Preparation of Lead, Lead-Alloy and Other Salts from Exhausted Grids of Some Rechargeable Lead Batteries

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Graphical Abstract

Metals of lead and some lead alloys, lead oxide, nickel and cobalt were recovered from exhausted grids of electrolyte-free rechargeable lead batteries by combining hydrometallurgy and pyrometallurgical method. The spent grids were leached in hot 2 M and 5 M nitric acid. The unleached fraction was heated with sodium carbonate to produce lead oxide. The leachants were analyzed by Inductively coupled plasma mass spectrometry (ICP). Lead was precipitated as hydroxide on cold with ammonia. Nickel and cobalt metals in solution were extracted by solvent extraction using LEWATIT MP 600 ion exchange resin. Metals loaded by the organic phase were stripped by HCl. Metal hydroxides were reduced with ascorbic acid or hydrazine hydrate to ultrafine free metals. Lead alloys were prepared by encapsulating the alloying metal oxide or organic salts in the host lead metal and heated at 800°C. The end products were investigated with Energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray fluorescence (XRF), ICP and scanning electron microscope (SEM). Results revealed that the spent grids contain 94.2% lead, aluminium 0.12%, nickel 0.05% and cobalt 0.053%. The particle size of the reduced metals was found in range of 15-60 um. LEWATIT MP 600 ion exchange resin is specific adsorbent for nickel and cobalt. Distribution constant (Kd) value of the stripping step decreased in the order Ni and Co. Lead-Al-Mg alloy was prepared by heat treatment of terminal taps at 500°C. The obtained lead alloys were investigated with EDX and SEM. Lead calcium alloy was homogeneous and contain calcium particles with 5 ums.

Keywords: Rechargeable batteries; Pure lead; Secondary lead-aluminum-magnesium alloy; Nickel and cobalt; Hydrometallurgy

Introduction

Rechargeable batteries usually used for temporary power supply in general and in case when the main power shutoff accidentally. The Bureau of Mines [1] has investigated an electrolytic recycling process to recover lead and improve secondary recovery of metals and minerals from scrap batteries. Metallic fraction of the crushed batteries were directly melted and cast as anodes for electro refining. The sludge is leached with ammonium carbonate [(NH₄)₂CO₃] and ammonium bisulfite (NH₄HSO₃) to convert lead sulfate (PbSO₄) and lead dioxide (PbO₂) to lead carbonate (PbCO₃). The lead metal grids and lugs are separated from the sludge by ball milling, washing, and screening by the Betts process using waste fluosilicic acid as the electrolyte. Battery is made of groups of plates connected together by external flag terminal made of lead alloy [1]. Lead oxide(s)/sulphate powders filling in the grids openings to form the electrically active material. In the charged state, the negative plate paste is lead-calcium grid loaded with lead sulphate. The positive electrode is lead dioxide. Both of these lead materials are in a spongy form to optimize surface area and thereby maximize the electrical capacity. The conductivity media is potassium hydroxide in low quantity just sufficient to moisten the electrode paste. In the discharging state, the negative lead plate loses electrons and get oxidized to a higher lead oxidation state.
Lead-calcium alloy provides benefits of good grid density, conductivity and tensile strength. It reduces water consumption over life of battery, it also reduces electrolyte and hydrogen gas evolution. Better self-discharge characteristics (typically 0.05% per day at 25°C) is attained with this alloy together with stable rate under float charge over the life of the battery and constant current draw [2]. Chen et al. reported recovery of lead from fly ash of waste lead-acid batteries [3]. The Pb forms are PbSO₄ and lead oxy sulphate Pb₃OSO₄. Nitric acid and sodium hydroxide were used for leaching of the fly ash sample. At a S/L of 60 gl⁻¹, the leach ability of Pb was 43% and 67% in 2 M acidic and basic solutions, respectively. Anglesite is soluble in NaOH whereas lanarkite is mildly soluble in HNO₃. Lead metal was electrolytically recovered from the leach solution with the help of an electrolytic cell fitted with graphite coated with titanium (Ti-DSA) anodes and stainless-steel cathode. Properties of anodes deposited with lead dioxides were analyzed by cyclic voltammetry. Junqing et al. recovered with this method, in which high purity metallic Pb is directly produced by electrolyzing PbO obtained from waste lead acid batteries in alkaline solution [4]. A hydrometallurgical process has been proposed [5,6] to recover valuable metals from spent lithium-ion batteries in citric acid media. A process was reported the steps of calcinations of a spent paste treated with an alkali carbonate or hydroxide or any mixture thereof, and elemental sulphur at temperature of up to 600°C, followed by washing with water. The heat treated and washed paste was dissolved in an alkali molten electrolyte, and lead was electro-won from the alkali molten electrolyte. The spent electrolyte was reused from a spent paste treated with an alkali carbonate or hydroxide or any mixture thereof, and elemental sulphur at temperature of up to 600°C, followed by washing with water. The heat treated and washed paste was dissolved in an alkali molten electrolyte, and lead was electro-won from the alkali molten electrolyte. The spent electrolyte was reused from the process [7]. Molten flux salts displayed good thermal stability and solvent properties; these characteristics helped their use in materials preparation [8], solar power plants [9], and the getting rid of paints or coating from metal surfaces [10]. An up to date technology, adapted a molten salt to the smelting processes of antimony and bismuth through the use of sodium hydroxide and a mixed molten salt in the NaOH-Na₂CO₃,2CaO system [11]. Separation of minor elements using Lewatit exchange resin was reported by Badawy et al. [12].

