RECOVERY OF LEAD FROM WASTE BATTERY PASTE

Tasneem Abbasi

Department of Chemical Engineering
Pondicherry Engineering College, Kalapet
Pondicherry 605 014, INDIA

ABSTRACT

As a part of our initiatives to obtain lead from waste battery paste, thereby attempting the dual gain of pollution control as well as resource recovery, extensive studies were conducted of which the gist is presented in this paper.

An electrolytic method was employed in which the lead paste was suspended in sodium hydroxide as electrolyte. Effect of several parameters : current density, temperature, time, lead ion concentration, sodium hydroxide concentration, agitated bath, and cathode material on the cathode potential, current efficiency, and nature of deposits, was studied. The possible reasons for the observed effects were also studied on the basis of which a mechanism for lead deposition has been elucidated.

The optimum conditions for lead recovery were found to be : temperature 60°C, current density 7A/dm², concentration of sodium hydroxide 600 g/liter, time of electrolysis 120 min.

INTRODUCTION

Used lead acid batteries form an important secondary source of lead, especially in countries which are not otherwise rich in lead resources. The treatment of used acid batteries for recovering lead is important from the point of view of lead production as well as pollution abatement as otherwise the battery scrap leads to serious disposal problems (Abbasi et al 1999). The lead in used batteries is in the form of grid plates and pole bridges made up of lead-antimony alloy (5-12 % antimony) and paste consisting mainly of antimony-free lead, lead oxide, and lead sulfate.

There have been attempts, especially pyrometallurgical, to recover lead from waste batteries (Abbasi 2000, Abbasi et al 1998) but none has achieved the benefit-cost advantage which can motivate large-scale processing of waste batteries for lead recovery. The present investigation has been undertaken in this context.
EXPERIMENTAL

The experimental set up is illustrated in Figure 1. Waste battery paste was analyzed by standard methods (APHA 1997) The composition was: lead monoxide: 27.77%; lead sulfate: 63.08%; free lead: 7.44%; total lead: 75.42%; Antimony: 2.55%.

All the experiments were carried out after stirring the solute (lead sulfate, lead monoxide, lead waste battery paste) in sodium hydroxide at 70° -80° C for half an hour. Before each experiment the cathode was cleaned thoroughly with hydrochloric acid and washed.

The lead deposits obtained after each experiment were washed liberally with water, then with 2% acetic acid, washed again with water, and dried in a vacuum furnace at 100 °C for 1 hr.

Figure 1. The experimental set-up for the electrolytical lead recovery

RESULTS AND DISCUSSION

Due to limitation of space, most data tables and several figures are not given here. The author shall be pleased to make them available should you ask. The gist of findings are presented here.
Reaction mechanism of lead deposition

The cathodic reaction taking place during electrolysis may involve lead or lead compounds in the solid (suspended) state, or it may proceed after the dissolution of lead or lead compounds.

Our studies show that the nature of lead deposits changed with the variation of such parameters as sodium hydroxide concentration and temperature, which influenced the dissolution of lead bearing material. This indicates that cathodic reactions were taking place after the dissolution of lead or its compounds in sodium hydroxide. The probable chemical reactions, therefore, are:

1. $\text{PbSO}_4 + 4\text{NaOH} = \text{Na}_2\text{SO}_4 + \text{Na}_2\text{PbO}_2 + 2\text{H}_2\text{O}$
2. $\text{PbO} + 2\text{NaOH} = \text{Na}_2\text{PbO}_2 + \text{H}_2\text{O}$
3. $\text{Pb} + 2\text{NaOH} = \text{Na}_2\text{PbO}_2 + \text{H}_2$

All three reactions generate sodium plumbite. The ionization of sodium plumbite during electrolysis may lead to plumbous ion ($\text{Pb}^{2+}$), biplumbite ion ($\text{HPbO}_2^-$), plumbite ion ($\text{PbO}_2^{2-}$), plumbic ion ($\text{Pb}^4+$), acid metaplumbite ion ($\text{HPbO}_3^-$), metaplumbite ion ($\text{PbO}_3^{2-}$), and orthoplumbite ion ($\text{PbO}_4^{4-}$). The potential – pH diagram for the system lead – water indicates that under the highly alkaline condition of the bath ($[\text{NaOH}] > 2\text{M, pH} \sim 14$), the predominant lead – containing ion is the biplumbite ion ($\text{HPbO}_2^-$); the concentration of other lead containing ions being insignificant.

