STUDIES ON THE ELECTROWINNING OF ZINC FROM ZINC SULPHATE ELECTROLYTE

R.A. Gohar, K.R. Kazmi and K. Hussain

PCSIR Laboratories Complex, Lahore 54600, Pakistan

Studies have been reported on the electrowinning of metallic zinc from a zinc sulphate electrolyte. The electrolyte was prepared by roasting of zinc sulphide concentrate followed by leaching and purification of the resultant solution. This communication presents the results on the optimization of electrowinning parameters like current density, electrode spacing, acid concentration and addition agents. The purity of the metal obtained is 99.74%.

Key words: Electrowinning, Electrolyte, Hydrometallurgy.

Introduction

The hydrometallurgical production of metallic zinc is quite an established industry and infact about 80% of the primary zinc production in the world is through this route [1]. The R&D effort in this industry is mainly oriented towards refinements in the existing technology. Thus, Duly and Krumb [2] reviewed the current practices in electrowinning and refining of copper, nickel and zinc from the point of view of their respective energy requirements. Ettel and Gordon [3] proposed a dimensionally stable anode with a low oxygen overpotential which could also permit reducing the gap, could possibly save as much as 0.5V and also reduce the cooling requirements.

Jochens *et al.* [4] reported that bubbling of air could reduce the contamination of zinc by lead. Classents [5] found that application of periodic reverse current was beneficial at high current densities provided the reverse pulse was short enough to avoid anode corrosion. Robinson and O'Keefe [6] reported the influence of relative amounts of glue and antimony in solution on the morphology of the zinc deposit and current efficiency. They showed that the glue and antimony combination of 0.08 mgl^{-1} Sb and 30 mgl^{-1} of glue resulted in an average of 90.9% current efficiency (C.E.) and characteristic zinc morphology. Sagiyama *et al* [7] reported that surface roughness, morphology and crystal orientation of zinc electrodeposit increased by decreasing mass transfer in electrolysis and bath conditions. He observed that stacked platelet crystals were formed parallel to the substrate by increasing mass transfer conditions. Cole [8] also studied the surface morphology and orientation of zinc deposits, obtained from pure, addition free acid and synthetic electrolyte containing 65 gl^{-1} Zn^{+2} and 200 gl^{-1} H$_2$SO$_4$. He observed that temperature and current density variation influenced the orientation and current efficiency in a systematic manner-hexagonal platelets grew preferentially with a basal plane aligned parallel to substrate at a high temperature and current efficiency (C.E. 95%). Bannear and McNicol [9] reported that C.E. increased as the zinc acid ratio. For the full scale operations suitable zinc acid ratio and other factors like spent electrolyte, acidity, power efficiency and impurities like Sb or Ni have also impact upon the plant performance.

In Pakistan, lead-zinc deposits occur in Balochistan and NWFP. This paper reports on the finidings regarding the electrowinning of metalic zinc from a zinc sulphate electrolyte prepared from a zinc sulphide concentrate [10]. The concentrate was obtained by flotation of NWFP lead-zinc ore containing upto 7% zinc [11].

Experimental

The electrolyte. The bulk electrolyte was prepared by roasting of a zinc sulphide concentrate followed by leaching of the resulting zinc oxide with H$_2$SO$_4$ and purification of the solution. The neutral solution so obtained was reconstituted to contain 50 gl^{-1} zinc (Zn) and 147.2 gl^{-1} H$_2$SO$_4$ and was called the cell solution. 400 ml cell solution was used in each test.

Electrolytic cell. A 500 ml pyrex glass beaker was used as electrolytic cell. It contained two lead anodes cut from 1 mm thick sheet each measuring 12.0 x 7.4 cm. The cathode measured 12.0 x 7.5 x 0.15 cm and was obtained from a commercially pure aluminium sheet. The cathode was dipped 7.0 cm in the electrolyte so that the total deposit area measured 105 cm^2.

Electrical supply unit. Electrical supply unit used was rectifier manufactured by the HBS Equipment Corporation, Los Angeles, California, USA. It could convert alternating current (A.C.) to direct current (D.C.). A D.C. output of 50 amp. at 6 V could be obtained.

Electrolysis. The principal variables studied were zinc and free acid contents of the electrolyte, electrowinning time, current density, cathode-anode spacing, glue concentration (7.50-58 mgl^{-1}) added as water solution and antimony concentration (0.0-0.06 mgl^{-1}) added in the electrolyte as potassium antimony tartrate solution.

Results and Discussion

Effect of zinc concentration in the electrolyte. Table 1 shows the effet of the initial zinc concentration on the electrowinning (E.W.) of zinc from electrolytic cell solution. It is seen that the recovery of zinc increases with increasing zinc concentration. At a concentration of 50 g1^{-1} Zn^{+2}, the recovery of zinc is 83.60%. After that it becomes 75.91. These results indicate that the initial higher concentration of zinc in the electrolyte favours the transportation of zinc ions for deposition on the cathode surface. As the electrolysis proceeds and the electrolyte becomes depleted, a limiting concentration is reached beyond which no deposition takes place.

