Ultrasonic enhanced water washing method for extracting sodium fluoride from spent pot lining

Yongrong Qi\textsuperscript{1a}, Yuan Gong\textsuperscript{1b}, Haibin Wang\textsuperscript{1c}, Li Peng\textsuperscript{1d}, Liting Fan\textsuperscript{1e}, and Chunlei Li\textsuperscript{1f}\textsuperscript{*}

\textsuperscript{1}College of Petroleum and Chemical Engineering, Lanzhou University of Technology, Lanzhou, 730050, China
\textsuperscript{1a}1372189234@qq.com, \textsuperscript{1b}yuangong@lut.edu.cn, \textsuperscript{1c}2745034360@qq.com, \textsuperscript{1d}2523486685@qq.com, \textsuperscript{1e}1768487222@qq.com, \textsuperscript{1f}licl@lut.edu.cn.

Abstract—A large amount of spent pot lining (SPL) is produced by cryolite-alumina melting electrolysis process, and the fluoride content in the leaching solution is up to 6000 mg/L, which belongs to hazardous waste. If SPL is not handled effectively, it will cause great harm to the environment. Because the NaF rich in SPL is an important raw material for the synthesis of cryolite by carbonation, this paper uses SPL as the raw material to extract NaF. On the basis of exploring the process conditions of water washing leaching NaF, ultrasonic wave was introduced to enhance mass transfer and the effects of ultrasonic cavitation on water washing process was compared. The results show that ultrasonic waves can effectively shorten the time for water washing to reach equilibrium and further improve the efficiency of NaF leaching. Under the optimal process conditions determined by the experiment, when the ultrasonic power is 400 W, the time for washing to reach equilibrium is shortened from 50 min to 40 min, and the NaF leaching efficiency is increased from 67.25\% to 70.42\%. While improving the leaching efficiency, the water consumption is effectively reduced, and the purity of the recovered product NaF is 96.82\%. This research provides a technical reference for the harmless and low cost leaching of NaF from SPL in the aluminium electrolysis industry.

1. Introduction

In the process of aluminum electrolysis, the cathode lining will be corroded by molten aluminum and fluoride, and the service life is generally 5 to 7 years. Spent pot lining (SPL) is one of the hazardous wastes generated at the end of the cathode lining (1). In addition to its composition containing 60\% to 70\% C, it also contains a certain amount of NaF, Na\textsubscript{3}AlF\textsubscript{6}, CaF\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. At present, the annual SPL emissions of the global aluminum electrolysis industry are as high as 600,000 tons (2). A large amount of its accumulation and disposal can cause serious harm to the environment. For example, after SPL encounters water, the fluorine content in its leaching solution is as high as 6000 mg/L, which is much higher than the upper limit specified in the "Identification Standard for Hazardous Waste-Identification of Extraction Toxicity" (GB 5080.3-2007). The limit value (100 mg/L), the penetration of fluoride into soil, rivers and groundwater will produce harmful hydrogen fluoride gas, which will endanger the health of animals and plants and the ecological balance (3). Therefore, the comprehensive utilization of SPL resources is a key issue facing the aluminum electrolysis industry.

At this stage, typical SPL treatment processes: one is fire treatment, the rotary kiln calcination technology developed by Aluminum Corporation of China (4). SPL is heat treated through a rotary kiln, and the soluble fluoride content in the solid slag is reduced to below 50 mg/L, and the waste slag
can be used as a cement raw material (5). However, the main equipment of this process consumes a lot of energy in the rotary kiln, and the reported energy recovery rate is about 50 % (6). The second is wet treatment, including acid and alkali leaching (7) and flotation (8, 9). The former reacts with the insoluble salts/oxides in the carbon block with excessive acid and alkali to convert them into soluble salts and leaching to recover high grade carbon and electrolytes. Compared with fire treatment, the technical energy consumption is low, but there are more waste liquids after leaching. The flotation process is simple, mainly using the difference between the hydrophobicity and wettability of the electrolyte and carbon to separate the carbon in the SPL from other components, and the waste water is recycled. In order to improve the separation efficiency, the grinding and flotation operation control requirements are strict, and the carbon powder after flotation and the fluoride obtained from the ore slurry need to be deeply removed before high value recycling can be achieved (10). Under relatively mild conditions, the carbonation method (11) uses NaF and NaAlO\textsubscript{2} as raw materials to synthesize Na\textsubscript{3}AlF\textsubscript{6}. The overall reaction equation is as follows: \[6\text{NaF} + \text{NaAlO}_2 + 2\text{CO}_2 = \text{Na}_3\text{AlF}_6 + 2\text{Na}_2\text{CO}_3.\] Using SPL as a raw material to prepare NaF not only reduces the harm of SPL, but also can use NaF as a raw material to prepare cryolite. Then cryolite is used as a flux in the aluminum electrolysis industry to realize the recycling of resources.