The diffusion and hydrodynamic flow force the anions ($\text{HPbO}_2^-$) to move towards the cathode where these ions are reduced. We found higher percentage recovery with stirred baths compared to static baths, which indicates the importance of convective flows. The probable reaction is

$$\text{HPbO}_2^- + 3\text{H}^+ + 2\text{e} = \text{Pb} + 2\text{H}_2\text{O}$$  \[4\]

$$E_0 = 0.702 - 0.0886 \text{pH} + 0.0295 \log [\text{HPbO}_2^-]$$  \[5\]

At pH 14 the above reaction is feasible when the cathode potential value is more negative than $-0.0530$. The observed cathode potential values (-0.01 to $-1.70\text{V}$) distinctively show the likelihood of the above reaction.

Effect of various parameters on the electrolysis of waste batter paste

Effect of current density: The current efficiency did not vary much in the current density range of $2.5 - 10 \text{A/dm}^2$. Above $10 \text{A/dm}^2$ the current efficiency decreased rapidly with the increase in current density. With the increase in current density the effective metal ion concentrations in the vicinity of the cathode reduce and hydrogen evolution increases leading to reduced current efficiency. The experiments were carried out keeping the waste battery paste in suspension in the sodium hydroxide solutions and in all likelihood, as detailed during discussion on the mechanism of lead deposition, the electrolysis was preceded by dissolution of paste. The decrease of current efficiency may also be due to the fact that the rate of dissolution of lead compounds and free lead in sodium hydroxide becomes the rate-controlling factor.
The purity of lead obtained was about 90%. This low purity may be due to the presence of lead oxide in the deposits owing to the following reasons:

1. Occurrence of lead oxide in the lead deposits because of decomposition of mechanically held sodium plumbite (in the deposits) during drying. The likely reaction is

\[
\text{Na}_2\text{PbO}_2 + \text{H}_2\text{O} = \text{PbO} + 2\text{NaOH}
\]  

[6]

The observed value of current efficiency higher than 100% for current density of 7 A/dm\(^2\) is also probably due to the above-mentioned phenomena, i.e., mechanical inclusion.

2. The reactivity of electrolytic powders are in general greater than that of powders prepared by thermal processes. The particles in electrolytic powder consist of clusters of very small crystals (about 0.07 \(\mu\)m in diameter) which are under strained condition. This leads to higher reactivity causing oxidation. In the present investigation the oxidation was minimized by using a vacuum furnace during drying.

The nature of deposits was black spongy throughout the current density range studied. The analysis of deposits showed that it contained arsenic (0.056%), antimony (0.55%), copper (0.016%), and iron (0.001%) besides lead oxide.

The effect of temperature: With the increase in temperature the cathode potential is seen to decrease (become less negative). It is known that, for overpotential \(\eta\),

\[
\eta = \eta_c + \eta_a + \eta_R
\]

As a rule with the increase in temperature, \(\eta_c\), the concentration overpotential, \(\eta_a\), the activation overpotential, and \(\eta_R\), the resistance overpotential, are all reduced. This may be the reason for the observed lower cathode potential values at higher temperature in the present investigation.

The current efficiency increased with the increase in temperature up to 60\(^\circ\)C but beyond this temperature it decreased. This may be due to lower hydrogen overvoltage and higher rate of dissolution of deposited lead at higher temperatures.

At room temperature the nature of deposits was black spongy. In the temperature range 60\(^\circ\) – 100\(^\circ\) C the deposits were black spongy near the cathode while the outer portions were bright and flaky. The later may be due to lower activation polarization and higher concentration polarization. With time of electrolysis the concentration of lead ions in the electrolyte becomes less causing an increase in concentration polarization. The activation polarization is lower with higher temperature. When concentration polarization dominates over activation polarization, the flakes grow more or less perpendicularly from the electrode surface into the solution.