The aim of this work is to extract metal lead. Lead aluminium-magnesium alloy and some salts from exhausted plates and grids of electrolyte-free rechargeable lead batteries. Recovery of lead metal was performed using hydrometallurgical and pyro metallurgy whereas the alloying elements of aluminium and Magnesium were extracted by solvent extraction technique. Parameters influencing these processes such as temperature, time, pH value and mole ratio of the reagents were studied.

Materials and Methods

Experimental details

The used battery cells: A sample of about ten Kg of used rechargeable lead batteries was supplied by the waste collection stores, Cairo. The sample was washed with water and left to dry in normal ambient conditions. Figure 1 shows a photograph of the collected spent rechargeable acid lead batteries.

The chemicals

The chemicals used for leaching, precipitation, separation and salts preparation were chemically pure grade. Nitric, formic, acetic acids and carbonate, oxide and hydroxide of calcium, sodium, and potassium were of ADWIC production (Egypt). Table 1 summarizes the properties of chemicals used.

The solvents

Table 2 shows the properties of the implemented solvents.

The resin: An ion exchange resin Lewait MP 600 (Merck) was used for ion exchange experiments. It was converted to chloride form before use by thoroughly washing with 0.1-2 M HCl acid in a column for 3 days. It was then washed with aqueous ethanol (70%). The treated resin was then dried under vacuum at 25°C.

The dyestuff: 4-(2-pyridylazo) resorcinol (product of Merck) weighing 10 g of molecular weight amounting to 215.21 was used. A 0.02 M stock solution was prepared by dissolving 0.538 g in 0.25 L 0.1 M aqueous ethanol.

Standard: 0.2 M bi-sodium hydrogen phosphate Na₂HPO₄ and 0.1 M citric acid C₆H₈O₇.H₂O solutions were used as buffer solutions for pH control.

Method of leaching and preparation of lead-calcium alloy from spent lead battery (SLB)

Figures 2 and 3 shows a process flow sheet of the applied method to recover lead and lead-alloys from exhausted rechargeable acid.

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Table 1: Properties of the chemicals used in this study.

