Solubilization Kinetics of Lead Hydroxide Obtained from Sulfated-oxide Waste from Lead-acid Battery, in Acetic Acid in the Presence of Urea

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The paper presented the solubility study of lead hydroxide obtained from sulfate-oxide waste by dismantling unused car batteries, in solution of acetic acid and urea. The study is performed in order to determine the best working conditions for leaching and cementation of lead. Preliminary studies have shown that the use of acetic acid and urea represent the best compromise between solubilization types of lead (II) compounds and pH of solution, maintaining a specific proportion between water/acidic solution. The solution pH should be as low as possible to avoid separation of sparingly soluble hydroxides of iron during hardening reaction but not less than 3 to maintain a proper concentration of free acetate ions in solution.

Keywords: waste, car batteries, lead, hydroxide

Increased demand for lead-acid batteries, due to the increasing number of vehicles, together with stricter environmental regulations, has created the need to move, modernize and reconvert the processes for batteries production and also for the lead recycling in order to minimize their environmental impact.

At this moment, recovery of lead from spent lead-acid batteries is done through a pyrometallurgical method, causing environmental problems due to emissions of lead particles and sulfur dioxide [1]. Because of the laws becoming more stringent for these types of emissions there was a large research effort to find a hydro-metallurgical method for the replacement procedures for lead-acid battery recycling [2]. In particular, has been extensively studied the electro-hydrometallurgical method for recovery of metallic lead; in this regard there were designed several pilot plants.

Electrolytic extraction techniques of lead, either in acidic or alkaline environments, yet fail to overcome many technological problems or to avoid the formation of a passive lead dioxide anode [3,4].

The general scheme of recovering lead from spent batteries include combined operations mechanical, pyrometallurgical and hydrometallurgical. From accumulators after grinding in mills and ranking the screeners and dense medium, we obtain the following classes of materials: metallic fraction represented by grids, battery terminals and connectors, light fraction represented by plastic skeleton and separators, the fine fraction is represented by sulphate pulp and acid solution represented by plastic skeleton and separators, the fine fraction is processed and separated according to the reaction:

\[ \text{PbSO}_4 + 2\text{CaCl}_2 \rightarrow \text{CaPbCl}_4 + \text{CaSO}_4 \]  (1)

\[ \text{PbO}_2 + 2\text{H}_2\text{SO}_4 + 4\text{CaCl}_2 \rightarrow 2\text{CaPbCl}_4 + 2\text{CaSO}_4 + \text{H}_2\text{O} \]  (2)

\[ \text{PbO} + 2\text{CaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaPbCl}_4 + \text{CaSO}_4 + \text{H}_2\text{O} \]  (3)

\[ \text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 + 4\text{CaCl}_2 \rightarrow 2\text{CaPbCl}_4 + 2\text{CaSO}_4 + 2\text{H}_2\text{O} \]  (4)

In the process of solubilization can be processed and other metallurgical lead products (fuming oxides, volatile powder, carpets, a. s. o.)[5]. Lead compounds leaching yield is about 99.5% at 50°-60°C. Along with lead can pass into solution as chlorides and impurities such as Cu, Sb, Be and others. Pulp resulting from leaching is subject to precipitation of calcium sulphate in the form of gypsum (CaSO\textsubscript{4} 2H\textsubscript{2}O) by cooling and without stirring.

Precipitate containing 95% gypsum can be used for different purposes (especially in construction). Chloride solution remaining after precipitation of gypsum is subject to purification by cementation of lead powder:

\[ 2\text{SbCl}_3 + 3\text{Pb} + 3\text{CaCl}_2 \rightarrow 3\text{CaPbCl}_4 + 2\text{Sb} \]  (5)

\[ 2\text{BiCl}_3 + 3\text{Pb} + 3\text{CaCl}_2 \rightarrow 3\text{CaPbCl}_4 + 2\text{Bi} \]  (6)

\[ \text{CaCl}_2 + \text{Pb} + \text{CaPbCl}_4 \rightarrow \text{CaPbCl}_4 + \text{Cu} \]  (7)

Metals results with powder lead in excess, forms a lead cement used in developing of lead alloys and purified chloride solution is treated with lime to lead hydrolysis according to the reaction:

\[ \text{CaPbCl}_4 + \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Pb(OH)}_2 + 2\text{CaCl}_2 \]  (8)

Recovery of lead from lead hydroxide can be done through a two-step process (leaching and cementation in separate procedure) or in a single step process (leaching and cementation in a single procedure) [6,7].

Results and discussions

Solution of acetic acid and urea was prepared by dissolving urea in H\textsubscript{2}O/H\textsubscript{Ac} solution.

