

## 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 CO<sub>2</sub> and N<sub>2</sub> under high temperature, and the fluoride was converted into CaF<sub>2</sub>, 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.

**Table 1. The fluoride leaching toxicity content in different SPLs.**

Sample (Type)	A	B	C	D	E	F	G	H	I	J
Content (mg/L)	5756	1093	3123	184	6695	11 563	8572	6264	2666	4589

Table 1 showed that the leaching potential of fluoride in different SPL varied greatly, ranging from 184 mg/L to 11 563 mg/L, which was mainly related to the age of the electrolytic cell and the location. The F sample with the highest content was the waste cathode with the age of 7 years, and the D sample with the lowest content was the calcium silicate plate with the age of 5 years, which was at the lowest layer of the electrolytic cell.

The G sample and H samples were selected for XRD phase composition analysis. The G sample was a mixed sample of waste cathode and the H sample was a mixed sample of waste refractory. The phase composition of G sample is shown in Table 2. The phase composition of H sample is shown in Table 3.

**Table 2. The phase composition of G sample (waste cathode).**

Phase composition	NaF	LiF	CaF <sub>2</sub>	Na <sub>3</sub> AlF <sub>6</sub>	C	K <sub>2</sub> NaAlF <sub>6</sub>	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	LiAlO <sub>2</sub>
Content (%)	16.2	7	1.4	5.9	67.8	0.4	0.9	0.4

**Table 3. The phase composition of H sample (waste refractory).**

Phase composition	NaF	LiF	CaF <sub>2</sub>	Na <sub>3</sub> AlF <sub>6</sub>	Nepheline	Illite	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	$\beta$ -Al <sub>2</sub> O <sub>3</sub>
Content (%)	12.6	10.6	5.2	13.5	45.6	5	6	1.5

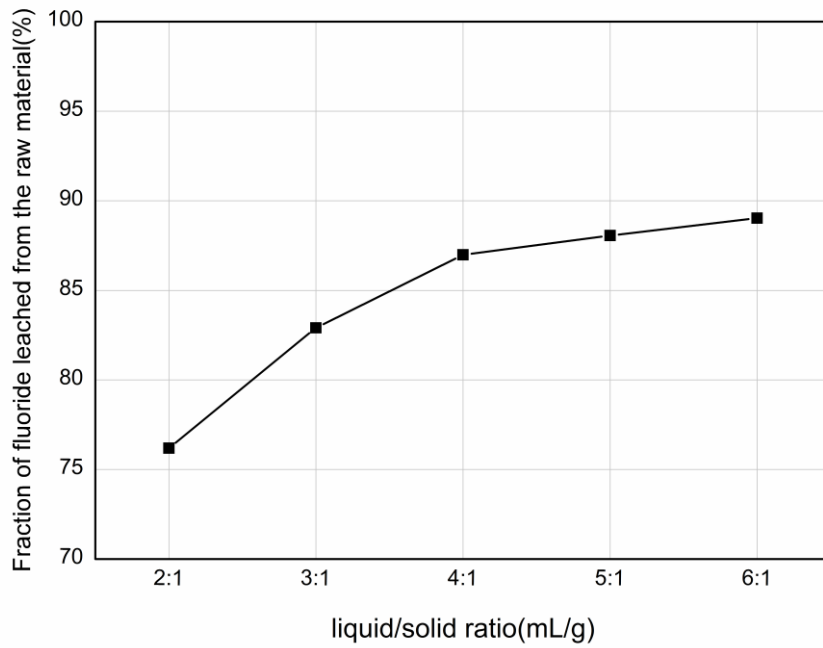
Table 2 and Table 3 showed that the carbon content was the highest in the waste cathode, and the content of aluminosilicate such as nepheline was the highest in the waste refractory. These were the components of the material itself. In addition, both the waste cathode and the waste refractory contained sodium fluoride, lithium fluoride, cryolite and calcium fluoride. These components were the components infiltrated from the aluminium electrolyte during the long-term operation of the electrolytic cell. The fluoride was mainly in the form of sodium fluoride and cryolite, and the fluoride with leaching potential was mainly in the form of sodium fluoride.

### 3.2 Effect of fluoride leaching in SPL

The H sample was crushed to a particle size below 0.15 mm and used as raw material.

