Leaching Treatment of Discarded Waste Cathodes in Aluminum Electrolysis

Junxue Zhao, Zhongyu Zhao, Liang Lu, Ruimeng Shi, Lisi Liang and Xiaoming Li

ABSTRACT

An industrial experiment was carried out by classifying the waste cathodes of aluminum electrolytic cells in Shanxi Province and investigating the effect of particle size and temperature on the leaching of soluble fluoride. It was discovered that NaF was the main dissolvent and could be effectively dissolved by four-stage leaching at 348 K and that the soluble fluorine could be decreased to the limit for hazardous solid waste. After the leaching of discarded water, the fluoride concentration in the final water was enriched to 17.69 g/L, and the effective enrichment of fluoride ion was realized.

INTRODUCTION

With the rapid expansion of electrolytic aluminum production capacity, waste cathode materials produced by the dismantling of aluminum electrolytic cells have been increasing annually [1-3, 5]. Waste cathodes contain a large amount of soluble fluoride, in which the fluoride ion concentration can reach 2000 mg/L or more (up to 6000 mg/L), which is far greater than the threshold value (50 mg/L) of the fluoride ion concentration in hazardous solid waste, known as the "invisible bomb"[4].

Samples were taken from the waste cathode site of an electrolytic aluminum production enterprise in Shanxi Province and analyzed through X-ray diffraction (XRD), chemical element analysis, and soluble F concentration, as shown in Tables I and II.

1Junxue Zhao, Zhongyu Zhao, Liang Lu, Ruimeng Shi, Lisi Liang, Xiaoming Li, College of Metallurgical Engineering, Xi'an University of Architecture and Technology, Shaanxi, China
It can be seen that the results of chemical analysis are close to that of XRD, that the fluorides are mainly Na$_3$AlF$_6$, CaF$_2$ and NaF and that the F$^-$ in the free state of sodium fluoride is 42% of the total F$^-$. 

There are no mature disposal technologies for these wastes, which are mainly disposed of in safe landfills. Achieving emission reduction, reducing harm, and applying comprehensive utilization are important issues that companies face. Furthermore, during the flotation process developed in recent years, the soluble fluoride in the waste cathode not only directly affects the process of separation but also complicates the treatment of beneficiation wastewater, and it is essential to remove the soluble fluoride in advance. Therefore, in this paper, an industrial test on the dissolution characteristics of fluorine in the waste cathodes from electrolytic aluminum production was conducted.

<table>
<thead>
<tr>
<th>TABLE I. SOLUBLE F CONCENTRATION OF SAMPLES.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO.</td>
</tr>
<tr>
<td>Value /mg·L$^{-1}$</td>
</tr>
<tr>
<td>NO.</td>
</tr>
<tr>
<td>Value /mg·L$^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE II. XRD AND CHEMICAL ELEMENTAL ANALYSIS OF SAMPLES.</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD</td>
</tr>
<tr>
<td>Content /%</td>
</tr>
<tr>
<td>Element</td>
</tr>
<tr>
<td>Content /%</td>
</tr>
</tbody>
</table>
TEST AND ANALYSIS

Experimental Scheme

The waste cathode material from electrolytic aluminum production was crushed down into three grain sizes: small (20-40 mm), medium (40-60 mm), and large (60-80 mm). A total of 3 square sinks (0.7×0.7×1.5 m in length, width and height, respectively), numbered as #1, #2, and #3, were designed and prepared. The leaching process is shown in Figure 1. Additionally, 3 square net cages (0.5 × 0.5 × 0.3 m in length, width and height, respectively shown in Figure 2) were prepared and used for loading materials. The liquid to solid mass ratio was 5:1, shown in Figure 3, and the water temperature was designed to be 288 K (room temperature) and 348 K (heating temperature). The waste-cathode F- dissolution experiment was conducted under different temperatures and particle sizes.