The studied working conditions ranged from 200-500 g / L urea, ratio H\textsubscript{2}O/H\textsubscript{Ac} between 0.25 to 3.50 v/v, temperature between 20-50°C and reaction time 1-3 h.
Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>t.10^{-3}, [s]</th>
<th>Pb, [g/l]</th>
<th>Pb acetate, mol/l</th>
<th>Acetic acid, mol/l</th>
<th>Acetic acid reacted, mol/l</th>
<th>Pb hydroxide, g</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.8668</td>
<td>0</td>
<td>70</td>
<td>20.6961</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>49.7738</td>
<td>0.2404</td>
<td>2.3839</td>
<td>0.4809</td>
<td>-</td>
<td>20.6961</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>85.2541</td>
<td>0.4118</td>
<td>2.0431</td>
<td>0.8237</td>
<td>-</td>
<td>35.4490</td>
</tr>
<tr>
<td>4</td>
<td>1.8</td>
<td>111.8126</td>
<td>0.5402</td>
<td>1.7865</td>
<td>1.0803</td>
<td>-</td>
<td>46.4921</td>
</tr>
<tr>
<td>5</td>
<td>3.6</td>
<td>162.4248</td>
<td>0.7847</td>
<td>1.2975</td>
<td>1.5693</td>
<td>-</td>
<td>67.5369</td>
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<tr>
<td>6</td>
<td>5.4</td>
<td>181.9659</td>
<td>0.8791</td>
<td>1.0187</td>
<td>1.7581</td>
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<td>75.6621</td>
</tr>
<tr>
<td>7</td>
<td>7.2</td>
<td>209.9319</td>
<td>1.0142</td>
<td>0.8385</td>
<td>2.0283</td>
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<tr>
<td>8</td>
<td>9.0</td>
<td>222.9732</td>
<td>1.0772</td>
<td>0.7125</td>
<td>2.1543</td>
<td>-</td>
<td>92.7132</td>
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<td>9</td>
<td>10.8</td>
<td>232.5988</td>
<td>1.1237</td>
<td>0.6194</td>
<td>2.2473</td>
<td>2.2991</td>
<td>96.7155</td>
</tr>
</tbody>
</table>

For example, in order to prepare 0.25 L containing 500 g/L of urea/acetate (ratio 2.7 v/v H₂O/HAc) were slowly dissolved 125 g of urea, at room temperature, in a solution containing 116.5 mL of water and 43 mL of glacial acetic acid. Urea/acetate (gr) ratio was approximately 2.8, the solution density being 1.15 kg/L and pH = 3.4.

70 g lead hydroxide was solubilized with an acetic acid solution (acetic acid in excess 20%). During solubilization, concentration of lead ions in solution was determined by atomic absorption spectroscopy of samples from solution taken from time to time throughout the reaction. Unreacted Pb(OH)₂ were collected by filtration, complete water washing and drying in the furnace before gravimetric determination.

The atomic absorption spectrometer with flame used was of type GBC 932 AB Plus (manufactured by GBC Scientific Equipment PTY Ltd. Australia).

All reaction steps were performed in a reaction system made from Pyrex flask of 500 mL double necked and round base, equipped with a condenser to condense the released vapours. During the reaction, the solution was agitated with a magnetic stirrer at about 100 rpm and heated in thermostatic bath.

The solubilization process of lead hydroxide, Pb(OH)₂ in acetic acid is a slow process, corresponding to a first-order kinetics, according to data [1], due to very low degree of acetic acid dissociation, about 4%. For increasing of solubilization rate, attempts were made to increase the acetate ions concentration in solution by using complex ions into the addition of urea:

\[
Pb(OH)_2 + 2HAc \rightarrow Pb^{2+} + 2Ac^- + 2H_2O \quad \text{fast process} \quad (10)
\]

Results and discussions

Experimental test results are shown in figures 1 and 2:

Working with experimental data using Jandel Scientific program and comparing the different kinetic equations we can conclude the process corresponds to a second-order kinetic process like:

\[
dx \over dt = k(\alpha - x)^2 \quad (11)
\]

or:

\[
k = \frac{1}{t} \left( \frac{1}{\alpha - x} - \frac{1}{\alpha} \right) \quad (12)
\]

where:

\( \alpha \) - is the initial concentration of acetic acid, mol/L,

\( x \) - amount of acetic acid consumed after time \( t \), mol/L,

\( k \) - rate constant of the process, L.mol⁻¹.s⁻¹

Equation (12) can be linearized, and the graphical representation is shown in figure 3.

\[
\frac{1}{\alpha - x} = kt + \frac{1}{\alpha} \quad (13)
\]

From the slope of the straight line (table 2), the rate constant for the process has the value of \( k = 1.172 \times 10^{-4} \text{L.mol}^{-1}.\text{s}^{-1} \)
To determine the best mathematical model that describes the solubilization process in the above conditions Jandel Scientific program was used (table 3), the data being presented below, resulting in equation (14), plotted in figure 4.

\[ y-1 = a + bx \quad (14) \]

where:
- \( y \) - acetate acid concentration, mol/L,
- \( x \) - reaction time, s.

\[ y-1 = 0.3488164 + 0.00011719108x \quad (15) \]

Comparing equation (5) with mathematical equation, (6), the values that should be compared are:

\[ k = 0.00011719108 \text{[l.mol}^{-1}\text{s}^{-1}] \], calculated and

\[ k = 1.172.10^{-4} \text{[l.mol}^{-1}\text{s}^{-1}] \], experimental.

There is a very good agreement with the model of experimental data.

Conclusions

In this paper, a new ecological and favourable method is proposed, to replace the traditional methods of recycling by melting of lead-acid batteries. Solubilization, up to approx. 99% of lead content in the pulp from lead-acid batteries has been achieved through a reaction using acetic acid and urea solution, and will use iron as a reducer for hardening lead. Reaction rate was found to be dependent on concentration of acetate ion in solution, which is why we used urea.

A hydrometallurgical plant using urea / acetate method, to recover metallic lead from exhausted lead-acid battery paste has several technological advantages compared with traditional technology pyrometallurgical technologies. The most obvious complication is the need of three units: a reactor and filter and crystallizer held at a temperature close to boiling temperature of the solution.

On the other hand, several advantages make this procedure very desirable: such as no gas emissions of...
SO_2, SO_3, NOX or powders containing lead, low power consumption, higher amount of metallic lead recovered per unit mass of thick mud (higher efficiency), lower operating costs, given the high costs of energy supply, treatment of toxic gas and discharge of lead containing furnace slag.

References
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