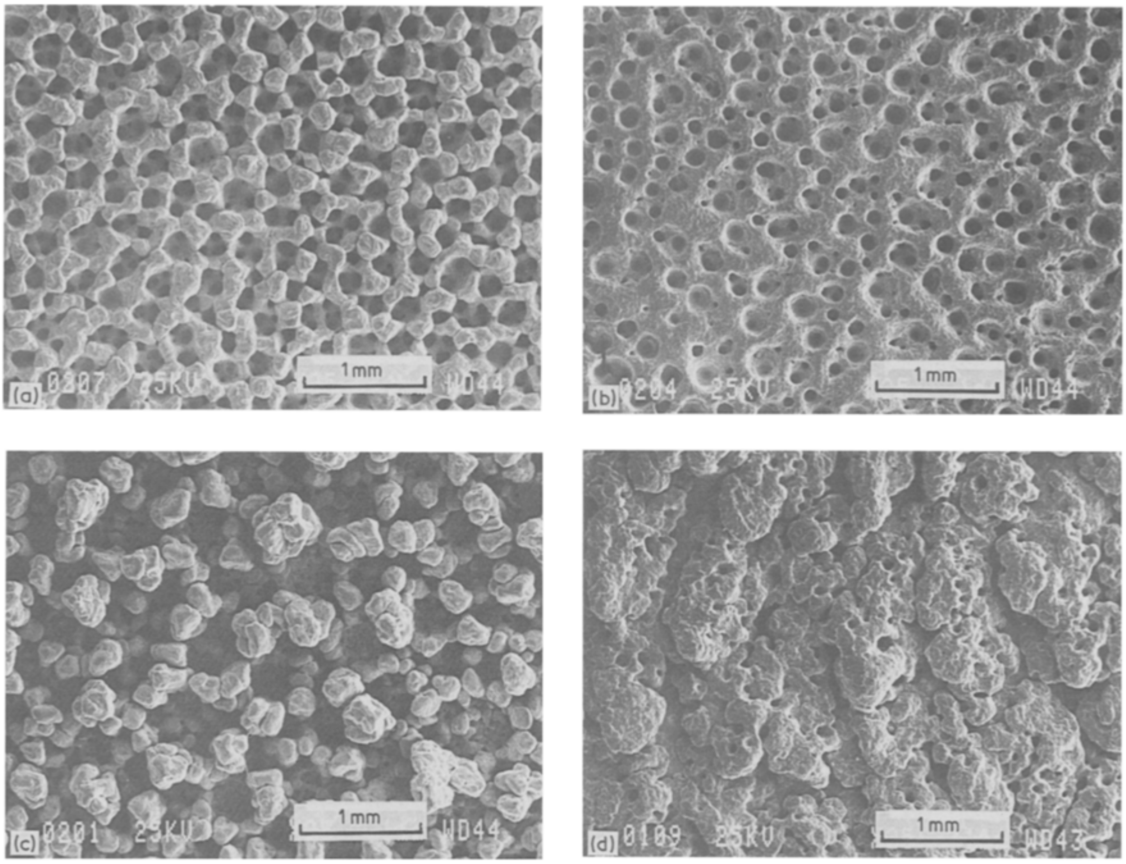

Fig. 12. Effect of 2-butyne-1,4-diol on zinc deposit morphology (16X) (a) Bath B; (b) Bath B + 2-butyne-1,4-diol; (c) Bath C; (d) Bath C + 2-butyne-1,4-diol.

