Process for stabilizing fluorine in electrolytic aluminum spent pot lining by roasting method

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**ABSTRACT**: Electrolytic aluminum Spent Pot Lining (SPL) contains excess soluble fluoride, which can cause harm to the environment and human body when it seeps into the ground with rainwater. Therefore, it is necessary to convert the soluble fluoride into a chemically stable insoluble substance. In order to stabilize the fluoride ions of soluble fluoride, a roasting process is adopted. Through thermodynamic calculations and experiments, four factors of suitable calcium salt, calcium salt to SPL ingredient ratio, roasting temperature and time are determined to obtain the best operating conditions. The experimental results show that when the calcium salt is CaCl\(_2\), the ingredient ratio is \(m(\text{CaCl}_2)/m(\text{SPL})=0.5\), the roasting temperature is 750°C and the roasting time is 5h, the amount of F-leaching is 10.64ppm, meeting the national requirements for the amount of F-leaching in electrolytic aluminum solid waste. Finally, the process route of roasting stable fluorine was determined according to suitable operating conditions.

1. **Introduction**

At present, the aluminum smelting industry generally uses the Hall-Elut method, also known as the electrolytic alumina molten salt method, to produce aluminum\(^1\). The emergence of electrolytic aluminum technology has increased aluminum output and greatly improved people's quality of life. However, in the electrolytic aluminum production process, a large amount of electrolyte cryolite (\(\text{Na}_3\text{AlF}_6\)) and alkali (\(\text{NaOH}\)) penetrated into the carbon lining material, causing the inner wall of the electrolytic cell to be corroded and cracked\(^2\). Therefore, the aluminum electrolytic cell needs to be completely repaired every 1800 days. The lining material removed during the complete repair process is called Spent Pot Lining (SPL), which is composed of cathode carbon blocks, refractory bricks and insulation materials\(^3\).

Due to the difference in the nature of the components in SPL, there is often no reasonable treatment method, so landfill and slag dumping are common treatment methods in the past\(^4\). However, the soluble or...
hydrolysolyed fluoride in SPL will cause serious harm to the ecological environment when encountering groundwater. In 2016, the National Hazardous Waste List has defined the waste residues generated from the repair and disposal of the electrolytic cell during the electrolytic aluminum process as hazardous waste, and the hazardous code is HW48-321-023-48. In addition, the Environmental Protection Tax Law of the People's Republic of China that came into effect on January 1, 2018 stipulates that an environmental protection tax of 1,000 yuan will be levied per ton of hazardous waste[5]. For electrolytic aluminum production enterprises, the harmless treatment of SPL cannot be delayed.

In order to recycle the carbon materials in SPL, LI Nan et al. used the flotation method to optimize the conditions to obtain a carbon material with a purity of 78.50%, the recovery rate was 84.90%, and the cryolite recovery rate was 86.86%. Although this method is conducive to the recovery of carbon and fluorine resources, it is difficult to achieve high carbon recovery and purity for SPL with low carbon content. Xie Wuming et al.[6] mixed SPL into the Red Mud, which reduced the Fe$^{3+}$ in the red mud by roasting, and optimized the operating conditions to make the iron recovery rate reach 88.84%. The soluble fluoride in SPL can be converted into cuspidine (3CaO·2SiO$_2$·CaF$_2$) by this method to achieve the purpose of stabilizing fluorine.

This research is based on the roasting treatment of SPL, using calcium salt to convert soluble fluoride such as NaF into insoluble and stable CaF$_2$. Firstly, the most suitable calcium salt was selected by thermodynamic calculation and experiment. Secondly, through orthogonal experiment analysis of temperature, ratio and roasting time, the optimal operating conditions are obtained. Finally, the process route of roasting stable fluorine was determined.

2. Experiment

2.1. Equipments and reagents

The instruments used in this experiment are ball mill, muffle furnace (SG-XL1800), HY-8 speed regulating oscillator, PHS-3C PH meter. The experimental reagents CaCl$_2$, CaSO$_4$ and CaCO$_3$ are all analytically pure, and the water used in the process is distilled water.

2.2. Sample source and preparation

The overhaul slag in this study is all from Lanzhou Branch of Aluminum Corporation of China. After crushing the SPL sample, ball milling is performed. The ball milling particle size is shown in Figure 1. The ball-milled SPL was baked at 105°C for 10 hours, then cooled and sealed for storage.

It can be seen from the figure1 that the particle size of the sample is less than 100μm and most of it is maintained at about 15μm. The particle size has a significant impact on the fluorine stabilization effect of SPL. In the electrolytic aluminum production process, the electrolyte penetrates into the
carbon block to make the carbon and electrolyte tightly embedded. When the particle size is too large, part of the NaF is wrapped by the carbon block to isolate it from the calcium salt.

