

ELECTROREFINING OF LEAD FROM SCRAP LEAD ACID BATTERY

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Lead acid battery finds application system and the disposal of its scraps is one of the environmental problems all over the world. Pyrometallurgical operation currently employed generates emission of oxides of sulphur and particulate lead causing atmospheric pollution. Electrolytic route is investigated as an alternative to recover lead. The route comprises breaking the scrap batteries and separating the portions of metallic lead and lead compounds. The metallic portion is cast into anodes and electrorefined in lead fluoborate medium. The purity of final cathode is analysed by mass spectrometry. Addition of levelling agent and grain refiner in proper proportion avoids dendritic growth. Over potential measurement is found to be useful in monitoring the concentration of additive in the electrolyte during electrorefining of lead.

Keywords: Recovery of lead, scrap batteries, electrorefining.

INTRODUCTION

Lead acid battery is an important automotive battery system and its annual production is around 4 million units from which 40,000 tonnes of lead can be recovered. Pyrometallurgical route currently practiced suffers from environmental problems like emission of lead particulates and oxides of sulphur. As an alternative, various process for the recovery of lead have been reported [1-4].

An alternative route based on electrohydro metallurgical principle is investigated. The scrap batteries are crushed and separated into fractions of metallic lead and lead compounds. The metallic portion is cast into anodes for electrorefining. The active material consisting of lead compounds is desulphurised, leached with fluoboric acid and lead is recovered by electrowinning from the solution.

In this paper certain aspects like distribution of lead fraction, electrorefining of metallics, monitoring of the electrolyte additives and generation of antimony slime during electrorefining have been examined.

EXPERIMENTAL

The battery plates were crushed and separated into metallic and non metallic portion using a

sieve. The metallic portion was melted, cast into anodes and electrorefined in a PVC cell containing lead fluoborate solution of 60-80 g.l⁻¹ lead, 80-100 g.l⁻¹ free fluoboric acid, 40 g.l⁻¹ goulac and 2.0 g.l⁻¹ gelatin. Lead starter sheet served as cathode and a current density of 200 Am⁻² was employed. After a period of 5-7 days, the cathode lead was analysed for its purity level by mass spectrometry. During electrorefining operation, the anode slime was removed periodically and its antimony content was analysed.

Cathode overpotential measurements were made using a thin lead sheet and pure lead foil of area 2 cm² as anode and cathode respectively. Current density ranging from 100-800 Am⁻² was applied and the corresponding cathode over potential was measured using a lead reference electrode. Amount of gelatin was varied from 500-3000 ppm and the corresponding polarisation data were measured.

RESULTS AND DISCUSSION

Table I shows the data on distribution of metallic portion and non metallic portion after crushing and sieving. The top lead and metallic portion constitutes more than 50% of the total lead values in the scrap batteries.

The metallic fraction separated from the scrap batteries is found to contain 2-2.5% antimony. Electrorefining is an ideal method for separating the major impurity like antimony. During electrorefining of antimonial lead, lead goes into solution and gets deposited at the cathode while the antimony is retained in the form of slime on the anode surface. The typical operating condition for electrorefining is given in Table II.

The lead anode could be dissolved up to 75% of its initial weight as shown in Table III. The antimony values are retained in the anode slime and antimony content of the slime is 30-40 % . The ratio of slime to lead deposit was found to be in the range of 6- 14%.

As the anode dissolves, the metallic impurities form a spongy compact layer weighing 2.5-3.0% of the anode and preserve the same shape as the original anode. It is a true metallic sponge through which migration of lead ions take place. The cell voltage rises from 0.3 V to 0.45-0.50 V when the slime layer reaches certain thickness. This is due to the gradual rise in the resistance of the growing slime layer.