Jin Xiao (12) believes that ultrasonic waves have the characteristics of good directionality and long transmission distance in water. Because of their special effects, they have received extensive attention in hydrometallurgy. He uses ultrasonic assist and traditional alkaline leaching method to treat SPL to improve the leaching efficiency. Zhang (13) compared ultrasonic assisted leaching and conventional leaching to smelt germanium in the by product and found that the ultrasonic assisted leaching process has special advantages. Therefore, ultrasonic assisted leaching is an efficient and economical leaching method, which has been widely used in the leaching process.

In summary, this article first adopts the water washing method to explore the best process through single factor experiments. On this basis, ultrasonic waves are introduced to enhance mass transfer. Comparing the influence law of ultrasonic cavitation effect on the water washing process, the goal of shortening the leaching time and improving the leaching efficiency is finally achieved. In this paper, SPL is used as the raw material to discuss the feasibility of ultrasonic enhanced water washing for leaching NaF.

2. Experimental part

2.1. SPL sample preparation

SPL comes from an electrolytic aluminium plant in Gansu Province, and its X-ray diffraction analysis results are shown in Fig.1. The main components are C and NaF, and contain Na\textsubscript{3}AlF\textsubscript{6}, CaF\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. The relative composition is determined by semi quantitative analysis, as shown in Tab.1. The raw materials are crushed by a jaw crusher (PE 100×60, Shao Xing yin he Machinery Co., Ltd.), and then further crushed and refined by a high speed universal crusher (FW-135, Beijing Guang Ming Medical Instrument Co., Ltd.). The obtained particles are sieved into five groups (180~125 μm, 125~98 μm, 98~75 μm, 75~63 μm and <63 μm) by an electric vibrating sieve (8411 type, Shang Yu Geotechnical Instrument Factory, Shao Xing City), and placed in a constant temperature drying oven (101 -1 type, Shanghai Dong Xing Building Materials Testing Equipment Co., Ltd.) after drying at 105 ± 1 °C, bag it for later use.

| Composition (content (%)) | C      | NaF    | Na\textsubscript{3}AlF\textsubscript{6} | CaF\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | Others |
|--------------------------|--------|--------|--------------------------------------|----------------------|--------------------------------------|--------|
|                          | 69.28  | 28.09  | 1.29                                 | 0.65                 | 0.51                                 | 0.18   |
2.2. NaF leaching from SPL by washing method

Place 20 g of the prepared SPL sample in a 250 mL three necked flask, and conduct single factor washing test with particle size, time, temperature, and liquid to solid ratio as variables. Experimental conditions are shown in Tab.2 is provided. In the whole experiment process, a magnetic stirrer was used to fully stir to ensure that the sample was in full contact with deionized water, and the temperature of the system was controlled by a constant temperature water bath system. The suspension after washing and leaching is filtered through a glass sand core funnel (G 4, Changchun Glass Instrument Factory) to obtain a filter cake and a clear filtrate. The filter cake was dried in an oven at 105 ± 1 °C and then weighed. The filtrate was dried by taking one tenth of the filtrate and weighed to calculate the mass of NaF in the filtrate. The total mass of NaF is converted from the content of NaF in SPL. The leaching efficiency of NaF is calculated by the following formula:

$$\eta = \frac{m_1}{m_2} \times 100\%$$

Where: \(\eta\) is the leaching efficiency of NaF, %.  
\(m_1\) is the mass of NaF in the filtrate, g.  
\(m_2\) is the total mass of NaF in SPL, g.