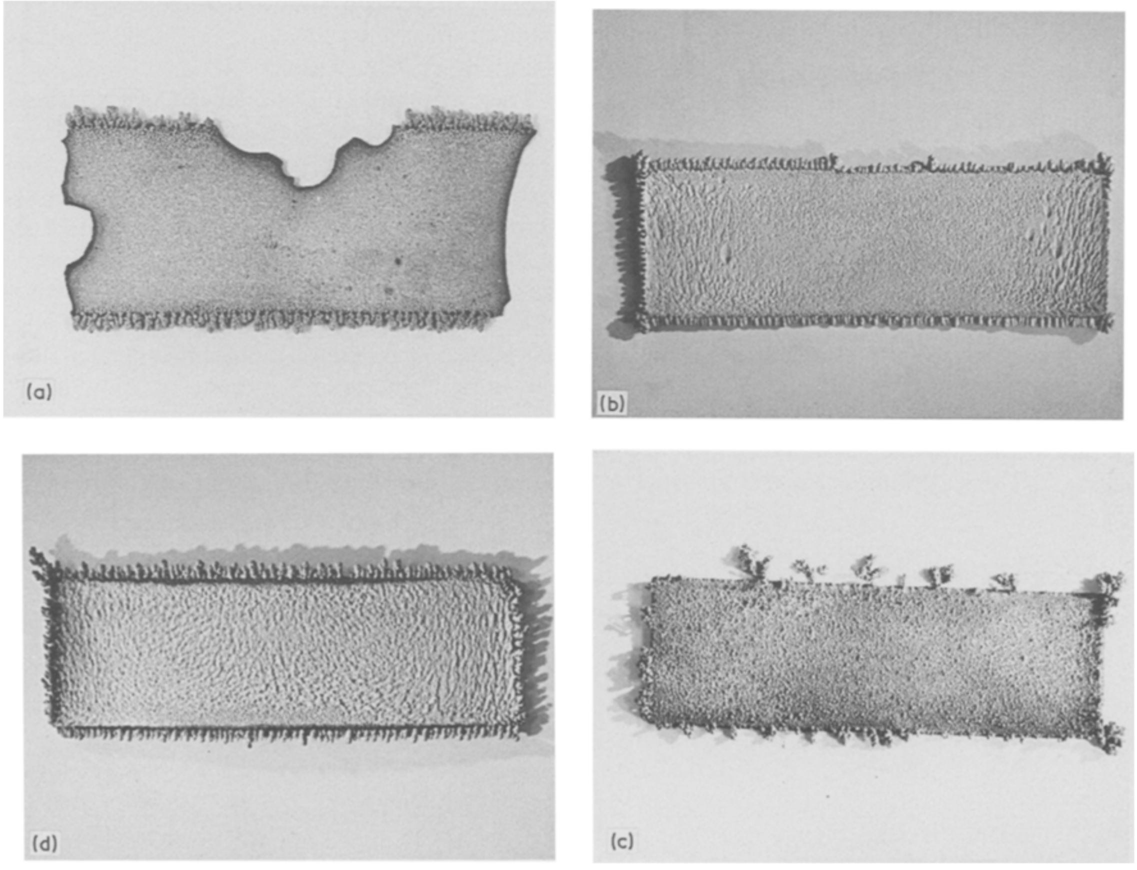

Fig. 13. Effect of nickel and 2-butyne-1,4-diol on zinc deposit (a) 1.1X; (b), (c) and (d) 0.9X: (a) Bath B + 15 $\mathrm{mg\,l^{-1}}$ Ni; (b) Same as (a) + 2-butyne-1,4-diol; (c) Bath C + 25 $\mathrm{mg\,l^{-1}}$ Ni; (d) Same as (c) + 2-butyne-1,4-diol.

expected with the mass transfer conditions used. Anomalous codeposition could also provide an explanation for the increase in the Ni content of zinc in the case of Cu + Ni combinations and for the detrimental synergy effects that have been reported. An interaction of Cu with this phenomenon should be considered.

The tests conducted in the more acidic solution (bath B) showed that the impurities can be classified in the following order of their detrimental effect: Sb > Co, Ni > Cu. The more aggressive behaviour of Sb is related to the probable mechanism of its action through hydride formation [22]. The codeposition of Sb with zinc has been reported in sulphate solution [24]. The higher Sb content observed in the chloride media results from the fact that at the low HCl concentration of bath A, a higher level of Sb can be tolerated in the electrolyte.

4.2. *Effect of 2-butyne-1,4-diol*

The lowering of the Ni content of zinc by 2-butyne-1,4-diol which is observed in chloride solutions agrees with the results reported in sulphate media by Mathieu and Piron [19]. Piron, Mathieu and D'Amboise have recently found that a cyclotrimer of 2-butyne-1,4-diol can form an insoluble complex with Ni ions in sulphate solutions [29]. Tests conducted for this study also demonstrated the precipitation of Ni ions with the additive in the chloride media. It should be emphasized that 2-butyne-1,4-diol was shown to have little effect on the rate of H_2 evolution on Ni either in sulphate [30] or chloride media [31]. The selective inhibition of the codeposition of Sb which permitted an increase of CE is also encouraging.

5. Conclusion

Zinc electrowinning tests in acidic chloride solutions have showed that the detrimental effects on current efficiency of metallic impurities are increased with higher acid concentration. In the case of Ni and Co, these effects are also more important with higher total chloride ion concentration. The low level of these metals in the zinc deposit can be related to the phenomenon of anomalous codeposition.

The use of 2-butyne-1,4-diol increased the current efficiency in the presence of Sb and Ni. The additive lowered the impurity contents of the zinc deposits.

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