Study on harmless and resource utilization of spent cathode carbon washing process

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Abstract. Spent cathode carbon is the main hazardous waste in the electrolytic aluminum industry, which seriously pollutes the environment. In this paper, the spent cathode carbon is treated by the water washing process to change it from hazardous waste to solid waste, so that the environment is protected and NaF is also utilized. The optimum conditions were determined by experiment: t=50 min, T=80°C, L/S = 20:1. The raw materials and the washed products were characterized by elemental analysis, X-ray fluorescence (XRF), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

1. Introduction
At present, alumina is mainly derived from the aluminum electrolysis industry [1], and a large number of solid hazardous wastes will occur each year along with the production of a large amount of alumina, the main one being the spent cathode carbon [2]. The spent cathode carbon is mainly caused by the infiltration of impurities such as NaF into the aluminum electrolytic cell, and the liquid in the groove leaks from the crack, causing the production to be stopped [3], so the cathode of the aluminum electrolysis plant will be replaced within 5~8a. [4]. Fluoride and cyanide in spent cathode carbons will cause great pollution to the environment with rainwater infiltration into the soil. Spent cathode carbons are also listed as hazardous wastes, so the disposal of spent cathode carbon has become an urgent problem for electrolytic aluminum plants [5-8].

Due to the toxicity of spent cathode carbons and the large amount of available resources [9, 10], the harmlessness and recycling of spent cathode carbon is important. The process of harmless treatment is mainly high-temperature combustion method, which achieves the purpose, but it causes a serious waste of available resources [11-13]. There are two kinds of resource processing: flotation method and chemical method. Because the surface of the spent cathode carbon adsorbs or embeds a nano or micron-sized electrolyte [14], the purity of the product obtained by flotation is too low to meet the recycling standards [15]. The chemical method usually obtains carbon powder and cryolite by acid-base treatment [16], then obtains SiC [17] or obtains AlF₃ by chemical treatment [18-20], but can not make full use of the available resources in the spent cathode carbon.

At present, the treatment of spent cathode carbons is rare. In this experiment, the steps of eluting salt by water are explored through the study of the composition of spent cathode carbons. The recovered NaF can also be reused. The cathode is changed from hazardous waste to solid waste, which has great significance for environmental protection and resource utilization.
2. Experimental

2.1. Material
The raw material are from Gansu Dongxing Aluminum Co., Ltd., and the raw material are analyzed by elemental analysis, XRF, XRD and SEM are shown in Table 1 and Figure 1, 2. The main substances are C, NaF, SiO₂, CaF₂ and Al₂O₃ combined with XRF and XRD. It was found by SEM that the surface of C was surrounded by a layer of disordered sheet-like material. According to the process of the electrolytic aluminum plant, the substance was NaF, and the content by XRD analysis was 43.81%.

| Element | F | Na | Fe | Al | Si | Ca | C | Others |
|---------|---|----|----|----|----|----|---|--------|
| Content/% | 12.16 | 36.01 | 0.81 | 1.76 | 2.01 | 10.60 | 33.62 | 3.03 |

![Figure 1. XRD analysis of spent cathode carbon.](image1)

![Figure 2. SEM picture of spent cathode carbon.](image2)

2.2. Experimental procedures
From the above analysis, it can be seen that the surface of the spent cathode carbon is coated with NaF. Stacking spent cathode carbon in the open air will cause great pollution to the environment. According to the characteristic that NaF is soluble in water, the water-eluting salt is used to be harmless. The spent cathode carbon after washing is tested for Leachate F⁻ according to GB/T 15555.11-1995.

2.2.1. Time single factor experiment. Weigh 10g of spent cathode carbon in a three-necked flask, set the temperature to 80 °C, add 250g of deionized water at a liquid-solid ratio of 25:1, and conduct experiments under 10min, 30min, 50min, 70min, 90min respectively. The results are shown in Figure 3.
2.2.2. Temperature single factor experiment. Weigh 10g of spent cathode carbon in a three-necked flask, set the time to 50min, add 250g of deionized water at a liquid-solid ratio of 25:1, and conduct experiments under 40°C, 50°C, 60°C, 70°C, 80°C respectively. The results are shown in Figure 4.

![Figure 3](image1.png)  ![Figure 4](image2.png)

**Figure 3.** Effect of 10,30,50,70,90min on desalination rate.  **Figure 4.** Effect of 40,50,60,70,80°C on desalination rate.

2.2.3. Liquid-solid ratio single factor experiment. Weigh 10g of spent cathode carbon was taken in a three-necked flask, the set time was 50 min, and the temperature was set to 80 °C, and experiments were carried out at liquid to solid ratios of 5:1, 10:1, 15:1, 20:1, and 25:1 respectively. The results are shown in Figure 5.

