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Current-Potential Effects of Trace Impurities in Zinc Sulfate Electrolyte

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The influence of combinations of impurities on the current-potential curves for electrolysis of zinc has been studied by a method described by Mantell and Ferment. The experiments show that for the single impurities antimony and β-naphthol there is a quantitative relationship between transition current and impurity concentration. For mixtures of the impurities cobalt, antimony, and β-naphthol the effects upon the current-potential curves show no law of additivity related to the effect of the single impurities. For mixtures the hydrogen overvoltage is reduced to a considerable degree.

Some of the trace impurities in the zinc sulfate electrolyte studied most extentisely are cobalt, antimony, and β-naphthol. Investigations concerning the relationship between cathode potential, current efficiency with respect to zinc and the amount of impurities in the electrolyte have been reported[1–5].

We have studied the effect of said impurities – single and in combinations – upon the current-potential curve. The method – described by Mantell and Ferment[6] for the manganese electrolyte – is based upon the curve produced by continuously changing the cathode potential at a programmed rate. Starting with a clean aluminium cathode the initial cathode potential is adjusted to yield zero current. The potential drive is then started and the current is recorded as a function of the cathode potential.

EXPERIMENTAL

The electrolytic cell consisted of a 400 ml Pyrex beaker and a cover of polyethylene plastic.

The cathode was a commercial aluminium alloy (analysis: 3.8 % Cu, 0.3 % Fe, 0.3 % Mg, 0.6 % Mn, 1.0 % Pb, 0.6 % Si, and 0.2 % Zn) and the anode a lead-silver (1 % Ag) alloy. Both electrodes were moulded in plastic.

The potential applied was measured by means of a saturated calomel electrode and a Luggin capillary and transformed to the Normal Hydrogen Scale. The distance between the cathode and the capillary tip was constant, 1 mm.

The potentiostat used was a Beckman Electroscan 30. The voltage variation was -60 mV/min.

Between each run the cathode surface was polished with different grades of suspended alumina of which the finest had a particle size of 0.05 μ.

The reagents used was of *p.a.* quality. The standard electrolyte contained 125 g/l Zn and 80 g/l H_2SO_4. Cell temperature 30°C.

RESULTS

The standard curve is shown in Fig. 1. Its particular form depends on the alloying metals of the cathode. This was demonstrated by a test with pure (99.998 %) Al-cathode. No current was then observed before the cathode potential was close to the reversible potential for zinc-deposition. From then it rose sharply and followed the form of the standard curve. The current at the point A at the standard curve is called the transition current.

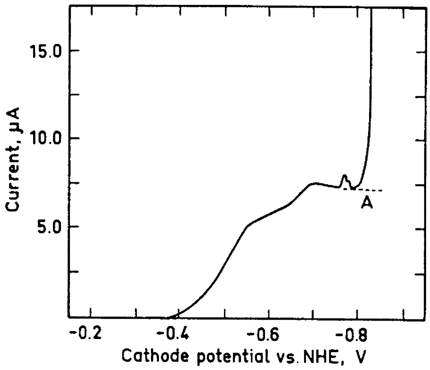

Fig. 1. Standard current-potential curve.

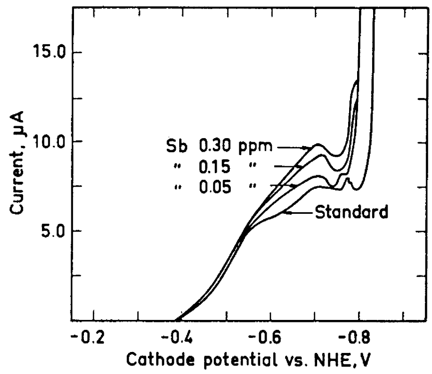

Fig. 2. Effect of antimony concentration.

Single impurities. Figs. 2 – 4 show the effect of the single impurities cobalt, antimony, and β-naphthol. Following the argument of Mantell and Ferment

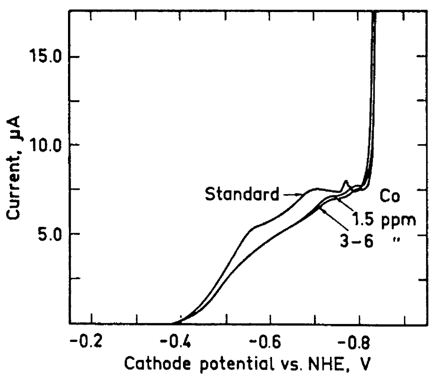

Fig. 3. Effect of cobalt concentration.

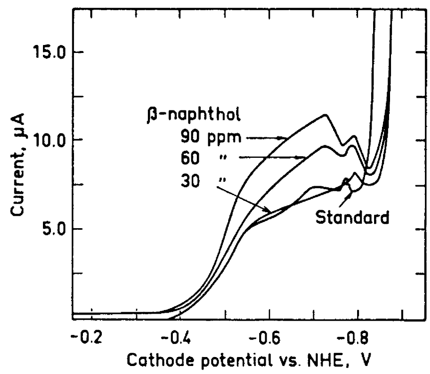

Fig. 4. Effect of β-naphthol concentration.

antimony and β-naphthol decrease the hydrogen overpotential of the base metal, while cobalt surprisingly under the existing conditions seems to increase it.

Antimony and β-naphthol show a correlation between transition current and impurity concentration. Cobalt has little effect. Antimony shifts the deposition potential in the positive direction while β-naphthol has the opposite effect.