Effect of free acid (H_2SO_4) content. Table 2 shows the effect of free acid content of the bath. It is observed that as the acid content increases, the recovery of zinc also increases. At an acid concentration of 147.2 g/l, the recovery of zinc is 83.60%. At higher concentrations of the acid, the recovery becomes almost constant.

Effect of time. In order to optimize the time required to obtain maximum recovery, a set of experiments was carried out. The results are shown in Table 3. It is seen that for a time of 60 mins, the electrolytic recovery of zinc is 83.60%. An increase in the duration of electrolysis beyond 60 min does not affect the yield of metal.

Effect of cathode-anode distance. Table 4 shows the effect of varying cathode to anode spacing from 0.5-3.0 cm. From this table it is seen that the recovery increases to 83.60% at 2.5 cm. After that when the space is increased, the recovery falls.

Effect of current. Table 5 shows the effect of total current on the recovery of zinc. It is seen that at a total current of 15 amps. the deposition of zinc is favoured with a recovery of 83.60%.

Effect of current density (c.d.). The variation in cathode/ anode current density ratio has been affected by changing the cathode area which causes the total current distribution to increase or decrease. The results shown in Table 6 indicate that with the increase in cathode c.d., the recovery of zinc increase. A cathode current density of 1575.63 amp/m^2 produces a recovery of 83.95% zinc.

Effect of additives. The effect of antimony and glue additions in varying amounts on the morphology of the zinc deposit was observed and noted. It was seen that at 0.04mgl^{-1} antimony, the deposit appeared to be more compact and of finer grain size than the deposit from addition-free electrolyte. The effect of increaseing the amount of antimony on the physical appearance of the zinc deposits is summarised in Table 7. It was noted that at higher antimony concentration, i.e. 0.06 mgl^{-1} the zinc deposit was seen to consist of large rounded platelets.

TABLE 1. EFFECT OF VARYING ZINC IN THE ELECTROLYTE.

Zinc (g/l)	Zinc deposited (calculated) (g)	Recovery %	C. E. %
40	31.22	78.06	68.28
45	36.00	80.00	78.72
50	41.80	83.60	91.4
55	41.75	75.91	91.29

Electrolysis conditions: Current 15A, volts 3.5, time 60 min. temperature 35°C, cathode c. d 1428.57 Am^{-2}, cathode anode spacing 2.5 cm.

TABLE 2. EFFECT OF FREE ACID CONTENT.

H$_2$SO$_4$ (g/l)	Zinc deposited (calculated) (g)	Recovery %	C. E. %
0.0	39.00	78.00	85.28
36.8	39.90	79.80	87.25
73.6	41.25	82.50	90.20
110.4	41.75	83.50	91.20
147.2	41.80	83.60	91.40
182.0	41.77	83.55	91.35

Electrolysis conditions: Same as above , Zinc 50g/l.

TABLE 3. EFFECT OF VARYING TIME IN ELECTROLYSIS.

Time (min.)	Zinc deposited (calculated)(g)	Acid g/l	Recovery %	C. E. %
15	8.50	153.10	17.00	74.34
30	20.00	165.40	40.00	87.46
45	31.12	171.50	62.25	90.74
60	41.80	177.60	83.60	81.40
75	41.80	183.75	83.60	89.90
90	41.80	196.00	83.60	88.45

Electrolysis conditions: Same as above, Zinc 50 g/l, H$_2$SO$_4$ 147.2 g/l.

TABLE 4. EFFECT OF VARYING CATHODE/ ANODE SPACING.

C-A distance (cm)	Zinc deposited (calculated)(g)	Recovery %	C.E. %
0.5	20.50	41.00	44.83
1.0	28.72	57.45	62.82
1.5	30.97	61.95	67.72
2.0	35.85	71.70	78.41
2.5	41.80	83.60	91.40
3.0	33.10	66.20	72.40

Electrolysis conditions: Same as above (Zinc 50g/l, H$_2$SO$_4$147.2g/l, time 60 min.).

TABLE 5. EFFECT OF VARYING TOTAL CURRENT.

Total current (A)	Cathode c.d. (A.m^{-2})	Anode c.d. (A.m^{-2})	Zinc deposited (calculated) (g)	Recovery (%)	C.E. (%)
5	476.19	482.63	10.25	20.50	67.24
10	952.38	965.25	24.15	48.30	79.21
15	1428.57	1447.88	41.80	83.60	91.40
20	1904.76	1930.50	41.80	83.60	68.55
30	2857.14	2995.75	41.77	83.55	45.71

Electrolysis conditions: Same as above (Zn 50g/l, H$_2$SO$_4$ 147.2g/l, time 60 min. C-A distance 2.5 cm.)

