Soda-lime Sintering Process for Aluminium Electrolytic Carbon Dross

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Abstract

This paper discusses an experimental study of the sintering process of aluminium electrolytic carbon dross. In the first step, after flotation of carbon dross, a certain proportion of carbon dust is introduced into the sintering slurry, Then, in the rotary kiln sintering, the carbon burns and gives heat. At the same time, the alkali metal reacts with the fluorine and gives calcium fluoride, which enters the Leached washed sinter and is solidified in the subsequent process. The experimental results show that when 2 % of flotated carbon slag is added to raw materials in the sintering process, the fluoride content in flue gas during sintering process is 0.53 mg/Nm3, the leaching toxicity of fluorine in leached washed sinter after the sinter dissolution is less than 67.78 mg/L, and the dissolution rate of alumina and sodium oxide in the sinter does not decrease.

Keywords: Sintering process, Hazardous waste treatment, Aluminium electrolytic carbon dross, Harmless, Recycling.

1. Introduction

Carbon dross is a solid waste produced by shedding anode surface and entering electrolyte during electrolytic aluminum production. On November 15, 2020, it was included in the National Hazardous Waste List (2021 edition) issued by the Ministry of Ecology and Environmental Protection of China.

The main components of carbon slag are electrolyte and carbon, in which carbon accounts for 20 - 42 %, electrolyte fluoride accounts for 58 - 80 %, carbon slag has the dangerous characteristics of leaching toxicity (fluoride), carbon sludge is the product of the flotation of carbon slag to remove fluoride salt, also has leaching toxicity.

If the valuable element sodium can be extracted from carbon mud and the combustion heat energy of carbon in it is sufficient, the hazardous waste can be reused, harmless and reduced. In recent years, Chalco Zhengzhou Non-ferrous Metal Research Institute has carried out the experimental study on the co-treatment of carbon sludge in the sintering process for alumina production by alkali and lime sintering and achieved satisfactory results.

Schematic diagram of experimental process is shown in Figure 1.

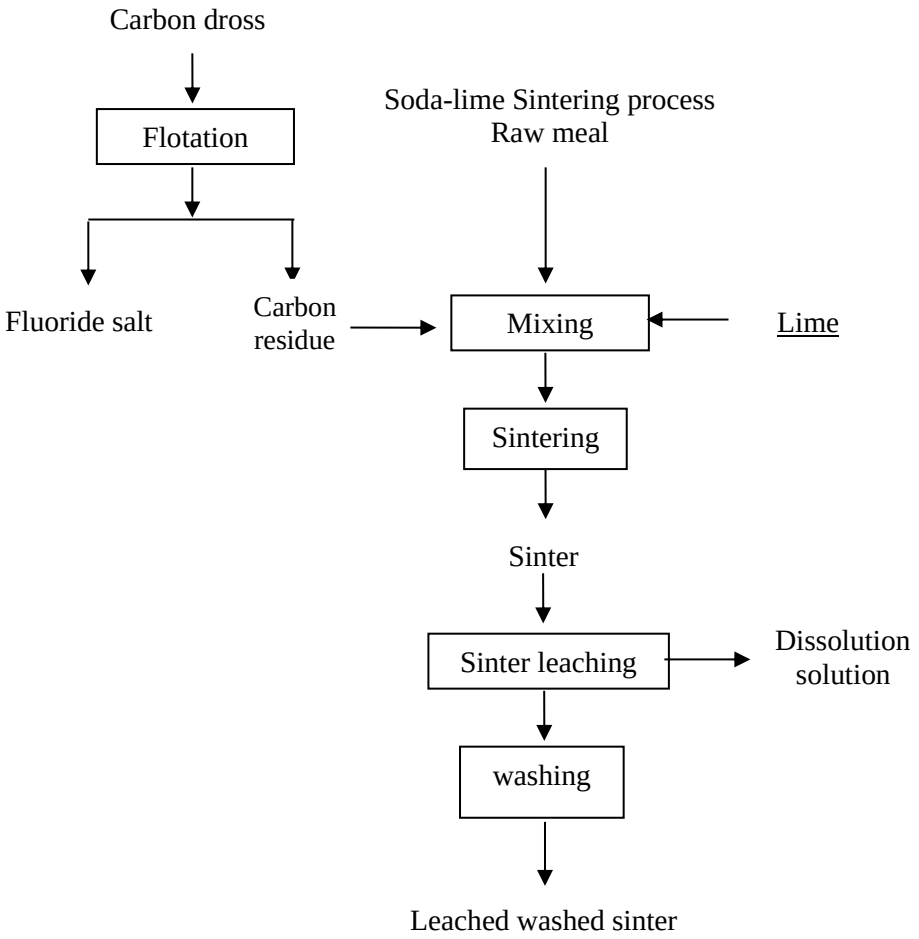


Figure 1. Schematic diagram of experimental process.