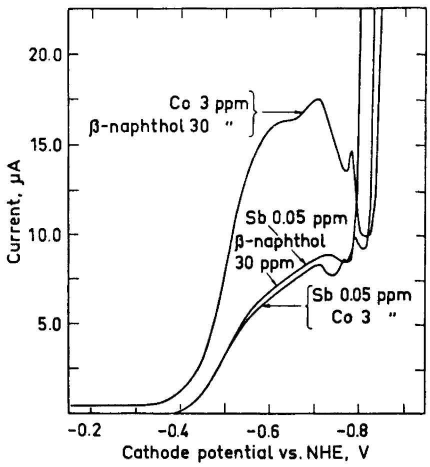

Fig. 5. Effect of combination of impurities.

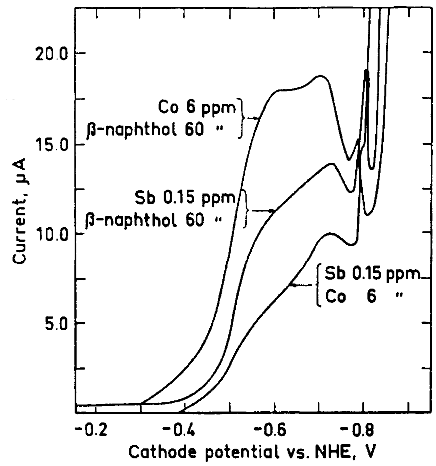

Fig. 6. Effect of combination of impurities.

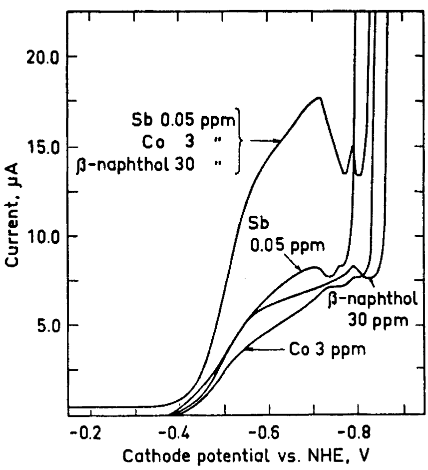

Fig. 7. Effect of combination of impurities.

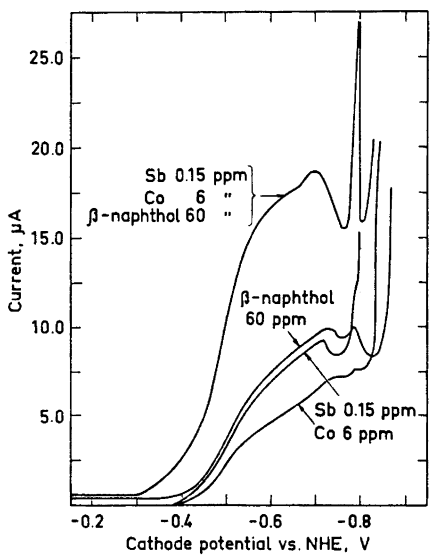

Fig. 8. Effect of combination of impurities.

Binary mixtures of impurities. Current-potential curves for pairs of impurities are shown in Figs. 5 and 6. The effect upon the curves does not follow an additive law related to the effect of single impurities.

Ternary mixtures of impurities. With all three impurities present (Figs. 7 and 8), this effect is even more marked. This is in agreement with reports for electrolysis of zinc. According to Turomshina and Stender[2] and Steintveit and Holtan[4] presence of only one impurity may not reduce the current efficiency at all, but when to or three are present simultaneously they may be very harmful.

The effect of binary and ternary mixtures upon the transition current is shown in Table 1.

Table 1. Effect of combinations of impurities upon the transition current.

Impurity, ppm	Transition current, μA
Standard	7.4
a. 0.05 Sb	7.7
b. 3 Co	7.6
c. 30 β-naphthol	7.7
a+b	7.7
a+c	9.2
b+c	9.9
a+b+c	13.4
d. 0.15 Sb	8.5
e. 6 Co	7.6
f. 60 β-naphthol	8.5
d+e	9.5
d+f	13.7
e+f	11.1
d+e+f	16.0

CONCLUSIONS

1. For the single impurities antimony and β-naphthol there is a quantitative relationship between transition current and impurity concentration.
2. For mixtures of the impurities cobalt, antimony, and β-naphthol the effects upon the current-potential curves show no law of additivity related to the effect of the single impurities.
3. Presence of the three impurities cobalt, antimony, and β-naphthol simultaneously reduces the hydrogen overvoltage to a considerable degree.

REFERENCES

1. Turomshina, U. F. and Stender, V. V. *J. Appl. Chem. USSR (English Transl.)* **28** (1955) 347.
2. Turomshina, U. F. and Stender, V. V. *J. Appl. Chem. USSR (English Transl.)* **28** (1955) 447.

3. Levin, A. J., Pomosov, A. V., Krymakova, E. E. and Falicheva, V. J. *J. Appl. Chem. USSR (English Transl.)* **31** (1958) 569.
4. Steintveit, G. and Holtan, Jr., H. *J. Electrochem. Soc.* **107** (1960) 247.
5. Znamenskii, G. N. and Stender, V. V. *J. Appl. Chem. USSR (English Transl.)* **33** (1960) 2692.
6. Mantell, C. H. and Ferment, G. *Trans. Met. Soc. AIME* **236** (1966) 718.

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