Table IV shows the purity level of electrorefined lead metal. As the cell voltage goes beyond 0.4 V, the antimony in the slime tends to go into solution and antimony content of lead deposit went even upto 0.77% affecting the purity of the lead deposit

TABLE I: Distribution of lead fractions

Battery capacity Ah	Wt. of battery Kg	Top lead portion Kg	Metallic portion Kg	Active material portion Kg
60	22.5	2.8	5.9	7.7
60	20.5	2.0	3.9	7.6
60	22.5	3.3	7.4	7.6
135	42.0	4.4	8.4	23.4
135	47.0	5.1	12.5	15.6
135	42.0	4.7	5.8	18.5
180	55.2	4.8	11.0	18.3
180	60.9	5.6	12.8	17.8

TABLE II: Typical operating conditions for electrorefining

Electrolyte	: Lead fluoborate solution containing 60-80 g.l ⁻¹ lead, 80-100 g.l ⁻¹ free fluoboric acid, 4.0 g.l ⁻¹ goulac and 1.5 g.l ⁻¹ gelatin
Anode	: Cast lead
Cathode	: Lead starter sheet
Current	: 10 A
Current density	: 200 Am ⁻²
Current efficiency	: 97%
Cell voltage	: 0.2 to 0.4 V
Duration	: 120-140 hours
Energy consumption	: 0.1-0.15 Kwhr/Kg

obtained during electrorefining operation. So the cell voltage is to be kept below 0.4 V to get better purity. This could be achieved by periodic removal of antimony slime either by scrapping the anode surface or by using air sparging.

Dendrites comprising lead tree growth and needle shaped formations are very common with deposits of lead during electrorefining. Addition agents like

TABLE III: Material balance in electrorefining

Anode Kg	Time Hrs	Lead deposited Kg	Undissolved portion Kg	Slime Kg	Slime/Pb deposit ratio Wt%	Sb content in the slime , %
9.10	168	6.18	2.48	0.40	6.5	32
7.45	114	4.42	2.45	0.58	13.1	37
8.20	143	4.20	3.23	0.77	18.3	36
8.20	150	5.47	2.15	0.55	10.1	42
8.50	151	5.84	2.22	0.58	9.9	35
8.10	151	6.21	1.80	0.40	6.4	41
5.25	99	3.52	1.25	0.48	13.6	36

lignin sulphonate (goulac) as grain refiner and gelatin as levelling agents are found useful in overcoming this problem.

Fig. 1 shows the polarisation curves for electrodeposition of lead from lead fluoborate electrolyte. The nearly linear polarisation/current density relationship suggests that the addition agents form a voltage barrier at the cathode surface and due to adsorption of additives on to the plating surface, there is rise of cathode potential. This cathode over potential rises to 150 mV when gelatin is present at 2000 ppm as compared to a potential value of 50 mV when there is no addition agent is present at a current density of 200 A m^{-2} . In other words a 50 mV rise is not large enough to cause uniform current density on all parts of the surface but a 150 mV does produce the required leveling action.

The slope of the polarisation curve for the addition of 500 ppm gelatin is found to be $0.3 \text{ mV A}^{-1} \cdot \text{m}^2$ and this increases to $0.6 \text{ mV A}^{-1} \cdot \text{m}^2$ for a gelatin concentration of 2000 ppm. It is reported [7] that an excellent polarisation curve refers to an approximately linear polarisation curve with a slope of $0.43 \text{ mV A}^{-1} \cdot \text{m}^2$ at 200 A m^{-2} . Hence addition of 2000 ppm of gelatin was found optimum based on the polarisation studies.

Fig. 2 shows the over potential time curves for electrodeposition of lead. When deposition is carried out for a longer duration, the polarisation of lead is found to decrease indicating the consumption of gelatin with time. When polarisation measurements were made, degradation of additives takes place linearly as function of time during couple of hours. It is

TABLE IV: Analysis of electrorefined lead

Sb %	As %	Cu %	Sn %	Bi %	Fe %
0.016	0.010	0.020	0.0041	0.0003	0.0024
0.770	0.004	0.001	0.0001	0.0008	0.0008
0.020	0.003	0.010	0.0060	0.0004	0.0010

reported [8] for copper electrorefining that gelatin is decomposed after 12 hours.

The adsorption of gelatin decreases the amount of free and active sites and often acts as inhibitors. They adsorb on the cathode surface where they involve in the electrochemical deposition of lead. These additives restrict the growth of existing grain and this forces the deposition to take place via the formation of new nuclei. The organic additive is adsorbed selectively on the active growth site and drive the natural growth direction to alter. It is also possible that the additives react with lead in forming a complex in the cathode film and in such a case it effects the lead polarisation process [7].

