Experimental Study About Recovering Metal Lead By Direct Electrolysis Waste Lead Paste

Jiageng Xiao¹, Yusheng Zhang

School of Tianjin University of Technology, Tianjin, China

*Corresponding author e-mail: xjg1832954045@163.com

Abstract. The scraped lead paste is the major pollution in the lead-acid battery industry, to solve this problem, how to dispose and utilize the waste lead paste is studied in this review study. Under acidic conditions, use the way of direct electrolysis to carry out Solid phase electrolysis of waste lead paste. The effects about three typical factors on electrolysis efficiency and energy consumption of electrolysis was studied, including the amount of lead paste, current density and sulfuric acid density. Through the design of orthogonal test to determine the optimum technological parameters. The technology has good economic value and environmental benefits, and it is easy to promote and apply.

1. Introduction
The treatment of waste lead paste is the key to the recycling of waste lead-acid battery[1]. For the treatment of waste lead paste, the main technical methods used in the production process of recycled lead are direct high-temperature smelting or high-temperature smelting after desulfurization [2-4]. The pre-desulfurization technology has greatly alleviated the environmental pollution caused by direct smelting, but this method needs to add a large number of chemical reagents and produce low economic value by-products such as Na₂SO₄ at the same time[5-7]. Around the problems in the process of paste treatment, many scholars are exploring the wet reduction technology of lead paste without pyrometallurgy. However, most of the current wet-processes have disadvantages such as long process flow, large consumption of chemical auxiliary agent and high energy consumption. In this paper, the wet direct electrolysis method is proposed to treat the waste lead paste in the acid condition. The sulfuric acid with high reuse value can be obtained at the end of the process, which can be used as the raw material of electrolyte or lead-acid battery. By optimizing the amount of paste, current density and sulfuric acid density, the optimal parameters of electrolysis efficiency and energy consumption are obtained, to recover lead in high efficiency and low consumption.

2. Experimental design

2.1. Test materials and devices
The waste lead-acid battery used in the test is from Chaowei power supply corporation scrap batteries. In the pre-treatment stage, the waste lead-acid battery is disassembled for acid washing, drying and separation. Grind the waste lead paste, and the lead paste powder passes the 120 target sieve. The
results showed that the content of PbSO$_4$, PbO$_2$, PbO, Pb and others were 65.42%, 28.53%, 4.51%, 0.87%, 0.67%.

2.2. Test principle and method

2.2.1. Test principle. On the cathode plate of the electrolytic cell, because the lead paste contains PbO$_2$ and a small amount of metal lead, after adding sulfuric acid in the electrolyte, the electrolytic cell actually constitutes a primary battery with discharge capacity. Due to the strong oxidize ability of PbO$_2$, as the lead is oxidized to lead dioxide, it is also reduced to lead dioxide, and the system discharges outward. At this time, there is voltage in the electrolyzer. When a small amount of lead in the waste paste is oxidized completely, the discharge reaction ends. The main reaction formula of cathode plate after power on is shown in (1)—(5):

\[
PbO_2 + 4H^+ + SO_4^{2-} + 2e^- = PbSO_4 + 2H_2O
\]

\[
PbSO_4 + 2e^- = Pb\downarrow + SO_4^{2-}
\]

\[
PbO + 2H^+ + 2e^- = Pb\downarrow + H_2O
\]

\[
Pb^{2+} + 2e^- = Pb\downarrow
\]

\[
2H^+ + 2e^- = H_2\uparrow
\]

The reaction formula of anode plate is shown in formula (6):

\[
2H_2O + PbSO_4^{2-} - 4e^- = O_2\uparrow + H_2SO_4
\]

The formula for calculating the energy consumption of electrolysis is shown in formula (7):

\[
W = \frac{VIT}{n} \times 10^3
\]

The calculation formula of electrolytic efficiency is shown in formula (8):

\[
\eta = \frac{m}{V \times 1000}
\]

2.2.2. Test method. In order to explore the influence of four typical factors, such as the amount of waste lead paste, the current density, the sulfuric acid density and the distance between the anode and the cathode, on the electrolytic efficiency and energy consumption of metal lead recovery by direct electrolysis of waste lead paste, the optimal parameters were obtained by controlling single factor variables and orthogonal test, and the minimum energy consumption of high efficiency lead recovery was obtained.