![Figure 1. Process flow chart.](image1)

![Figure 2. Net cage with waste cathode. Figure 3. Square sink for leaching.](image2)
Results and Discussion

CHANGE IN FLUORINE ION CONCENTRATION IN LEACHING SOLUTION

The fluoride ion concentration in the three tanks was continuously measured by a BPX-932 fluorine ion meter. The results are as follows:

Figure 4. F-concentration changes during leaching from level I to III in each tank.

(a) #1 leaching at 288 K; (b) #1 leaching at 348 K; (c) #2 leaching at 288 K
(d) #2 leaching at 348 K; (e) #3 leaching at 288 K; (f) #3 leaching at 348 K
Figure 5. XRD diffraction patterns of waste cathodes before and after water leaching.

It can be seen from Figure 4.(a) to (f) that after the water leaching of waste cathodes with different particle sizes at different temperatures, the F- concentration reached 13.26 g/L at 288 K and 17.69 g/L at 348 K in the final water; additionally, the F- leaching rate reached 62%, achieving the effective enrichment of fluoride ions.

In the process of leaching from grades I to III, a “jump” phenomenon in F-concentration was detected during the experiment because of the nonuniform concentration of F- in the leachate, indicating that the external diffusion of the dissolution process was insufficient. Therefore, it is recommended to add blowing or mechanical stirring into the industrial leaching process.

PHASE DETECTION AND MORPHOLOGY OBSERVATION

(a) Leaching three times at 288 K; (b) Leaching three times at 348 K

Figure 6. Waste cathode microstructure.
The XRD phases of the samples before and after leaching was detected, and the results are shown in Figure 5.

XRD analysis shows that, except for carbon, fluoride in waste cathode materials was generally in the forms of Na$_3$AlF$_6$, CaF$_2$ and NaF. Among them, NaF readily dissolves in water, and Na$_3$AlF$_6$ and CaF$_2$ are insoluble compounds. Therefore, with a decrease in grain size, the content of NaF in the carbon residue after leaching was gradually reduced and the content of Na$_3$AlF$_6$ and CaF$_2$ remained unchanged.

The microstructure of waste cathode before and after leaching is shown in Figure 6.

Through the contrast in sample microstructures in Figure 6, it is obvious that after the leaching of the waste cathode with electrolytes, the inner hole in the sample increases. With the leaching temperature increased, the internal surface of the waste cathode exhibits flocculent structure, and the hole is obviously larger. This is consistent with the dissolution results of fluoride in the leaching process, indicating that the pores are formed after the dissolution of fluoride.

**GRINDABILITY DETECTION**

Carbon residues were crushed, sieved, and weighed into 50-g samples with pore sizes of 0.63-1.25 mm, for the original and grade I-III water-quenched samples. The grindability index was calculated by the following one-dimensional linear regression equation [GB/T 2565-2014]:

$$HGI=6.95\Delta m+12.71$$  \hspace{1cm} (1)

It can be seen from Figure 7 that the grindability index of the waste cathode after water quenching was remarkably improved, which corresponds to the increase in pore size. The smaller the particle size is, the more complete the dissolution and the greater the grindability index.

The spent cathode after the dissolution treatment will require grinding if it is subjected to selective treatment. The water-quenching pretreatment will facilitate subsequent grinding. Moreover, dissolution can reduce the impact on the selection process, and wastewater with a high fluorine content is advantageous for centralized treatment.

**HAZARD ASSESSMENT OF WAST CATHODES AFTER QUENCHING**

According to the requirements in the "Dangerous Waste Identification Standard - Identification of Leaching Toxicity" (GB5085.3-2007), the leaching toxicity of the waste cathode samples after the third-stage leaching was identified, and the NaF concentration was determined to be 85 mg/L. The threshold for the identification of dangerous solid waste is 100 mg/L. Therefore, through three-stage dissolution, waste cathodes can be converted into a general solid waste.
KINETIC ANALYSIS OF LEACHING PROCESS

To further explore the relationship between particle size and reaction kinetics, field samples (small: 20-40 mm, medium: 40-60 mm, large: 60-80 mm) were used to determine the leaching rate of different particle sizes at room temperature (288 K), and the internal diffusion control kinetic equation was substituted [6].

\[ 1-\frac{2}{3}\alpha - (1-\alpha)^{2/3} = kt \]  

\( \alpha \) - Leaching rate;  
\( k \) - Apparent reaction rate constant;  
\( t \) - Reaction time.