Addition agents are often used to increase the ampere efficiency of a zinc cell and to improve the physical character of the deposit. One theory on the use of addition agents is that certain substances added to the electrolyte combine with the unwanted impurities present and cause them to precipitate with the anode sludge [12].

It appears from the experimental results that a current efficiency of 93.48% can be achieved. It may, however, be pointed out that, theoretically, higher current efficiencies may be attained by using concentrated electrolytes with low acid concentrations and that electrolysis should be carried out at high current density and low temperature [14]. But, as electrolysis progresses, the zinc concentration in the solution is reduced, its acidity increases, and current efficiency decreases, making difficult the complete recovery of zinc (Table 3). A

TABLE 6. EFFECT OF CATHODE/ANODE CURRENT DENSITY VARIATION.

Cathode c.d. (A.m^{-2})	Anode c.d. (A.m^{-2})	Zinc deposited (calculated) (g)	Recovery (%)	C.E. (%)
1316.25	1447.88	38.17	76.35	83.50
1428.57	"	41.80	83.60	91.40
1575.63	"	41.97	83.95	91.82
1885.22	"	41.97	83.95	91.82
2142.86	"	41.97	83.95	91.82

Electrolysis conditions : Same as above (Zn 50g/l, H$_2$SO$_4$ 147.2g/l time 60 min. C-A distance 2.5 cm, total current 15A).

TABLE 7. EFFECT OF ADDITION AGENTS OF ZINC DEPOSITION.

Additive (mg/l)		Zinc deposited (calculated) (g)	Recovery %	C.E. %	Appearance of the deposit
Sb	Glue				
0.00	0.00	41.97	83.95	91.82	Scattered, big granules on plate.
0.02	0.00	42.00	84.00	91.84	Unsmooth granules on plate.
0.04	0.00	42.07	84.15	91.99	Smooth plate deposited bright.
0.06	0.00	42.00	84.00	91.84	Bright brittle deposit.
0.00	7.50	42.20	84.40	92.31	Light greyish deposit.
0.00	15.00	42.30	84.60	92.49	Light greyish loose deposited.
0.00	30.00	42.47	84.95	92.89	Smooth greyish deposit easily stripped.
0.00	58.00	42.05	84.10	91.95	Thin film of glue formed on the deposit.
0.04	30.00	42.75	85.50	93.48	Smooth bright greyish deposit easily stripped.

Electrolysis conditions: Same as above (Zn 50g/l, H$_2$SO$_4$ 147.2g/l, time 60 min. C-A distance 2.5 cm, total current 15A, Cathode c.d. 1575.63 A.m^{-2}

lack of available ions in the electrolyte produces an effect at least similar to a lowering of the hydrogen over voltage [12]. Continuous E.W. can compensate this effect. At the same time, due to an increase in the current density, the anode oxygen overvoltage and consequently the value of anode potential increases. Working with anodes which give high overvoltages for oxygen evolution strongly oxidizing conditions may be established and oxygen-rich compounds such as persulphates, manganese dioxide and lead dioxide may be produced [13].

Formation of lead dioxide on the anodes, as it has been observed and examined indicates that the recovery of zinc beyond 85.5% might not have been achieved due to anodic oxidation. About the formation of lead dioxide, it follows from the standard electrode potentials that the first to form is lead sulphate which produces a thin film of nearly insoluble crystals on the anode. The area of the lead electrode is, as a result decreased, the current density rises, and so does the anode potential. The next to form in the pores of the lead sulphate is lead dioxide followed after another increase in the anode potential by the release of oxygen the principal reaction at the anode [14].

Moreover, as the electrodes were commercially pure "Local- Cell" action might have been set up which contributed to the resolution of zinc. This is because a detrimental impurity of electrode metal existing even in trace amounts may seriously lower the hydrogen overvoltage at this point [12].

Current efficiencies approaching 100% are difficult to obtain as there are a number of factors affecting the current efficiency. Hydrogen evolution is one such factor. It was observed during electrowinning experiments that hydrogen did evolve at the cathode as a secondary product affecting not only current efficiency but also the morphology of the deposit. The purity of zinc obtained is 99.74%

Conclusion

The results of the test work reported in this communication indicate that it is possible to obtain a smooth, coherent and easily stripped zinc deposit at a current efficiency of 93.5%.

The electrolyte containing 50 g/1 zinc, when submitted to electrolysis for 60 min. at an applied voltage of 3.5 V, total current 15A, H$_2$SO$_4$ concentration 147g/1, cathode anode spacing 2.5 cm, cathode current density 1575.6A/m², addition agents 0.04 mg/1 antimony and 30mg/1 glue, will result in a metal recovery of 85.5%.

These results have been obtained using commercially pure aluminium sheet cathode and lead anode. Lead-0.75% Ag anodes were not available for use in experimental work. The electrolyte required cooling during electrolysis and temperature was maintained at 35°. It was observed that stirring of

the electrolysis bath helped in dis-engagement of O_2 resulting in improved current efficiency and metal recovery.

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