CONCLUSION

The scrap lead acid battery is found to contain more than 50% of the total lead values as metallic fractions in the form of lead antimony alloy. These fractions on electrolytic refining yield lead of high

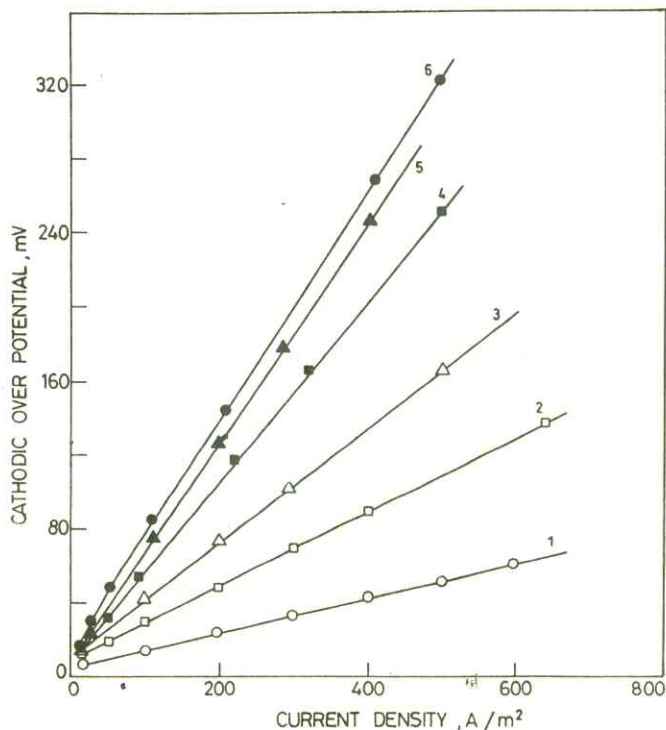


Fig. 1: Galvanostatic polarisation curves for electrodeposition of Pb from lead fluoborate solution containing 50 g.l^{-1} Pb, 150 g.l^{-1} fluoboric acid and 4 g.l^{-1} goulac with additions of (1) 0 ppm (2) 100 ppm (3) 500 ppm (4) 1000 ppm (5) 2000 ppm and (6) 3000 ppm gelatin

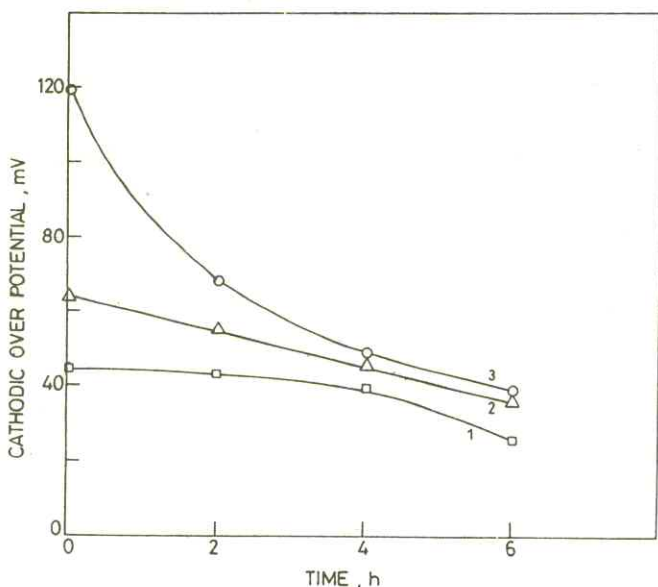


Fig. 2: Cathodic overpotential-time curves for electrodeposition of Pb from lead fluoborate solutions (1) 50 g.l⁻¹ (2) 70 g.l⁻¹ (3) 100 g.l⁻¹ Pb²⁺ with additions of 4 g.l⁻¹ goulac and 2 g.l⁻¹ gelatin

purity with generation of value added antimony slime. During electrorefining antimony is separated in the form of slime which contains 30-40 % antimony. The cell voltage should be maintained below 0.4 V, otherwise the antimony

in the slime tends to go into solution and the antimony content in the electrodeposit increases even up to 0.77%. The cathode over potential measurement is found useful in monitoring the concentration of additives like gelatin in the electrolyte. Addition of 2000 ppm of gelatin is found optimum in improving the physical nature of lead deposit.

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