Additionally, the relationship between \( 1-\frac{2}{3}\alpha - (1-\alpha)^{2/3} \) and \( t \) of the leaching reaction at different particle sizes was plotted, and the experimental data were linearly fitted with the a custom formula in the software Origin 8.5, as shown in Figure 8. Furthermore, the leaching kinetic equations for different particle sizes can be obtained, as shown in Table 3 below.

Figure 7. Comparison of grindability index.

Figure 8. Diagram of the relationship between \( 1-\frac{2}{3}\alpha - (1-\alpha)^{2/3} \) and leaching time at different particle sizes.
The leaching kinetic equations at different particle sizes are given in Table III.

<table>
<thead>
<tr>
<th>Size, mm</th>
<th>Kinetic equations</th>
<th>Apparent reaction rate constant, k/min⁻¹</th>
<th>Linear correlation coefficient, R</th>
</tr>
</thead>
<tbody>
<tr>
<td>20~40</td>
<td>$1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} = 0.652 \times 10^{-3} t$</td>
<td>$0.652 \times 10^{-3}$</td>
<td>0.98</td>
</tr>
<tr>
<td>40~60</td>
<td>$1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} = 0.596 \times 10^{-3} t$</td>
<td>$0.596 \times 10^{-3}$</td>
<td>0.98</td>
</tr>
<tr>
<td>60~80</td>
<td>$1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} = 0.156 \times 10^{-3} t$</td>
<td>$0.156 \times 10^{-3}$</td>
<td>0.99</td>
</tr>
</tbody>
</table>

It can be seen from Figure 8 and Table III that in a certain particle size range, $1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3}$ has a linear relationship with the leaching time $t$ (linear correlation coefficient $R \geq 0.97$), which indicates that the leaching process of soluble F⁻ at different particle sizes belongs to the internal diffusion control type.

Furthermore, according to the linear relationship in Figure 8, the leaching kinetic equations at different particle sizes can be obtained, as shown in Table III. It can be seen that the controlling factor in the leaching reaction of waste cathode material in the aluminum electrolytic cell conforms to an internal diffusion control process. The smaller the reaction particle size is, the larger the reaction rate constant.

Compared with the previous kinetic analysis of the waste cathode leaching process with small particle size (0.075-1.000 mm) [7], the selected kinetic model is in good agreement with the experimental results.

**CONCLUSIONS**

(1) The primary content of fluoride in the anode carbon residue of the aluminum electrolysis cells was in the form of Na₃AlF₆, NaF, CaF₂, etc. NaF was the major soluble fluoride.

(2) The F⁻ concentration reached 13.26 g/L at 288 K and 17.69 g/L at 348 K in the final water, while the F⁻ leaching rate reached 62%, achieving the effective enrichment of fluoride ions.

(3) The NaF concentration of the waste cathode samples after third-stage leaching was determined to be 85 mg/L < 100 mg/L (the critical solid waste identification threshold).

(4) After water leaching, the pore size and grindability index of the waste cathode increased significantly; this was beneficial to subsequent separation.

(5) Through kinetic analysis of the waste cathode leaching process of aluminum electrolysis cells, a rate control model was established to further determine that the NaF leaching kinetic rate control process was an internal diffusion control process.

(6) The above results indicate that fractional leaching is a pretreatment method that is conducive to subsequent processing and comprehensive utilization.
ACKNOWLEDGEMENTS

This research was supported by Scientific and Technological Research Projects for Social Development (2015SF259)、Shaanxi Natural Science Basic Research Project (2014JM7249) and the Natural Science Foundation of China (51674185, 51674186, 51174155).

REFERENCES