#### 3.2.1 Effect of Leaching Times on Leaching Effect of Fluoride

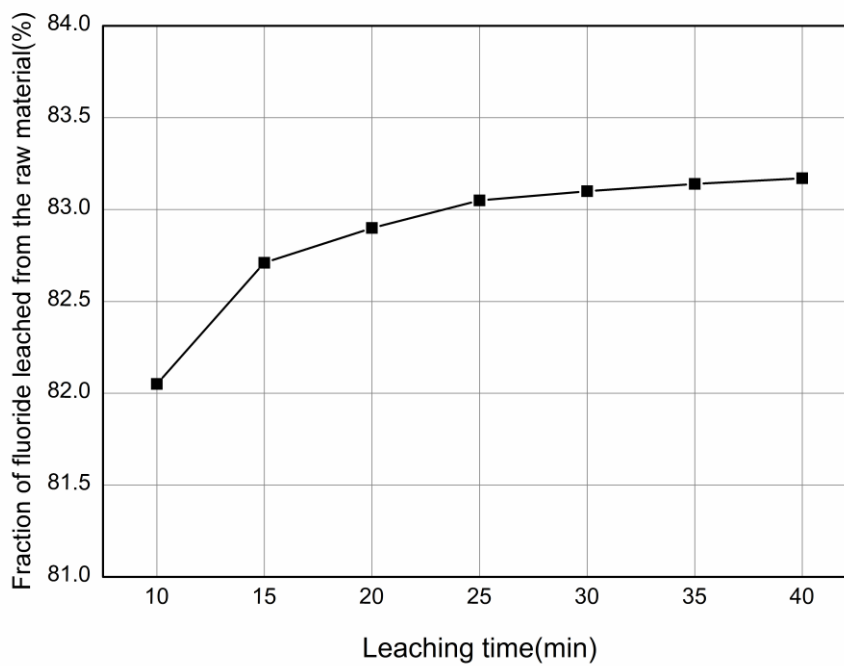
At room temperature, the liquid/solid ratio was controlled at 3:1, and the leaching time was 30 minutes. The effect of leaching times on fluoride leaching was studied. The results are shown in Figure 1.



**Figure 2. Effect of liquid/solid ratio on fluoride leaching.**

### 3.2.3 Effect of Leaching Time on Leaching Effect of Fluoride

At room temperature, the leaching times was controlled at 2 times, and the liquid/solid ratio was 3:1. The effect of leaching time on the leaching effect of fluoride was studied. The results are shown in Figure 3.



**Figure 3. Effect of leaching time on fluoride leaching.**

Figure 3 shows that the leached fractions were 82.05 %, 82.71 % and 83.14 %, respectively, when the leaching time was 10 minutes, 15 minutes and 35 minutes. When the leaching time increased by 25 minutes, the fraction of leaching only increased by 1.09 %. The leaching reaction rate was fast and the leaching time had little effect on the leaching rate. Considering the stability of the leaching reaction and the disposal efficiency, the leaching time was 20–25 minutes.

### 3.3 Study on Desilication and Crystallization of Fluorine-Containing Leaching Solution

The H sample was subjected to 2 times of leaching at a liquid/solid ratio of 3:1 for 20 minutes to obtain the first leaching solution and the second leaching solution. The second leaching solution was used to react with the H sample according to the liquid/solid ratio of 3:1 for 20 minutes, and the first leaching solution was used as the research object for this part.

#### 3.3.1 Desilication Pretreatment of Fluorine-Containing Leaching Solution

According to the standard of “sodium fluoride”, the fluorine, silicon, carbonate and sulphate in the solution were analysed. The results are shown in Table 4.

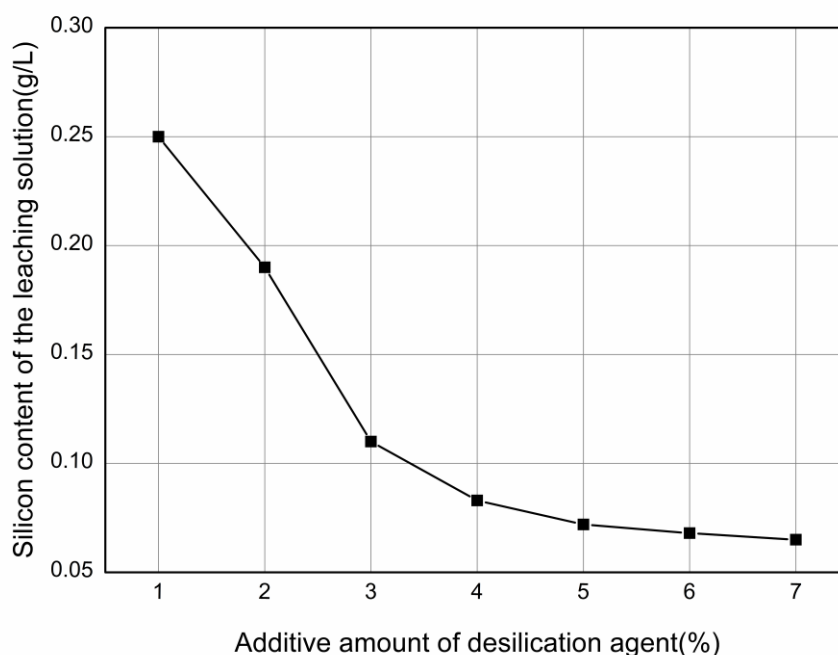
**Table 4. Ion content in leaching solution.**