2.3. Determine operating conditions

2.3.1. Determination of the type of calcium salt

Three different salts of CaSO\(_4\), CaCO\(_3\) and CaCl\(_2\) are used as reagents to stabilize fluorine. The Gibbs free energy was calculated before the experiment, the feasibility and difficulty of the reaction between each calcium salt and fluoride in SPL at different temperatures were calculated by thermodynamics. The calculation method is as follows\(^7\):

The formula of Gibbs-Helmholtz: \[
\Delta H^\theta = \int C_p dT
\]

\[
\Delta C_p = \Delta A_1 + \Delta A_2 \times 10^{-3} T + \Delta A_3 \times 10^{5} T^{-2} + \Delta A_4 \times 10^{-6} T^2 + \Delta A_5 \times 10^8 T^{-3}
\]

\[
\Delta A_k = \sum a_i A_i (\text{product}) - \sum j A_j (\text{reactant})
\]

\[
\Delta H^\theta = \Delta A_1 T + 1/2 \Delta A_2 \times 10^{-3} T^2 - \Delta A_3 \times 10^5 T^{-1} + 1/3 \Delta A_4 \times 10^{-6} T^3 - 1/2 \Delta A_5 \times 10^8 T^{-2} + A_6
\]

Incorporate formula (5) into formula (1) and integrate

\[
\Delta G^\theta = -\Delta A_1 T \ln T - 1/2 \Delta A_2 \times 10^{-3} T^2 - 1/2 \Delta A_3 \times 10^5 T^{-1} - 1/6 \Delta A_4 \times 10^{-6} T^3 - 1/6 \Delta A_5 \times 10^8 T^{-2} + A'_6 T + A_6
\]

In formula (1), \(\Delta G^\theta\) is Gibbs free energy, \(\Delta H^\theta\) is Enthalpy change; In formula (3), \(C_p\) is equal pressure heat capacity, \(A\) is the characteristic constant of each reactant and product, and its value is not affected by the ambient temperature; In formula (4), \(A_i\) and \(A_j\) are the coefficients before the product and the reactant in the reaction equation, respectively; \(A_6\) in formula (5) and \(A'_6\) in formula (6) are integral constants; Formula (6) is the calculation formula of Gibbs free energy. Putting different temperatures into formula (6) can calculate the Gibbs free energy of each reaction at the corresponding temperature, When \(\Delta G^\theta > 0\), the reaction can proceed at temperature \(T\), and when \(\Delta G^\theta < 0\), the reaction cannot proceed at temperature \(T\).

In order to verify the above calculations, three different calcium salts were used to calcinate at \(m(\text{calcium salt})/m(\text{SPL})=0.2\) and a temperature of 850\(^\circ\)C for 2 hours. Finally, according to GB/T 15555.11-1995, determine the leaching concentration of fluoride ions in the samples after each treatment, and select the most suitable solid fluoride calcium salt\(^8\).

2.3.2. Orthogonal experiment

In order to further obtain the optimal operating conditions and explore the degree of influence of each condition on the effect of stabilizing fluorine, an orthogonal table \(L_9(3^3)\) is designed from the three
factors of temperature, time and ratio, as shown in Table 1:

| Level | Temperature (A) | Time (B) | m(calcium salt)/m(SPL) (C) |
|-------|-----------------|----------|-----------------------------|
| 1     | 650°C           | 2h       | 0.2                         |
| 2     | 750°C           | 5h       | 0.35                        |
| 3     | 850°C           | 8h       | 0.5                         |

2.4. Characterization
The TG-DSC curve is produced by a comprehensive thermal analyzer to analyze the changes of SPL under operating conditions.

1 Results and discussion

3.1. Thermodynamics Research
The equations for the reaction of different calcium salts with NaF are as follows:

\[ \text{CaCl}_2 + 2\text{NaF} = \text{CaF}_2 + 2\text{NaCl} \]
\[ \text{CaCO}_3 + 2\text{NaF} = \text{Na}_2\text{CO}_3 + \text{CaF}_2 \]
\[ \text{CaSO}_4 + 2\text{NaF} = \text{Na}_2\text{SO}_4 + \text{CaF}_2 \]

The Gibbs free energy of each reaction at 700K, 800K, 900K, 1000K, 1100K, 1200K was calculated according to formulas (1) ~ (6).

The Gibbs free energy of the three different calcium salts in Figure 2 is less than zero when calcined at different temperatures. It is thermodynamically proved that these three salts are feasible to stabilize fluoride ions. The higher the temperature, the more negative the Gibbs free energy of each reaction, and the difficulty of the three calcium salts participating in the reaction is: \( \text{CaSO}_4 > \text{CaCO}_3 > \text{CaCl}_2 \). In order to further verify the above calculation, an experiment was designed to select the best calcium salt. The experimental results are shown in Figure 3.

