

Study on Utilization and Disposal Technology of Spent Potlining

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Abstract

Spent pot lining (SPL) is a solid hazardous waste, produced from electrolysis. The fluoride is the main toxic substance which also has relatively high recycling value. This paper comprehensively studied the existence form and content of the fluoride, the utilization and disposal technology of the fluoride in the spent pot lining. The research shows that the fluoride was mainly in the form of sodium fluoride and cryolite. The soluble fluoride was mainly present in the form of sodium fluoride which can be recovered by leaching, desilicization and crystallization. The small amounts of fluoride that cannot be leached can be solidified into calcium fluoride to meet the requirement of identification standards for hazardous wastes. The leaching process reacted at room temperature, the leaching times was 2–3 times, the leaching liquid/solid ratio was 3:1, and the leaching time was 20–25 minutes. The desilication with the volume percentage of about 4 % should be added in the desilicization process. The liquid/solid ratio and reacting time was 3:1 and 20–25 minutes in the solidified process, respectively. The addition of the fluorine-fixing agent was more than 1.6 times greater than the theoretical value. The purity of the sodium fluoride products reached 98 % which can be used in the electrolytic cell.

Keywords: Spent pot lining, Fluoride, Utilization, Disposal.

1. Introduction

Spent pot lining (SPL) is a solid waste produced from the aluminium electrolysis process after a cell is taken offline and delined. SPL mainly comprises of waste cathodes and waste refractories [1–4]. The SPL contains excessive toxic substances such as inorganic fluoride and cyanide, which are extremely harmful to the environment, and it has been included in the “National Hazardous Waste List” in China. It is calculated that, depending on the line amperage, for an electrolytic cell with the life of 5 to 8 years, the amount of SPL is 10-20 kg/t Al, and the amount of production is very large.

At present, the harmless disposal and resource utilization technology of SPL mainly includes hydrometallurgical method, pyrometallurgical method and synergistic utilization [5–12]. In the hydrometallurgical method, the fluoride was converted to cryolite, sodium fluoride and calcium fluoride by leaching, crystallization and precipitation. In the pyrometallurgical method, the cyanide was oxidized and decomposed into CO₂ and N₂ under high temperature, and the fluoride was converted into CaF₂, and the harmless residue was used elsewhere or landfilled. The synergistic utilization technology included cement kiln synergy and waste cathode synergy. The valuable components such as carbon, aluminium, silicon and fluoride were synergistically utilized by the cement kiln. The carbonaceous components of the waste cathode were used for steelmaking and mineral wool production.

The harmless disposal of SPL cannot meet the requirements of China's environmental protection policy. The "General Principles for Hazardous Waste Identification Standards" stipulates that "Unless the relevant national regulations and standards stipulate otherwise, the solid wastes generated after the disposal of hazardous waste with toxic and hazardous characteristics still belong to hazardous waste". The utilization of SPL is a good method. On the one hand, the valuable components can be extracted and transformed into products to improve economic benefits. On the other hand, the "General Principles" stipulates that "Solid waste generated during the hazardous waste with toxic and hazardous characteristics is no longer identified as hazardous".

In this paper, the content, phase composition and recycling process conditions of the fluoride were comprehensively studied. The solidification treatment of a small amount of fluoride in the filter residue was studied. The related process parameters of fluoride recovery and solidification were obtained. The cyanides in the solution were removed by oxidation in the room temperature, and the oxidant does not contaminate the solution.

2. Experimental

Firstly, the toxic substance fluoride in the SPL was analysed, and the content was obtained. Secondly, the phase composition of SPL was analysed, and the existence form of the fluoride was obtained. Thirdly, the utilization of soluble fluoride in SPL was studied. The cyanides were removed by oxidation before if they were present, and then the effects of leaching times, liquid/solid ratio and leaching time were studied by measuring the leaching rate of fluoride, and the relevant leaching process conditions were determined. Fourthly, the filtrate was desilicized and crystallized, and composition of the crystals were determined. Fifthly, the filter residue was treated with fluorine fixation. The effects of fluorine-fixing agent, liquid/solid ratio and reacting time were studied by measuring the leaching toxicity of fluoride in the filter residue, and the relevant fluorine-fixing process conditions were determined.

$$\text{Leaching fraction} = \left(1 - \frac{m_r \times C_r \times 100}{m_f \times C_f \times 100} \right) \times 100 \% \quad (1)$$

where:

- m_r the weight of raw material, g
- C_r the soluble fluorine content of raw material, g/L
- m_f the weight of the filtrate after leaching, g
- C_f the soluble fluorine content of the filtrate after leaching, g/L
- 100 conversion coefficient, L/g