Ion	Fluorine	Silicon	Carbonate	Sulphate
Ion content(g/L)	16.95	0.36	0.004	0.003

Table 4 showed that the fluoride ion in the leaching solution reached 16.95 g/L, which was close to the saturated concentration. The content of silicon ion was 0.36 g/L, and the content of carbonate and sulphate was very low. The first level standard of “sodium fluoride” requires that the content of sodium fluoride is more than 98 %, the content of silicon dioxide is less than 0.5 %. By calculation, the fluorine/silicon ratio should be above 190:1, but the test shows that the fluorine/silicon ratio was only 47:1, which was far lower than the theoretical value. It also showed that the content of silicon ion was too high, which negatively affects the quality of the product. Therefore, the leaching solution should be desiliconized.

A desilication agent was added to the leaching solution. The reaction was carried out at room temperature for 30 minutes. The amount of desilication agent was increased in steps: 1 %, 2 %, 3 %, 4 % and 5 % of the volume of the leaching solution. The content of silicon ions in the leaching solution after the reaction was determined. The results are shown in Figure 4.

Figure 4 shows that with the increase of the amount of desiliconizer, the silicon content in the solution decreased rapidly and then gradually stabilized. When the amount of desilication agent was 3 %, 4 %, 5 % and 6 %, the silicon content in the solution decreased to 0.11 g/L, 0.083 g/L, 0.072 g/L and 0.068 g/L, respectively. According to the fluorine content of 16.95 g/L in the leaching solution, the silicon content should be reduced to 0.089 g/L. Therefore, the amount of desiliconizer added was 4 % of the volume of the leaching solution.



**Figure 4. Effect of desilication agent addition on desilication.**

### 3.3.2 Study on Crystallization of Desilication Leaching Solution

The leaching solution after desilication was evaporated and crystallized. The index of crystal sodium fluoride was determined according to the standard of “sodium fluoride”. The results are shown in Table 5.

**Table 5. The index of crystal sodium fluoride.**

The index	NaF	SiO <sub>2</sub>	CO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	Insolubles in water
The standard (%)	98	0.5	0.37	0.3	0.7
Yield (%)	98.58	0.36	No detection	0.12	0.58

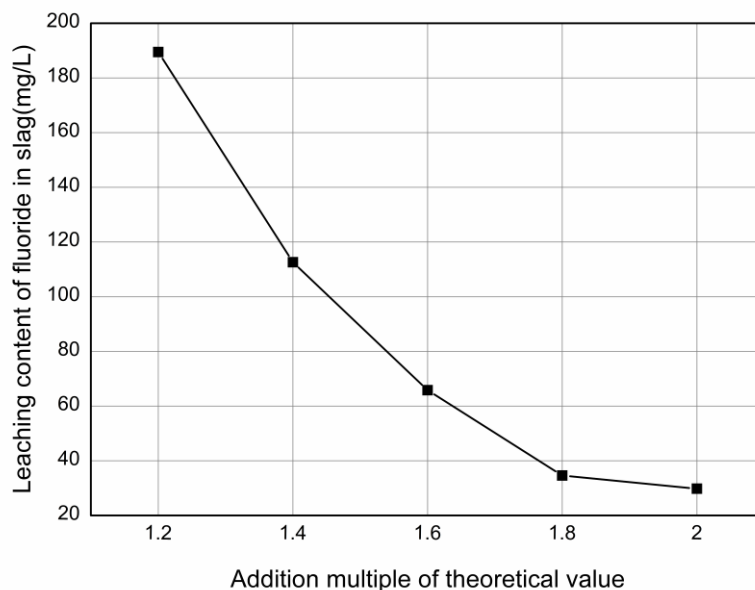
Table 5 shows that the crystal sodium fluoride product had a high purity and reached the first-level standard of “sodium fluoride”.