| no | particle size range (μm) | time (min) | temperature (°C) | liquid solid ratio (mL/g) |
|----|-------------------------|------------|------------------|--------------------------|
| 1  | 180～125                | 60         | 30               | 10:1                     |
| 2  | 125～98                 | 60         | 30               | 10:1                     |
| 3  | 98～75                  | 60         | 30               | 10:1                     |
| 4  | 75～63                  | 60         | 30               | 10:1                     |
| 5  | <63                    | 60         | 30               | 10:1                     |
| 6  | 75～63                  | 10         | 30               | 10:1                     |
| 7  | 75～63                  | 20         | 30               | 10:1                     |
| 8  | 75～63                  | 30         | 30               | 10:1                     |
| 9  | 75～63                  | 40         | 30               | 10:1                     |
| 10 | 75～63                  | 50         | 30               | 10:1                     |
2.3. Extraction of NaF from SPL by ultrasonic enhanced washing method
Under the optimal water washing process conditions, the enhancement of the ultrasonic cavitation effect on the NaF leaching process was explored, and the experimental variables were set as ultrasonic time and ultrasonic power. The specific process conditions are shown in Tab.3.

Tab.3 SPL ultrasonic enhanced water washing test conditions

| No | particle size range (μm) | time (min) | temperature (℃) | liquid solid ratio (mL/g) | ultrasonic power (W) |
|----|-------------------------|------------|-----------------|--------------------------|---------------------|
| 1* | 75~63                   | 10         | 80              | 10:1                     | 480                 |
| 2* | 75~63                   | 20         | 80              | 10:1                     | 480                 |
| 3* | 75~63                   | 30         | 80              | 10:1                     | 480                 |
| 4* | 75~63                   | 40         | 80              | 10:1                     | 480                 |
| 5* | 75~63                   | 50         | 80              | 10:1                     | 480                 |
| 6* | 75~63                   | 60         | 80              | 10:1                     | 480                 |
| 7* | 75~63                   | 40         | 80              | 10:1                     | 80                  |
| 8* | 75~63                   | 40         | 80              | 10:1                     | 160                 |
| 9* | 75~63                   | 40         | 80              | 10:1                     | 240                 |
| 10*| 75~63                   | 40         | 80              | 10:1                     | 320                 |
| 11*| 75~63                   | 40         | 80              | 10:1                     | 400                 |
| 12*| 75~63                   | 40         | 80              | 10:1                     | 480                 |

3. Results and Discussions
3.1. Determination of the best washing process conditions
Fig.2 explores the variation trend of the leaching efficiency of NaF in SPL with condition variables. It can be seen from Fig.2 (a) that when the particle size is 180~125 μm, the leaching efficiency of NaF is 40.63 %, and when the particle size is reduced to 75~63 μm, the leaching efficiency can reach to 64.49 %. Within the experimentally set particle size range, the leaching efficiency of NaF first increases rapidly with the decrease of particle size and then tends to level off. Therefore, the particle size range of 75~63 μm is selected as the optimal particle size for the leaching process. Because the smaller the particle size, the greater the total specific surface area, and the greater the contact area with water, so the higher the leaching efficiency. Due to the high hardness of SPL, it is difficult to grind. When the particle size is reduced to 63 μm, grinding is not continued to reduce the particle size.
As shown in Fig. 2 (b), as time goes by, the leaching efficiency of NaF gradually increases from 57.69 % at 10 min to 62.71 % at 50 min. Leaching time was prolonged to 60 min, NaF leaching efficiency increase of only 0.08 %. This means that under this condition, the leaching efficiency of NaF in SPL reaches the maximum. It is difficult to increase the leaching efficiency by continuing to extend the reaction time. Therefore, this study chose 50 min as the best washing time.

As shown in Fig. 2 (c), when the temperature is 30 °C, the leaching efficiency of NaF is 62.71 %. As the reaction temperature increases, the leaching efficiency gradually increases. When the reaction temperature is 80 °C, the leaching efficiency reaches 67.25 %. As the leaching temperature rises to 95 °C, the leaching efficiency of NaF increases to 68.16 %. During the leaching process, the leaching efficiency of NaF is higher, because NaF is easily soluble in water, and the solubility increases with temperature (14). Therefore, increasing the temperature is conducive to the dissolution of NaF. Considering the high temperature will cause evaporative water loss, so the choice of the optimum temperature of 80 °C.