<table>
<thead>
<tr>
<th>Product</th>
<th>Properties</th>
<th>Purpose</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$COOH</td>
<td>90%</td>
<td></td>
<td>Riedel-de Hein</td>
</tr>
<tr>
<td></td>
<td>Sp. Gr. 1.044-1.049</td>
<td></td>
<td>ADWIC</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>Sp.GR.1.18 (AR)</td>
<td>Leaching Process</td>
<td>Riedel-de Hein</td>
</tr>
<tr>
<td></td>
<td>Min. assay 36%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fuming 69%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>H$_2$SO$_4$ 95-97% Extra pure</td>
<td></td>
<td>ADWIC</td>
</tr>
<tr>
<td>HCl</td>
<td>Sp.GR.1.18 (AR)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca carbonate</td>
<td>99.3, 1.6 um</td>
<td>Synthesis process</td>
<td>Green Egypt</td>
</tr>
<tr>
<td>Ca oxide</td>
<td>3.34 g/cm$^2$, 1.57 um</td>
<td></td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>NaOH (Sodium hydroxide)</td>
<td>Pure reagent for analysis</td>
<td>Synthesis process</td>
<td>United Co for chemicals and</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>25% Pure reagent for analysis</td>
<td></td>
<td>Med. Preparations</td>
</tr>
<tr>
<td>AgNO$_3$ (Silver Nitrate)</td>
<td>Pure reagent for analysis</td>
<td>Chloride ion determination</td>
<td>44.4</td>
</tr>
<tr>
<td>Mono-distilled water</td>
<td>Hausa</td>
<td>Chemical reactions</td>
<td>2.2</td>
</tr>
<tr>
<td>Tap water</td>
<td>Tiv</td>
<td>Other purposes</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 2: Properties of the solvents used in this work.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Acetic acid</td>
<td>(0.1 M-1 M)</td>
</tr>
<tr>
<td>(2) Ethanol/water</td>
<td>10%-75%</td>
</tr>
<tr>
<td>(3) Acetone/water</td>
<td>25%-75%</td>
</tr>
<tr>
<td>(4) Diethyl ether</td>
<td>50%</td>
</tr>
</tbody>
</table>

Determination of lead and other metals in the exhausted grids

Lead, calcium and other metals content in the exhausted grids were determined by XRF. Leaching was carried out by 3 M nitric acid. The obtained leachant was analyzed by ICP. The unleached residue was also analyzed by XRD.

Figure 2: A conceptual process flow sheet to method to recover lead and lead alloys from exhausted rechargeable spent plates of the battery.
Description of the method used

The resin was de-mineralized by packing 1 g of the resin in a glass column through which HCl acid (2 M-0.01 M) was passed for nearly three days to assure that all the resin converts to the chloride form. It was leached with 1 L of 1% (NH4) OH followed by 1 L of 4% sodium sulfate solution. The pH of the prepared metal salt solution(s) (≈ 100 mL) was adjusted to the required value by addition of the buffer solution before starting the adsorption experiments. The pH-adjusted solution was then run through the resin in the column. Ion exchange experiments were conducted by packing 0.2 g Lewatit MP 600 in the column. Solution containing the metal ions was then poured onto the top of the column and allowed to flow at a rate of 0.5 mL/min. The solution was recycled through the column for completely satisfying adsorption of the metal ions.

The effluent was collected in a separating flask. Chloride content in the aliquots from each leach was determined by titration against standard 0.05 N silver nitrate using potassium chromate as indicator. Stripping of the loaded metals was conducted by eluting with 4 M HCl solution. The collected chloride solutions were separately concentrated by evaporation under vacuum. Chloride was either electrolyzed to prepare the respective metal or converted to insoluble carbonate that was reacted with the acid of concern (inorganic or organic) to prepare the required salt.