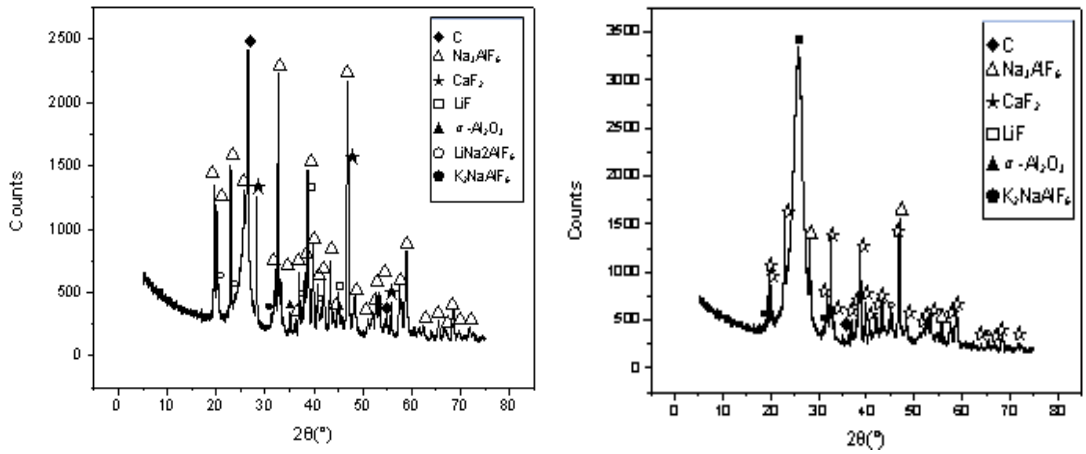
2. Physicochemical Properties of Carbon Slag and Carbon Sludge

2.1 Chemical Composition and Phase Composition

The chemical compositions of Carbon dross and Carbon residue are shown in Table 1.

Table 1. Chemical composition of carbon slag (%)

The sample	Al	O	Si	Mg	Na	K	Ca	Fe	C	S	F
Carbon dross	11.75	3.87	0.48	0.48	19.58	2.53	0.25	0.017	23.02	0.42	37.22
Carbon residue	3.97	5.46	0.68	0.27	7.62	0.53	1.02	0.14	60.81	1.50	17.26



Carbon dross Carbon residue

Figure 2. XRD patterns of Carbon dross and Carbon residue

The main toxic element of carbon dross is F, and Na_3AlF_6, K_2NaAlF_6, Li_2NaAlF_6 and LiF and CaF_2 minerals exist respectively, and the content of fluorine minerals is high. The carbon residue is produced by the flotation of carbon dross, in which the toxic element is also F. Na_3AlF_6, K_2NaAlF_6 and LiF and CaF_2 minerals exist respectively. Compared with the carbon dross, the content of fluorine minerals is decreased, while the carbon content is increased.

2.2 Leaching Toxicity of Carbon Dross and Carbon Residue

The leaching toxicity analysis was carried out according to the solid waste leaching toxicity leaching method (GB 50861-1997), and the leaching was detected by the lightning magnetic PXSJ-216 ion selective electrode. Solid phase fluorine content was determined by distillation - thorium nitrate titration volumetric method.

The results of leaching toxicity of carbon residue and charcoal sludge are shown in Table 2.

Table 2. Leaching toxicity test results

The sample	The test items	
	Inorganic fluoride mg/L	Cyanide mg/L
Carbon dross	365.2	0.01
Carbon residue	426.5	0.009

The leaching toxicity of F in both of them exceeded the limit of 100mg/L.

3. Addition of Lime to Fix Fluorine and its Mechanism

3.1 Addition of Lime to Fix Fluoride

Carboniferous and lime were used as ingredients, and the addition of lime (calculated by CaO) was 18.42% and 34.08%, respectively. The sintering temperature was 1250℃, Time at the sintering temperature is 0.5 hours. The results are shown in Table 3.

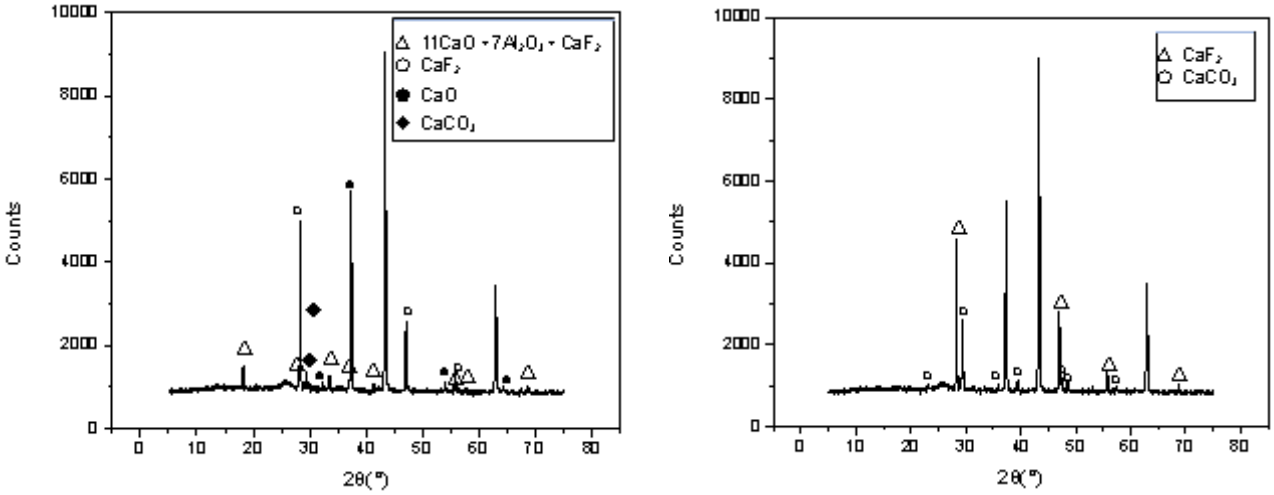
Table 3. Carbon residue ingredients and sinter dissolution solution