As shown in Fig. 2 (d), when the liquid to solid ratio is 5:1 mL/g, the leaching efficiency of NaF is 55.53 %. As the liquid to solid ratio increases, the leaching efficiency gradually increases. When the liquid to solid ratio is 10:1 mL/g, the leaching efficiency reaches 67.25 %, and then increasing the liquid to solid ratio has little effect on the leaching efficiency. When the liquid to solid ratio is greater than 10:1 mL/g, the influence of the solvent on the dissolution efficiency of NaF gradually decreases, and the leaching efficiency remains basically unchanged. Therefore, the best liquid solid ratio is selected as the liquid solid ratio of 10:1 mL/g.

In summary, the optimal process conditions for leaching NaF in SPL by water washing method are 75-63 μm in particle size, washing time 50 min, washing temperature 80 °C, and liquid solid ratio 10:1 mL/g. At the same time, the leaching efficiency is 67.25 %.
3.2. *The effect of ultrasonic cavitation on the leaching efficiency of NaF*

Fig. 3 discusses the relationship between the leaching efficiency of NaF in SPL under ultrasonic enhancement and the ultrasonic time and ultrasonic power. It can be seen from 3(a) that when the ultrasonic time is extended from 10 min to 40 min, the leaching efficiency increases from 63.54 % to 70.48 %. Further extension of the ultrasonic time has little effect on the extraction efficiency. At 60 min, the extraction efficiency only increased by 0.08 %. Therefore, 40 min is selected as the best ultrasound time. From the leaching results shown in Fig. 2 (b) and Fig. 3 (a), the leaching time under ultrasonic strengthening is significantly shortened, and the leaching efficiency is significantly increased. This is because under the action of ultrasound, there is a perturbation effect (12), which is a kind of fluctuation caused by the action of ultrasound on solid particles. The weak disturbance in the microspores increases the dissolution rate of NaF in the microspores, which is difficult to achieve by mechanical stirring. During the leaching process, due to the synergistic effect of cavitation and perturbation effects, the NaF and C in the SPL are separated faster and more thoroughly, so that the leaching efficiency is improved.

Fig.3 The relationship between the leaching efficiency of NaF in SPL and (a) ultrasonic time and (b) ultrasonic power

As shown in Fig. 3 (b), at 80 W, the leaching efficiency is 59.98 %, and when the ultrasonic power is increased to 240 W, the leaching efficiency increases to 62.82 %. At this time, the leaching efficiency is lower than that obtained by the optimal water washing process. This is because there is no mechanical stirring in the ultrasonic process, and because the ultrasonic power is low, it cannot produce enough cavitation effect to affect the dissolution of NaF in SPL (15). When the ultrasonic power was 240 W~400 W, the cavitation effect began to effectively affect the dissolution of NaF in SPL with the increase of ultrasonic power, and the leaching efficiency increased sharply. Higher ultrasonic power was helpful to improve the take efficiency. The ultrasonic power has a turning point at 400 W. Under the existing experimental conditions, when the power is greater than 400 W, the leaching efficiency does not change much. Therefore, 400 W is selected as the best ultrasonic power.
The NaF obtained in the experiment was subjected to XRD analysis. It can be seen from Fig.4 that both the water washing method and the ultrasonic enhanced water washing method have only the characteristic peak of NaF, and the half-value width is extremely narrow. It shows that the obtained are all high purity NaF, and the crystallization is intact, and the impurity content is small. XRD semi quantitative analysis shows that it can reach more than 95 %. Comparing the two characteristic peaks of NaF obtained in the process, it can be seen that the peak intensity of the latter is obviously stronger than that of the former, and it can be seen that the NaF obtained by the ultrasonic enhanced water washing method is better.

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) The best process parameters obtained through the water washing experiment are: particle size 75~63 μm, time 50 min, temperature 80 ℃, liquid-solid ratio 10:1 mL/g. The best process parameters obtained by the ultrasonic enhanced washing method are: ultrasonic time 40 min, ultrasonic power 400 W. The final NaF leaching efficiency is 70.42 %.

(2) This article introduces ultrasound on the basis of water washing experiment, and studies the influence of ultrasound time and ultrasound power on the leaching efficiency. It can be seen from the experimental results that ultrasound can not only shorten the leaching time of NaF in SPL, but also improve the leaching efficiency of NaF. It provides new ideas for the resource utilization of SPL.

(3) The next step will be based on the study of NaF leaching in SPL, for the aluminum ash produced in the process of aluminum electrolysis, NaAlO$_2$ will be prepared by aluminum ash alkali sintering, and Na$_3$AlF$_6$ will be synthesized by carbonization, in order to achieve the best utilization of its resources.

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