Study on Transformation and Migration of Antimony Impurity in Wet Recovery of Waste Lead Paste

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Abstract. The existing forms of antimony impurities in lead paste were analyzed, and the migration and transformation rules of antimony impurities in the process of recovering waste lead paste by leaching with organic acid system were studied. The experimental results show that when the dosage of leaching agent is constant, the more impurities transfer to the filtrate with the extension of reaction time. The conversion rate of antimony is relatively high, reaching about 97.0%. Cycle experiments show that with the increase of cycle times, the antimony content in the liquid phase decreases. By the third cycle, the proportion of antimony entering the filtrate is only 38%, and most antimony impurities enter the solid phase.

1. Introduction
In the production of waste lead-acid batteries, and pretreatment processes such as crushing and screening, the main components of waste lead-acid batteries divided into four parts: lead pole, lead alloy grid and waste electrolyte, lead paste and organic matter. The main component of lead paste is sulfate which is difficult to decompose (its mass fraction is about 50% ~ 60%), and there is high valence PbO2 oxide. The lead paste is the difficulty and hotspot of lead battery recovery [1]. Kumar of Cambridge University and others proposed a wet process for treating waste battery lead paste with citric acid, that white lead citrate crystals were obtained by simulating the reaction of lead with sodium citrate solution in one component [2]. Yang Jiakuan and others have conducted in-depth research on the simulated and actual wet recovery of lead paste, however, their main concern is the recovery of lead and not enough attention is paid to the removal of impurities. Lead powder for traditional industrial batteries is directly ball-milled from lead ingots with extremely low impurity content. However, Sb, Fe, Ba and other impurities will be introduced in the process of corrosion crushing and separation of waste lead-acid batteries [3]. If impurities cannot be effectively removed in the wet leaching process, the quality of the final lead powder will be affected. In battery production, the content of impurities in lead powder is required to be high, so it is important to study the changes of impurities during leaching. Gao Linxia and others have studied the migration and transformation of zinc-added simulated lead paste in citrate sodium citrate system [4]. On the other hand, the author takes the antimony impurity with the highest content in lead paste as the object to study the leaching transformation and migration law of antimony impurity in the actual lead paste in sodium citrate system.

2. Determination of Impurity Content in Lead Paste and Analysis of Main Impurity Forms
The lead content in the lead paste was determined by chemical titration. As can be seen lead is the main component of the lead paste, and ω(Pb) reaches 74.50%; The main components of impurity elements are iron and antimony, ω(Sb) is 0.10%, ω(Fe) is 0.24%.
The lead used in the battery manufacturing process is generally electrolytic lead, and the purity is generally not less than 99.994%. Antimony impurity in lead paste mainly comes from grid. At present, lead-antimony alloy is a typical material for preparing lead storage battery grids, and antimony content in the alloy is generally 3.5% ~ 6.0%. Grid is an important component of lead storage battery. It not only supports active substances as a carrier, but also conducts and collects current. The positive grid is easily corroded during the charging and discharging of the battery. In the process of crushing waste lead storage batteries, many lead-antimony alloys fall off the power grid due to corrosion and enter the lead paste. From the battery reaction and subsequent crushing process, it is concluded that antimony impurity mainly exists in the form of metallic antimony, and may also contain antimony sulfate and antimony oxide due to being in sulfuric acid system.

3. Transformation of lead paste
Taking \((C_6H_5O_7)\cdot H_2O-Na_3(C_6H_5O_7)\cdot 2H_2O\) as leaching system, referring to the previous experimental results, sodium citrate and citric acid are required for leaching lead sulfate, and the molar ratios of sodium citrate, citric acid and lead sulfate are 2: 1 and 1: 1 respectively, citric acid is required for leaching lead dioxide, lead oxide and metal lead, and the molar ratios of lead dioxide, lead oxide, metal lead and citric acid are 4: 1, 1: 1 and 1: 1 respectively. Lead paste is leached out if use 10.0 g, the theoretical reaction ratio shown in Table 3 is obtained according to the contents of main components in Table 2 shown the lead paste, i.e. 12.5 g of Na3 \((C_6H_5O_7)\) \(2H_2O\), 15.24 g \((C_6H_6O_7)\cdot H_2O\), and 6 ml of \(H_2O_2\) solution \((\omega(H_2O_2)=30\%\) in \(H_2O_2\) solution) are required for leaching lead paste is 10.0 g.