### 3.4 Study on Fluorine Dioxation of Filter Residue after Leaching of SPL

At room temperature, the H sample powder was dissolved 2 times according to the liquid/solid ratio of 3:1 for 20 min. The second leaching residue was the research object in this part. The fluoride leaching toxicity of the second leaching residue was 1072 mg/L.

#### 3.4.1 Effect of the Amount of Fluorine-Fixing Agent on Fluoride Fixation

At room temperature, the liquid/solid ratio was controlled at 3:1, and the reacting time was 30 minutes. The effect of the amount of fluorine-fixing agent was studied. The results are shown in Figure 5.



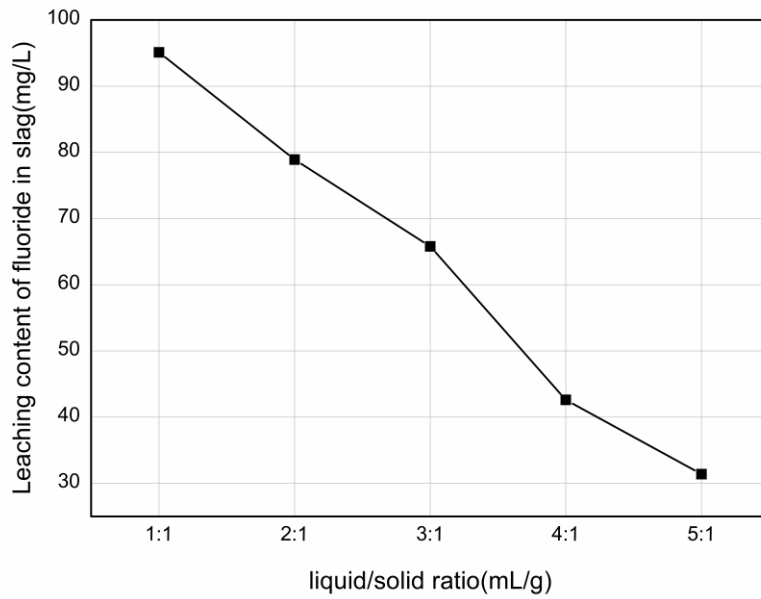
**Figure 5. The effect of the amount of fluorine-fixing agent on fluorine fixation.**

From Figure 5, it can be seen that with an increased addition of fluorine-fixing agent, the leaching content of fluoride in the filter residue gradually decreased. When the addition of fluorine-fixing agent was 1.4 times, 1.6 times and 1.8 times of the theoretical value, the leaching content of fluoride was 112.6 mg/L, 65.8 mg/L and 34.6 mg/L, respectively. According to the requirements of “Hazardous Waste Identification Standard Leaching Toxicity Identification”, the leaching content of fluoride must be reduced to below 100 mg/L. Therefore, requirement was met by adding an amount of fluorine-fixing agent of 1.6 times the theoretical value.

### 3.4.2 Effect of Liquid/Solid Ratio on Fluoride Fixation

At room temperature, the reacting time was controlled at 30 minutes, and the amount of fluorine-fixing agent added was 1.6 times of the theoretical value. The effect of liquid/solid ratio was studied. The results are shown in Figure 6.

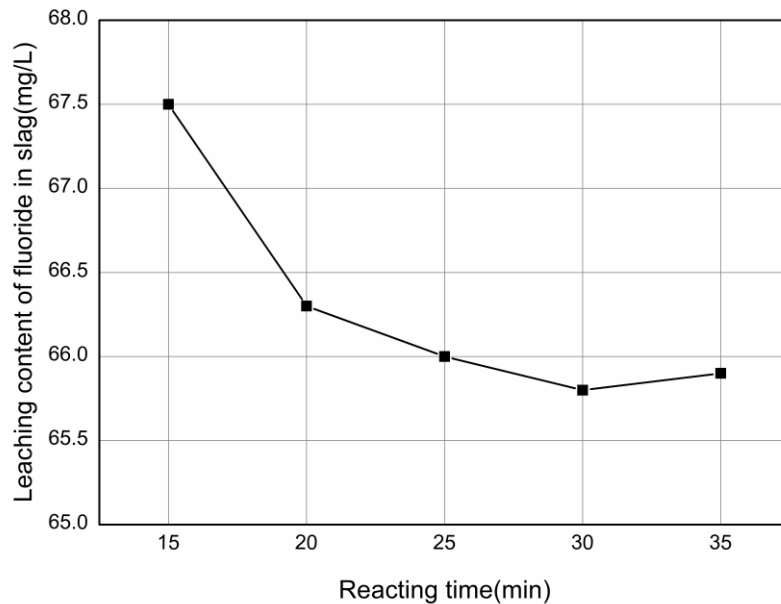
Figure 6 shows that with the increase of liquid-solid ratio, the leaching toxicity content of fluoride in the filter residue gradually decreased, which was related to the reaction of fluorine-fixing agent, and the increase of liquid volume had a certain leaching dilution effect on fluoride. According to the requirements, it was more appropriate to work with a liquid/solid ratio of 3:1.