The effect of sodium hydroxide concentration: The results are presented in Table VII (Fig. 4). The change in sodium hydroxide concentration from 200 to 800 g/liter showed an increase in current efficiency from 34.2 to 50.2%. Black spongy deposits were obtained in all cases and the purity of lead was about 90%.
The increase in current efficiency with the concentration of sodium hydroxide is possibly due to the increase in solubility of lead and its compounds. Our experiments on different constituents of the paste reveal that the current efficiency remained practically consistent in case of lead sulfate while it increased with increase in sodium hydroxide concentration when lead or lead monoxide were electrolyzed. The reason for this observation is that the solubility of lead sulfate in sodium hydroxide is high even at low alkali concentrations and the increase in solubility with increase in alkali concentration is not substantial. The dissolution of lead or lead monoxide, on the other hand, increase markedly with the increase in alkali concentrations resulting in a similar trend for current efficiency.

The current efficiency-sodium hydroxide concentration curves level off at, and beyond, the sodium hydroxide concentration of 600 g/liter, and this value is taken as the optimum concentration of sodium hydroxide.

The effect of time: The results show that the current efficiency remained practically constant up to 120 min and then decreased slowly up to 210 min. After 210 min the current efficiency fell steeply, probably due to unavailability of lead-containing ions for deposition. The cathode potential increased after 210 min as concentration polarization probably arose from insufficient number of lead-containing ions. The weight percent recovery of lead was 91.9%.

Effect of static bath, agitated bath, and rotated cathode: The deposit of lead on the stationary cathode in the static bath was nonadherent and spongy. It readily peeled off even while the cathode was taken out of the cell. On the other hand the lead deposit in the agitated bath and on the rotating cathode was adherent, spongy, compact, and could be handled easily. It may be due to the fact that rotation of cathode and stirring of the bath reduces the thickness of the electrical double layer, leading to compact and adherent deposits.

The cathode potential in case of the rotated cathode was less than in the case of the static cathode. This unexpected observation may be explained on the basis of contact resistance (electrical contact to the rotating electrode) and/or improper contact of luggin tip (of reference electrode) with the rotating cathode, which might have developed.

The current efficiency of the static bath-static cathode system (91.5%) was found to be between that of agitated bath-static cathode system (98.1%) and agitated bath-rotated cathode system (83.7%). The higher efficiency, in the case of agitated bath-static cathode system compared to that of static bath-static cathode system is expected, but the low value of current efficiency in the case of the rotating cathode was probably due to the loss of deposited lead by dissolution and/or peeling off during rotation of the cathode.

Effect of cathode material: The value of current efficiency for nickel, stainless steel, graphite, and mild steel cathodes were close to each other, about 99%, but the value for the lead cathode was 85.87%. This low value is likely to be due to passivation of the lead cathode.

Effect of chilled cathode: When the cathode was chilled during electrolysis, the lead deposit consisted of fine powder and granules. Electrolytic deposition is a nucleation and growth process. As the cathode is chilled, the growth of the crystals at the cathode surface is hastened.
resulting in fine powder. Since the heat conductivity of lead is not high, the cooling of the deposited powder is not efficient after a few layers have been deposited. Subsequent deposits are thus granular. The purity of lead was 96%, which was higher than the purity of spongy deposits obtained in earlier experiments. The granular and powdery deposits were easier to wash which possibly reduced the formation of lead oxide during drying and favorably effected the purity of lead.

CONCLUSIONS

1. The deposition of lead takes place at the cathode after the dissolution of lead or lead compounds in sodium hydroxide and the ion responsible for lead deposition is the biplumbite ($\text{HPbO}_2^-$) ion.

2. The optimum values for the various parameters are: current density 7 A/dm$^2$, concentration of sodium hydroxide 600 g/liter, temperature $60^\circ$C, time of electrolysis 120 min.

3. A current efficiency of 97% is achieved when the electrolysis is carried out under near-optimum conditions (current density 5 A/dm$^2$, concentration of sodium hydroxide 400 g/liter, temperature $60^\circ$C, time of electrolysis 120 min).

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REFERENCES