The method to determine the leaching potential was based on the "Solid Waste Leaching Toxicity Leaching Method Sulfuric Acid Nitric Acid Method". Specifically, the raw material of SPL was crushed to a sieve that could pass through a 9.5 mm pore size, and 150 g of the sample was placed into one 2 L extraction bottle. According to the liquid/solid ratio of 10:1, 1500 mL of pure water was added, and the bottle cap was tightly fixed on the flip-type oscillator. The rotation speed was 28–32 rpm, and it was shaken at 21–25 °C for 18 h. The fluoride ion content in the filtrate was determined by ion chromatography, which was the leaching toxicity content of fluoride in SPL.

3. Results and Discussion

3.1 The Content and Composition of SPL

The soluble fluorine content in different SPL was determined according to the determination method of leaching toxic substances. The fluoride leaching potential of different SPLs is shown in Table 1.

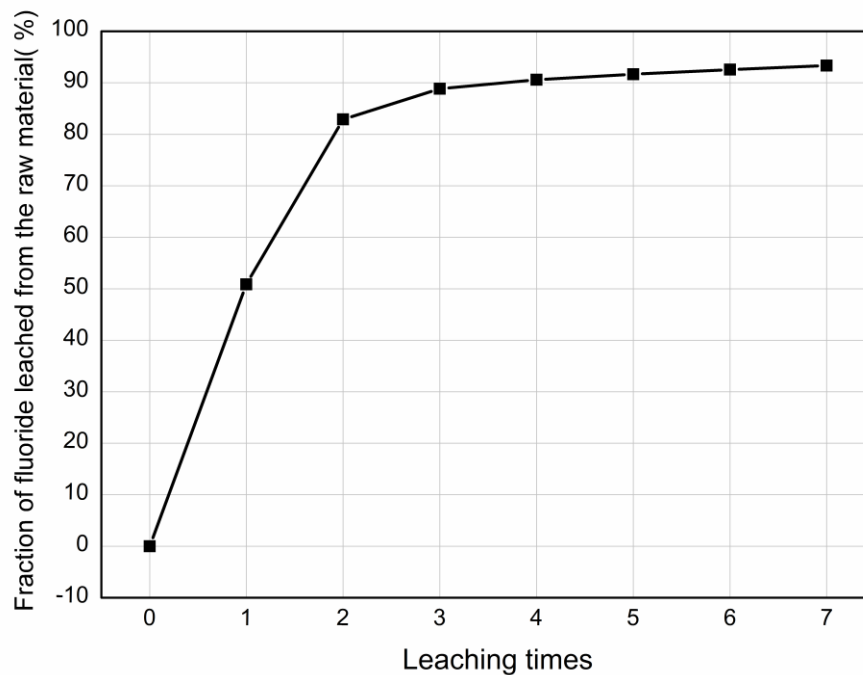


Figure 1. Effect of leaching times on fluoride leaching.

Figure 1 showed that with the increase of leaching times, the fraction of fluoride that was leached increased rapidly and then gradually stabilized. The leaching fractions of 1–4 times were 50.8 %, 81.6 %, 88.9 % and 90.6 %, respectively. The fraction of leaching increased by 31 % from 1 time to 2 times. The fraction of leaching increased by 7.3 % from 2 times to 3 times. The leaching rate only increased by 1.7 % from 3 times to 4 times. Considering the leaching process flow, water balance and equipment investment, the optimum number of leaching times was determined to be 2-3 times. Generally, a material containing fluoride levels below 7000 mg/L can be leached 2 times, and a material with fluoride content higher than 8000 mg/L can be leached 3 times. The leaching times were adjusted according to the raw materials.

3.2.2 Effect of Liquid/Solid Ratio on Leaching Effect of Fluoride

At room temperature, the leaching time was controlled at 30 minutes, and the leaching times were 2 times. The effect of liquid/solid ratio on the leaching effect of fluoride was studied. The results are shown in Figure 2.

Figure 2 showed that with the increase of liquid/solid ratio, the leaching potential of fluoride increased rapidly and then gradually stabilized. When the liquid/solid ratio was 2:1, 3:1, 4:1 and 5:1, the fractions of leaching were 76.2 %, 82.9 %, 87.0 % and 88.1 %, respectively. When the liquid/solid ratio increased from 3:1 to 4:1, the fraction of leaching increased by 4.1 %. When the solid/liquid ratio increased from 4:1 to 5:1, the fraction of leaching only increased by 1.1 %. Considering the increase of leaching potential and system water balance, the optimum liquid/solid ratio was determined to be 3:1.