From the data in the figure, it can be seen that \( \text{CaCl}_2 \) has the best fluorine stabilizing effect, and the leaching amount is 361.02 ppm. Compared with the raw sample F leaching amount of 5200.03 ppm, although \( \text{CaSO}_4 \) and \( \text{CaCO}_3 \) also have the effect of stabilizing fluorine, the F leaching amount is 2016.26 ppm and 4665.99 ppm respectively, but it is far inferior to \( \text{CaCl}_2 \). This result is seriously inconsistent with that in Figure 2. The reason for this phenomenon can be analyzed by kinetics: The melting point of \( \text{CaCl}_2 \) is 772°C; the melting point of \( \text{CaCO}_3 \) is 1339°C; the melting point of \( \text{CaSO}_4 \) is
1450℃. When calcined at 850℃, the molten CaCl$_2$ can dissolve and react with NaF. CaCO$_3$ and CaSO$_4$ are still in a solid state, preventing effective collisions between molecules and making the reaction impossible. Because there is a small amount of low melting point salt (such as NaCl) in SPL, it can dissolve a small amount of calcium salt and NaF, so it has a weak fluorine stabilizing effect. In summary, CaCl$_2$ is the best calcium salt for fixing fluorine.

3.2. Orthogonal experiment

After using CaCl$_2$ as the calcium salt for stabilizing fluorine, in order to explore the influence of roasting temperature, time and ratio on the effect of fluorine fixation, the L$_{9}(3^3)$ orthogonal experiment was designed. The experimental results are shown in Table 2.

Table 2 lists the effects of stabilizing fluorine under different firing conditions. For the three factors of roasting temperature, roasting time and ratio, R (Range) represents the influence level of these three parameters. It can be seen from the table that the R level decreases in the following order: RC>RB>RA, indicating that the effect of stabilizing fluorine is most significantly affected by the ratio, followed by the roasting time and the temperature. Since KA2<KA3<KA1; KB2<KB3<KB1; KC3<KC2<KC1, the best group can be obtained as A2B2C3. Under this operating condition, the leaching amount of fluoride ion is only 10.64ppm, which meets the requirements of the country for solid waste of electrolytic aluminum. The requirement that fluoride ion leaching content is not higher than 100ppm$^{[9]}$. Similarly, the experimental results of R3, R4, and R7 also meet this requirement.

3.3. Characterization

In order to explore the quality and heat absorption and release changes of SPL during the roasting process, the TG-DSC curve was produced by a comprehensive thermal analyzer at a temperature of 0–850℃, a heating rate of 10℃/min, and an air rate of 50mL/min.
As shown in Figure 4. Two DSC endothermic peaks are observed at 150℃, which may be the evaporation of crystal water in SPL. There is a DSC endothermic peak at 230℃, and from 100℃ to 450℃, the TG curve slowly loses weight by 3%, indicating that cyanides have decomposed in this temperature range. A large and steep endothermic peak appears in the DSC from 450℃ to 850℃, and the TG curve drops rapidly by 18% in this interval. This can be considered as carbons in the SPL were oxidized. Therefore, SPL can be harmless and reduced under these operating conditions.

4. Design of process flow
In order to meet the national environmental protection requirements and realize the sustainable development of SPL harmless treatment, equipment investment and energy consumption should be reduced as much as possible. Therefore, a simple treatment process is required to obtain an ideal stable fluorine effect. In addition, the hazardous waste generated in the process of roasting method stabilization of fluorine should be treated safely. Figure 5 shows the roasting method to stabilize the fluorine process. The SPL particle size is less than 100 μm, so that the raw materials and the calcium salt are more fully contacted during the reaction, so that it can react with the calcium salt as much as possible. There are two suitable operating conditions: Roasting for 5 hours at 750℃ at a mixing ratio of m(CaCl₂)/m(SPL)=0.5, as an operating condition, the amount of F-leaching in SPL can be minimized; Roasting for 2 hours at 750℃ at a mixing ratio of m(CaCl₂)/m(SPL)=0.35, as an operating condition, can meet national environmental protection requirements while saving calcium salt input and roasting time, which not only improves SPL harmless treatment efficiency, and can reduce energy consumption. The gas absorption equipment is designed to prevent the toxic gas generated during the muffle furnace roasting process from being discharged. Na₂CO₃ solution can effectively absorb HF and HCN acid gas, and it is safer and low cost. SPL after roasting has a low soluble fluoride content and can be buried in the slag field.
5. Conclusions
(1) Through thermodynamic calculations and comparative experiments of three calcium salts, the most suitable calcium salt is determined to be CaCl₂.

(2) The best operating condition was obtained through orthogonal experiments: from the environmental protection aspect, R5 is the best combination, and its F⁻ leaching amount is 10.64 ppm; at the economic aspect, R4 is the best combination, but the amount of F⁻ leaching is 76.45 ppm. In actual operation, reasonable operating conditions should be selected in combination with economic investment and environmental protection.

(3) A laser particle size analyzer was used to analyze the particle size distribution of the SPL after ball milling, which showed that the particle size of most samples was concentrated around 15 μm; through TG-DSC analysis, it is concluded that the comprehensive weight reduction of SPL during the burning process is 18%, which achieves the reduction of SPL to a certain extent.

(4) Finally, using the above operating conditions, a process flow suitable for the harmless treatment of electrolytic aluminum SPL roasting method is proposed, and the simple treatment process is used to obtain the ideal stable fluorine effect.

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