During the test, the waste lead paste shall be placed on the surface of the cathode plate, spread evenly, and then compacted; the anode plate shall be installed, the distance between the anode and the cathode plate shall be adjusted, and sulfuric acid shall be added, and the electrolysis shall be powered on. Stop power on when reaching the end of electrolysis, record the power on time and average cell voltage. Take out the cathode plate, separate the electrolytic lead from the surface of the plate, conduct vacuum drying, and then plastic seal for storage. The waste acid is poured out from the electrolytic cell and analyzed after centrifugation. The sulfuric acid used in the test is analytical pure (molecular weight 98, concentration 98%).
3. Results and discussion

3.1. The effect of the amount of waste lead paste on the efficiency and energy consumption of electrolysis

Set the current density as 600 A/m², sulfuric acid density as 1.2g/cm³, the spacing between the anode and cathode plates as 12 mm, and the amount of lead paste added as 10, 20, 30, 40, 50, 60 g respectively. Explore the effect of the amount of waste lead paste added on the electrolysis efficiency and energy consumption, see Figure 1 for details.

![Figure 1. The effect of amount of added lead paste on electrolysis efficiency and energy consumption](image)

The electrolysis efficiency first increases with the increase of the amount of lead paste, then decreases, and the maximum value is obtained when the amount of lead paste is 30 g. When the amount of paste added is less than 30 g, the electrolytic reaction is less affected by the thickness of the paste layer, which can carry out efficient electrolytic reaction. The increase of the amount of paste per unit area makes the electrolytic efficiency increase, and the energy consumption of electrolysis decrease. With the continuous increase of the amount of paste, the thickness of the paste on the surface of the cathode plate increases, which makes it more difficult for the current to break through the paste layer, and the cell voltage increases. In addition, because of the edge effect of the electrode plate, the electrolytic lead occurs from top to bottom. When the paste layer is too thick, the metal lead formed by electrolysis is preferentially covered around the plate and on the top of the paste, forming an inverted bowl structure. The paste near the center area of the bottom of the cathode plate is wrapped in it, making it more difficult to participate in the electrolytic reduction reaction, greatly extending the electrolysis time, and making the energy consumption of electrolysis increase sharply. Even if the end point of electrolysis is reached, there is still some paste at the bottom of the plate that is not involved in the electrolysis. In order to ensure the high efficiency and low energy consumption of electrolytic lead, the most suitable amount of lead paste is selected when the amount of lead paste is 30g.
3.2. Effect of current density on electrolysis efficiency and energy consumption
The dosage of lead paste is 30 g, the density of sulfuric acid is 1.2 g / cm\(^3\), and the distance between plates is 12 mm. The current density is 200, 300, 400, 500, 600, 700 A/m\(^2\), to explore the influence of current density on electrolysis efficiency and energy consumption, see Figure 2 for details.

Figure 2. The effect of current density on electrolysis efficiency and energy consumption

It can be seen from Figure 2 that when the current density increases gradually, the electrolytic efficiency shows a trend of rising first and then declining, while the curve of electrolytic energy consumption is just the opposite. In this system, the current density is increased by increasing the current, which can make electrolysis. With the improvement of efficiency, the reduction process of lead compounds in lead paste can be realized more quickly. When the current density is 637 A / m\(^2\), the electrolysis time is the shortest; when the current density is too large, the reaction of electrolytic water is also enhanced, the hydrogen and oxygen generated escape with the bubbles, making the lead paste and sponge lead on the electrode plate suspend in the electrolyte again, slowing down the deposition rate of electro deposition lead, prolonging the electrolysis time, leading to the continuous increase of the energy consumption of electrolysis. In addition, due to the enhanced reaction of electrolytic water, a large amount of water in the electrolyte escapes in the form of H\(_2\) and O\(_2\), which greatly increases the concentration of sulfuric acid, while the high concentration of acid makes the conductivity drop, which is not conducive to the reduction of lead. Therefore, the current density of 637 A / m\(^2\) is the best condition.

3.3. Analysis of recovered products
After the test, the cathode plate is taken out from the electrolytic cell, the electrolytic lead is obtained from the surface of the cathode plate, and then the deionized water is used for full acid washing step, and then it is placed in the vacuum drying oven for full drying. Using jade software to analyze and compare the XRD spectrum, the results show that the more obvious peak type of the electrolytic products is crystal lead, without other obvious material crystals; in addition, the results of ICP-AES detection also show that the purity of the recovered metal lead is high, except for the trace metal impurities, the lead content is as high as 99.7%.
4. Conclusion
The best technological parameters of the acid direct electrolysis method for the treatment of waste lead paste are: the amount of waste lead paste is 30 g, the current density is 637 A / m². Under the optimal parameters, the electrolysis efficiency of the acid direct electrolysis method is about 1.20 kg / (m² · h), the energy consumption can be controlled below 1800 kW · h lead paste, and the purity of the obtained electrolytic lead is as high as 99.7%.

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