**Figure 6. The effect of liquid/solid ratio on fluorine fixation.**

### 3.4.3 Effect of Reacting Time on Fluoride Fixation

At room temperature, the amount of fluorine-fixing agent added was controlled at 1.6 times of the theoretical value and the liquid/solid ratio was 3:1. The effect of reacting time was studied. The results are shown in Figure 7.



**Figure 7. Effect of reacting time on fluorine fixation.**

Figure 7 showed that with the increase of reaction time, the fluoride leaching toxicity content in the filter residue gradually decreased. The fluoride leaching contents with reaction for 15 minutes,

20 minutes, 25 minutes and 30 minutes were 67.5 mg/L, 66.3 mg/L, 66 mg/L and 65.8 mg/L, respectively. When the leaching time increased by 15 min, the fluoride leaching content only decreased by 1.7 mg/L. The fluorine fixation reaction rate was fast, and the leaching time had little effect on the fluorine fixation. Considering the stability of the fluorine fixation reaction and the disposal efficiency, the reaction time was 20–25 minutes.

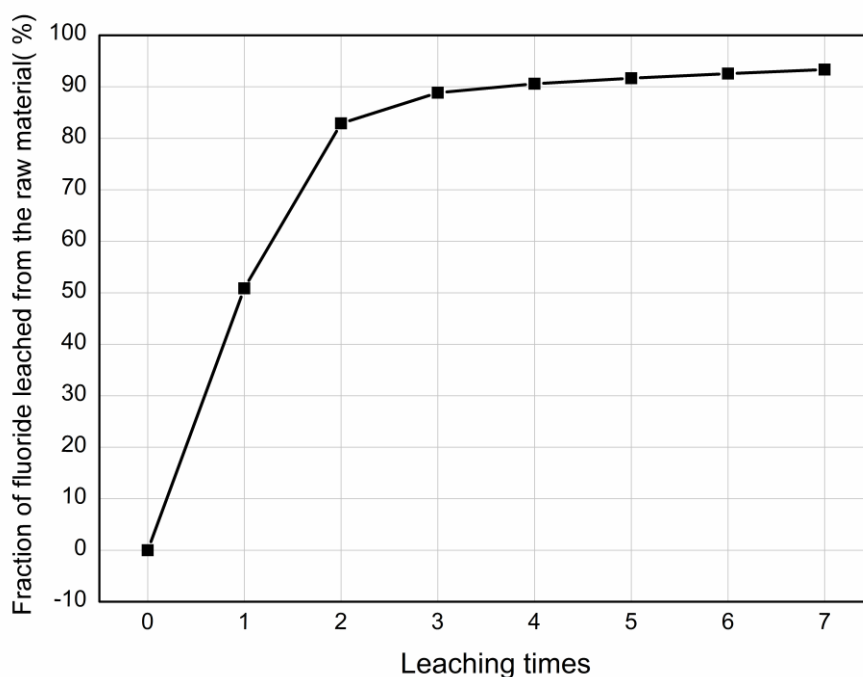
#### 4. Conclusions

From work presented in this paper, we can draw the following conclusions:

1. The fluoride in SPL was mainly in the form of sodium fluoride and cryolite. The soluble fluoride in SPL mainly exists in the form of sodium fluoride. The leaching potential of fluoride in different SPL samples varied greatly, ranging from 184 mg/L to 11563 mg/L, which was mainly related to the age of the electrolytic cell and the location.
2. The fluoride can be recovered by leaching, desilicization and crystallization. The leaching process reacted at room temperature, the leaching time was 2-3 times, the leaching liquid/solid ratio was 3:1, and the leaching time was 20-25 minutes.
3. The desilication with the volume percentage of about 4 % should be added in the desilicization process. The purity of the sodium fluoride products reached 98 %, which means it can be used in the electrolytic cell.
4. The small amounts of fluoride that cannot be leached can be solidified into calcium fluoride, in order to meet the requirements of the standard. In the solidification process, the liquid/solid ratio and reacting time was 3:1 and 20–25 minutes, respectively. The addition of fluorine-fixing agent was more than 1.6 times greater than the theoretical value.

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**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.