Methods of measurements

- Determination of chromium, zinc, cadmium and nickel ions was carried out with the help of a UV-visible atomic absorption spectrophotometer Milton Roy model 20-D for the resin and the metals ions determination.
- Determination of the pH value was carried out with a based bench pH meter (Hanna model 211) fitted with HF1131-B electrode. Measurements were conducted at 25°C ± 0.2°C.
- The exchange capacity of the resin εr was determined from the following relation [11].

\[
\varepsilon_r = \frac{V \cdot N \cdot W}{W} \times 100
\]

Where V is the volume, N is the normality, W is the weight of the resin sample.
- The distribution coefficient Kd was determined from the relation given by John et al. [13].

\[
K_d = \frac{\Delta C \cdot V \cdot \text{resin}}{C_{CHF}}
\]

Where ΔC is the change in concentration of the metal in solution before Ci and after the experiment CHF, V is the volume and g are the weight of the resin.
- Sorption extent (%) was determined from the relation related by Fethiya et al. [14].

\[
\text{Sorption} \% = \frac{\Delta C}{Ci} \times 100
\]

Method of preparation of the metals and their salts

The battery grids under investigation were dissolved in 1.1 stoichiometric ratio of 3 M nitric acid at room temperature till complete dissolution (usually takes time). The volume of the solution as adjusted to 250 ml by distilled water. The nitrate solution was hydroxylated with ammonia. The prepared nitrate or hydroxide salts were used to prepare free metals of lead or base metals by reduction with ascorbic acid or to prepare carbonate, chloride, sulphate, format, oxalate, citrate and acetate salts.

Results

Figure 4 shows the XRD of the lead paste. It is seen that the major content is lead sulphate, lead oxide while lead dioxide is minor.

This is very clear that lead compounds in grey plates were lead sulphate. The lead compounds in the brown plates were lead oxide and partly lead dioxide. Lead compounds decreased in the order sulphate, oxide and dioxide. With respect to the minor compounds, Ni and cobalt were present nearly in equal amounts (Figure 5).
It is seen that lead metal is the major element that constitutes 94.2% by weight. Other elements are in minor percentages. It is also seen that the weight percentage of these minor elements decreases in the order Si, Al, Ru, Zr, Co, Ni, Cu and Zn. The common elements in commercial use are Ni and Co and Zn. These were recovered by solvent extraction technique.

Figure 6 shows the extent of leaching lead from the spent plates using 2 M and 5 M nitric acid at room temperature. The use of sulphuric acid instead of nitric acid was discarded because the reaction stopped rapidly because lead sulphate is immiscible in water. It can be seen that leaching process takes time to react with lead compounds. The extent of leaching increases with time to give the maximum extent of 38.4% after 7 days with 2 N acid. More concentrated nitric acid (5 M) gives less extent of leaching (32%) (Figure 7).

Leaching of the grids loaded with brown lead powder using 2 M and 5 M nitric acid at 80°C shows that 5 M nitric is more reactive as compared to 2 M concentration. After 6 days the maximum extent of leaching amounts to 38% and 14% with 5 M and 2 M respectively.

Figure 8 shows the effect of nitric acid concentration on leaching lead sulphate and lead oxide at room temperature for 6 days. It is seen that lead sulphate displays higher extent of leaching compared to lead oxide up to 3 days. After 6 days lead oxide is more leached than lead sulphate (Figure 9).

It can be seen that with and the same metal ion concentration in the solution, the Kd value increases with the decrease in concentration. This statement is logic as given in equation (2). The values of the denominator decrease that gives a corresponding increase in Kd value. The effect of change in g value is less significant as compared to the change in C value.

Results given in Figure 10 with Co and Ni confirm the results obtained with Zn (Figure 9). Figure 11 shows the Effect of pH value on the Kd value with nickel ions. It can be seen that the effect of pH.

N becomes significant at values ≥ 8.5. At pH 9 the Kd value is highest. Figure 12 is confirms the same findings with Zn ions. Figure 13 shows the effect of type of solvent on the obtained metal powder after stripping. It is seen that solvent 2 gives Ni and Al in nano size. Solvent 1 gives the same effect with Aluminium. Other solvents give metals with larger size. Table 4 shows the prepared salts and its purity extent.