Ingredients (g)		**Dissolution solution (mg/ L)**		
Carbon residue	Lime	F^-	Cl^-	SO_4^{2-}
100	18.42	1460	270	1680
100	34.08	263	150	1488

As can be seen from Table 3, with the increase of lime content, F entering the dissolving (leaching) liquid decreases when the sinter is dissolved, indicating that lime has the effect of fixing fluorine.

3.2 Mechanism of Fluoride Fixation by Lime

The XRD patterns of raw material, sinter and leached washed sinter mixed with charcoal and lime are shown in Figure 3.



Sinter Leached washed sinter

Figure 3. Solid phase XRD pattern of carbon residue

Na_3AlF_6, CaF_2 and LiF are contained in the raw material of charcoal sludge, and the fluoride in sinter is CaF_2 and $11CaO•7Al_2O_3•CaF_2$, and the fluoride in Leached washed sinter is CaF_2. 11CaO•7Al2O3•CaF2 may be dissolved when the sinter is dissolved.

4. Main Test Results of Blending Charcoal Mud in Raw Materials of Sintering Process

The sintering method was used to add carbon residue at 2% or 3% of the raw material amount, and lime at a certain proportion of the carbon residue amount was added. The collaborative treatment was carried out according to the process flow in Figure 1, where the sintering temperature of sinter was 1250℃.

4.1 Determination of Sintering Flue Gas of Sinter

The flue gas produced in the sintering process is completely absorbed by the absorption bottle containing sodium hydroxide aqueous solution (concentration :1 mol/L), and then the Content of

F ion in the flue gas is determined by IC Flex930 ion chromatography of Swisscom, and then the content of F in the flue gas is calculated. The results are shown in Table 4.

Table 4. Measurement results of flue gas F emission

Ingredients	F, mg/Nm^3
Raw meal+2% Carbon residue	0.53
Raw meal+3% Carbon residue	1.34

It can be seen from Table 4 that F in flue gas increases with the addition of carbon sludge, and F in flue gas is 1.34 mg/Nm3 when the addition is 3%. Meet China's national industrial furnace air pollutant emission standard (GB4912-85).

4.2 Sinter Dissolution

The determination results of sinter dissolution rate and dissolution liquid by ion chromatography are shown in Table 5.

Table 5. Results of sinter dissolution

Ingredients	Dissolution rate (%)		Dissolution solution (mg/ L)		
	η_A	η_N	F^-	Cl^-	CN^-
Raw meal	94.18	97.41	7.2	8.9	0.005
Raw meal+2% Carbon residue	93.65	97.25	18.0	46.0	0.078

It can be seen from the results in Table 5 that the dissolution rates of alumina and sodium oxide in the sinter with the addition of 2% carbon residue did not change significantly compared with that of the sinter without adding carbon residue, indicating that the dissolution rates of alumina and sodium oxide in the charcoal sinter also reached those of ordinary raw material. At the same time, the content of F in the dissolution solution is low.

4.3 Leaching Toxicity of Leached Washed Sinter

The leaching toxicity of leached washed sinter was determined by the same method as that of carbon slag and carbon mud, and the results were shown in Table 6.

Table 6. Leaching toxicity test results of Leached washed sinter

Ingredients	Inorganic fluoride mg/L	Cyanide mg/L
Raw meal+2% Carbon residue	67.78	0.005

As can be seen from Table 6, the leaching toxicity of leached washed sinter F produced by adding 2% of raw material to carbon mud ingredients is 67.78 mg/L, which meets the limit value of China's national solid waste toxicity identification standard (GB5085.3-2007) ≤100 mg/L.

5. Conclusion

It is feasible to treat electrolytic aluminium waste sludge by alkali - lime sintering Resource, harmless and reduction, to achieve emission standards and efficient recycling and utilization of valuable elements.

Adding a certain proportion of lime to carbon residue can make F in fluoride salt transform into CaF_2 during sintering process, which has a good fluorine fixation effect.

Under the condition of adding 2% carbon residue to the raw material of the sintering process, both the flue gas discharged from the sintering process and the leached washed sinter discharged from the sinter dissolution meet the limit requirements of China's national standards, and more than 97% of the Na in the carbon residue can be recovered.