| Component | \(\omega/%\) | \(m/g\) | \(n/mol\) |
|-----------|--------------|---------|-----------|
| PbSO4     | 64.5         | 6.45    | 2.13\(\times\)10^{-2} |
| PbO2      | 29.5         | 2.95    | 1.24\(\times\)10^{-2} |
| PbO       | 4.5          | 0.45    | 0.20\(\times\)10^{-2} |
| Pb        | 1            | 0.1     | 0.048\(\times\)10^{-2} |

The dosage of 12.5 g Na3 \((C_6H_5O_7)\) \(2H_2O\) and 15.24 g \((C_6H_6O_7)\cdot H_2O\), calculated from leaching 10.0 g of lead paste, are defined as \(\alpha\). The effects of dosage of 0.5\(\alpha\), \(\alpha\), 1.5\(\alpha\) and 2\(\alpha\) on desulfurization rate and lead recovery rate of lead paste are studied. The results are shown in fig. 1. The desulfurization rate of PbSO4 gradually increases with the extension of the reaction time. As we can seen by fig. 1

| Lead paste composition | \(Na_3(C_6H_5O_7)\cdot 2H_2O\) dosage | \((C_6H_6O_7)\cdot H_2O\) dosages | \(H_2O_2\) solution dosage \((\omega(H_2O_2)=30\%\) ) |
|------------------------|--------------------------------------|----------------------------------|-----------------------------------------------|
|                        | \(n/mol\) | \(m/g\) | \(n/mol\) | \(m/g\) | \(n/mol\) | \(V/mL\) |
| PbSO4                  | 4.26\(\times\)10^{-2}            | 12.5    | 2.13\(\times\)10^{-2} | 4.47 | 0 | 0 |
| PbO2                   | 0       | 0       | 4.96\(\times\)10^{-2} | 10.29 | 5.4 \(\times\)10^{-2} | 6 |
| PbO                    | 0       | 0       | 0.20\(\times\)10^{-2} | 0.42 | 0 | 0 |
| Pb                     | 0       | 0       | 0.048\(\times\)10^{-2} | 0.01 | 0 | 0 |
| summation              | 4.26\(\times\)10^{-2}            | 12.5    | 7.338\(\times\)10^{-2} | 15.24 | 5.4 \(\times\)10^{-2} | 6 |
3.1 Influence of Time on Antimony Conversion in Leaching Process
During the experiment, the dosage of lead paste is 10.0 g each time, and the actual dosage of leaching agent is 1.5α, that is, 18.8 g of sodium citrate and 22.9 g of citric acid need to be added. However, the volume of H₂O₂ solution remains unchanged at 6 mL, and the solid-liquid mass ratio is 1/5. Set the rotation speed of the stirrer to 650 r/min, carry out the reaction at room temperature, sample at different reaction time nodes, filter and wash, and measure the antimony content in the filtrate[5]. Table 4 shows the experimental results. We can see from table 4, 79.15% of antimony impurities in the lead paste were transferred to the filtrate within the first 1 h of reaction, but the reaction speed slowed down step by step with the extension of reaction leaching time. When the reaction time reached 24 h, the antimony impurities transferred to the filtrate could reach 96.77%.

Table 4 Conversion rate of antimony impurity in paste leaching and conversion

| Extraction time/h | The total mass of antimony/mg | Antimony in the filtrate/mg | The mass fraction of antimony in filtrate/% |
|-------------------|-------------------------------|----------------------------|------------------------------------------|
| 1                 | 24                            | 18.996                     | 79.15                                    |
| 4                 | 24                            | 20.092                     | 83.72                                    |
| 9                 | 24                            | 22.06                      | 91.92                                    |
| 24                | 24                            | 23.224                     | 96.77                                    |

3.2 Leaching and Transformation Mechanism of Impurity Antimony in Leaching Process
During the use of the battery, the lead-antimony alloy grid is corroded, and antimony will enter the lead paste due to the subsequent crushing process, so there may be metal antimony, antimony oxide, and antimony sulfate. From the analysis results of antimony content in the leaching reaction process, it can be determined that most of antimony in the lead paste was transferred to the sodium citrate solution in the leaching process[6]. It is presumed that antimony citrate or sodium antimony citrate may be generated. The possible reactions are as follows:

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\begin{align*}
2\text{Sb} + 2\text{C}_6\text{H}_8\text{O}_7 & \rightarrow 2\text{SbC}_6\text{H}_5\text{O}_7 + 3\text{H}_2 \uparrow; \\
2\text{Sb} + 2\text{C}_6\text{H}_8\text{O}_7 + 2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 & \rightarrow 2\text{Na}_3\text{Sb(C}_6\text{H}_5\text{O}_7)_2 + 3\text{H}_2 \uparrow; \\
3\text{Sb} + 5\text{C}_6\text{H}_8\text{O}_7 + \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 & \rightarrow 3\text{NaSb(C}_6\text{H}_5\text{O}_7)_2 + 7.5\text{H}_2 \uparrow; \\
\text{Sb}_2\text{O}_3 + 2\text{C}_6\text{H}_8\text{O}_7 & \rightarrow 2\text{SbC}_6\text{H}_5\text{O}_7 + 3\text{H}_2\text{O}; \\
\text{Sb(SO}_4)_3 + 2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 & \rightarrow 2\text{SbC}_6\text{H}_5\text{O}_7 + 3\text{N}_2\text{SO}_4; \\
3\text{SbC}_6\text{H}_5\text{O}_7 + 2\text{C}_6\text{H}_8\text{O}_7 + \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 3\text{H}_2\text{O}_2 & \rightarrow 3\text{NaSb(C}_6\text{H}_5\text{O}_7)_2 + 6\text{H}_2\text{O}.
\end{align*}
\]
3.3 Influence of Leaching Solution Circulation on Transformation of Lead Paste and Antimony

3.3.1 Scheme of Circulation Experiment
In the leaching process, the dosage is 1.5α, i.e. citric acid is 22.9 g, sodium citrate 18.8 g, solid-liquid ratio 1/5. After reacting for 24 h at a temperature of about 20°C, filtering, solid-liquid separation to obtain crude filtrate for the next cycle experiment. Washing the filter cake to obtain washing liquid. Antimony content in crude filtrate and washing liquid was analyzed. Before the cyclic experiment, the consumption and loss of citric acid, sodium citrate and water are calculated according to the material balance equation to supplement this part of material to ensure the quality of the circulation system is basically unchanged.

3.3.2 Influence of Cycle Times on Conversion Rate of Lead Paste
In the leaching process of lead paste, the most important thing is the conversion of lead sulfate, and the conversion rate of lead sulfate actually represents the conversion rate of lead paste. The conversion rate of lead sulfate gradually decreases with the increase of filtrate circulation times. The conversion rate was 99.8% in the first experiment, and 92.11% in the second leaching, and during the third leaching, the conversion rate quickly decreased to about 80.20%. This may be due to the formation of sodium sulfate in the reaction process, and more residual sodium citrate and citric acid, which increase the viscosity of the filtrate, resulting in lower conversion rate of lead sulfate in the lead paste. With the increase of circulation times, the total amount of lead in the filtrate showed an increasing trend.

![Figure 2 Effect of cycle times on desulfurization rate](image)

3.3.3 Influence of filtrate circulation times on antimony impurity conversion
The influence of filtrate circulation times on antimony migration and transformation is shown in Table 5. With the increase of circulation times of the filtrate, the content of antimony impurities in the filtrate gradually increased, but the increase slowed down. The antimony content in the filter cake was relatively low in the first two cycles, but the antimony content in the filter cake increased rapidly in the third cycle. The mass of antimony impurity entering the liquid phase in the first cycle is 19.12 mg, the mass of antimony in the filter cake is 4.88 mg, and the mass fraction of antimony impurity entering the filtrate is about 79.6% of the total. The mass of residual antimony in the filter cake for the second time is 5.45 mg, and the mass fraction of antimony entering the liquid phase is about 77.3% of the total. The mass of residual antimony in the filter cake of the third cycle is 14.9 mg, and the mass fraction of antimony entering the filter cake is about 62% of the total, while the mass fraction in the liquid phase is about 38.0%, which is obviously decreased. This shows that two leaching cycles are feasible.
Table 5 Changes of antimony mass in filtrate and filter cake

| cycle index | Antimony in the filtrate/mg | The mass of antimony in a filter cake |
|-------------|----------------------------|-------------------------------------|
| 1           | 19.12                      | 4.88                                |
| 2           | 37.67                      | 5.45                                |
| 3           | 46.77                      | 14.90                               |
| 4           | 51.31                      | 19.46                               |
| 5           | 53.01                      | 22.30                               |

4. Summary
Antimony is the main impurity in lead slurry of lead-antimony alloy grid lead-acid battery, and its existing form is mainly in the form of metallic antimony, antimony sulfate or antimony oxide. In the leaching experiment of lead paste, it is shown that the leaching amount of antimony increases with the increase of the amount of leaching agent. When the dosage of reagent is increased by 1.5 times, the amount of antimony exudation increases with the extension of reaction time. It can be seen from the cycle experiment that with the increase of cycle times, the desulfurization rate of lead sulfate decreases with the increase of cycle times, and the amount of antimony entering the solid phase increases but the amount of antimony entering the liquid phase gradually decreases.

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