### Table 3: The XRF analysis of the elements present in the exhausted plates.

<table>
<thead>
<tr>
<th>Metal</th>
<th>wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>94.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.05</td>
</tr>
<tr>
<td>zinc</td>
<td>0.0030</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.053</td>
</tr>
<tr>
<td>Copper</td>
<td>0.0272</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.0727</td>
</tr>
<tr>
<td>Rhodium</td>
<td>0.0842</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.12</td>
</tr>
<tr>
<td>Silicon</td>
<td>5.389</td>
</tr>
</tbody>
</table>

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Figure 8: Effect of nitric acid concentration on leaching lead sulphate and lead oxide at room temperature for 6 days.

Figure 11: Effect of pH value on Kd value.

Figure 9: The Kd value for Zn from solution with different concentration of Zn as affected by the amount of the ion exchange resin.

Figure 12: Effect of pH value on the Kd value with Zn ions.

Figure 10: The Kd value for Zn from solution with different concentration of Co as affected by the amount of the ion exchange resin.

Figure 13: The effect of type of solvent.
Table 4: The prepared salts of lead and its purity extent.

The unleached fraction remaining after nitric acid leaching was analyzed by XRF, Table 5 shows the chemical composition of the residue.

Table 5: The chemical composition of the residue.

Discussion

Lead metal in battery plates is present in three forms; a grid made of lead alloy in the form of net shaped structure loaded with lead sulphate or lead oxide. Metal. Heating the terminal tap of the battery gives lead alloy composed of lead-aluminium-magnesium alloy as revealed from EDX pattern confirmed with SEM image given in Figure 14. It is composed of 95.83% wt Pb and 4.17% Al.

Results revealed that only 15-20% of lead is obtained by simple heating of all the grids even in reducing conditions. It becomes legitimate to apply modified method capable to produce high extent of lead recovery (Figure 15).

Unified Numbering System (UNS) designations for various pure lead grades and lead-base alloys is as follows [1].

- Pure leads L5xx00-L5xx99
- Lead-calcium alloys L5x700-L5x899
- Lead-strontium alloys L552xx-L55299
- X=0

Lead is a soft and ductile metal and lead alloys are used on large scale. The alloying elements may be antimony, tin, arsenic, and calcium are. Antimony is used to give greater hardness and strength, as in storage battery grids (0.5 to 25%), sheet, pipe, and castings. Antimony contents in the lead-antimony alloys are usually 2% to 5%.

Lead-calcium alloys are used in a number of applications, particularly, storage battery grids and casting applications. Pb-Ca alloys contain 0.03% to 0.15% Ca. aluminum is now added to calcium-lead and calcium-tin-lead alloys to stabilize calcium. Alloying tin to lead increases hardness and strength. However, lead-tin alloys are usually used for their good melting, casting, and physical properties as in type metals and solders.

Reduction of metals hydroxides: Ascorbic acid reduces hydroxide salts of lead and basic metals to free fine particles as follow (Figure 16).

\[ \text{Pb(OH)}_2 + 2 \text{ascorbic acid} \rightarrow \text{PbO} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{ascorbic acid} \]

**Figure 14:** The EDX and SEM of the melted terminal tap.
**Figure 15:** EDX pattern of lead alloy containing Ca, Al.

**Figure 16:** Reduction of metal hydroxides.
Conclusion

The output conclusion of this work is that exhausted rechargeable batteries are one of the essential resources for recovery of nonferrous metals such as lead and lead alloys. Other metals value (Ca, Al, Ni, Co) are present and were successfully recovered. The method used to achieve the goal of the study was simple and friendly. Preparation of lead alloys with calcium and aluminium has been matched applying the combined hydrometallurgy and pyrometallurgy methods. Valuable salts of lead including organic salts were also prepared in highly pure grade.

References