2.2.4. Desalination rate calculation method. The desalination rate calculation equation is as follows:

\[ \eta = \frac{m_1}{m_2} \]

In the equation: η is the desalination rate of the spent cathode carbon, m_1 is the mass of the salt removed, m_2 is the total salt mass in the spent cathode carbon the content by XRD analysis was 43.81%.

2.3. Characterization of spent cathode carbon
Characterization used in the experiments: elemental analysis is Flash 2000, Thermo Fisher Scientific, XRF is Magix PW2403, PANalytical, XRD is D/max-2004, Rigakn, SEM is JSM-6701F.

3. Results and discussion
3.1. Effect of various parameters on desalination rate

3.1.1. Effect of time on desalination rate. As can be seen from Figure 3 the desalination rate has been increasing with time. When the time reached 50 min, the desalination rate reached 74.06%. Then it tends to be gentle, 90min is 74.09%. This is because the time is too short, the soluble salt in the spent cathode carbon has not completely dissolved. When the time reached 50 min, the soluble salt was substantially dissolved, the desalination rate tended to be gentle, so selection time was 50 min.

3.1.2. Effect of temperature on desalination rate. As can be seen from Figure 4 the desalination rate increased with increasing temperature and reached 74.08% when it reached 80 °C. This is because the soluble salt is mainly NaF, and its solubility rises with increasing temperature. Considering the economic problems of industrial production, the temperature is selected to be 80 °C.
3.1.3. Effect of liquid-solid ratio on desalination rate. As can be seen from Figure 5 the desalination rate first increases with the increase of the liquid-solid ratio until it is gentle at 20:1 is 74.01%, because when the liquid-solid ratio is too small, the soluble salt in the spent cathode carbon can not be completely dissolved, with the solvent increases, the salt rejection rate increases. When the amount of water is much larger than the amount of soluble salt, the desalination rate is basically unchanged, so the liquid-solid ratio is selected to be 20:1.

![Figure 5](image1.png)

**Figure 5.** The effect of liquid to solid ratio of 5:1, 10:1, 15:1, 20:1, 25:1 on desalination rate.

3.1.4. Salt analysis. The obtained salt solution was placed on a hot plate to be evaporated until crystallization occurred, then placed in an oven to be dried for XRD detection. It can be seen from Figure 6 that the obtained salt is NaF with higher purity, it can be concluded that the NaF in the spent cathode carbon is removed by the water washing process, the purity of the NaF is 96.32% by XRD analysis, which has satisfied the aluminum electrolysis industry reuse standards.

![Figure 6](image2.png)

**Figure 6.** XRD analysis of salt.

3.2. Spent cathode carbon harmless treatment
The spent cathode carbon is classified as hazardous waste because the F- content is seriously exceeded. The desalting process is mainly removed into NaF, therefore, this process can also be used as a process of harmless treatment. According to GB/T 15555.11-1995, the F- in the spent cathode carbon eluate was tested, and the standard curve was as shown in Figure 7. The linear regression equation was: E=284.424-57.554logCF, R=0.9995.

![Figure 7](image3.png)

**Figure 7.** E(mv)-logCF (mg/L) standard curve.

![Figure 8](image4.png)

**Figure 8.** Soluble F in solids after multiple washings.

Multiple washing experiments under the optimum conditions, and the results are shown in Figure 8. It can be seen that the F- concentration of the spent cathode carbon which was not washed with water...
was 18375.48 mg/L, the F concentration was 93.48 mg/L after 4 times of water washing. According to GB/T 5085.3-2007, it is known that less than 100mg/L is solid waste, so the spent cathode carbon after 4 times of washing is solid waste. This method can treat hazardous waste as solid waste, and the washed salt can be reused, not only protects the environment, but also realizes resource utilization.

Characterization of spent cathode carbon after washing
The XRD and SEM of the spent cathode carbon after water washing are shown in Figures 9, 10. By comparing the XRD patterns before and after washing, it can be seen that NaF is removed during the water washing process. It can be seen from the SEM that the water-washing can basically wash off the surface-coated layer of the sheet-like substance, but there is still a small amount of impurities on the surface of the washed material. These are water insoluble substances that require further processing.

![Figure 9. Spent cathode carbon XRD after washing.](image)

![Figure 10. Spent cathode carbon SEM after washing.](image)

4. Conclusions
This article examines the spent cathode carbon from hazardous waste to solid waste, and the NaF recycling.

The optimal conditions for the experiment were determined by studying experimental factors, t=50min, T=80°C, L/S=20:1, the spent cathode carbon was measured after 4 times of water washing according to GB/T 15555.11-1995 dissolved F content, after the fourth water washing, it below the 100mg/L required by the national standard. This provides an idea for the recovery of a large amount of NaF in the spent cathode carbon, and lays a foundation for the reuse of the spent cathode carbon.

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