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Research on the Co-processing of Mixed Electrolytic Aluminum Waste in Circulating Fluidized Bed Boiler

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ABSTRACT

In this study, a mixed combustion system in a fixed bed is proposed to deal with electrolytic aluminum waste. The feasibility of the laboratory-scale fixed bed burner system is verified. The effect of different mixing proportions, temperatures (i.e. 900, 980 and 1050 °C) and the addition of limestone on the products of combustion and pollutant emission is investigated through SEM and XRD analysis. The results show that the combustion process and the physical characteristics of the product are exhibited by mixing with 7:3 (coal: waste) ratio at 900 °C. Adding limestone meets the requirements of using circulating fluidized bed boilers for mixed burning of electrolytic aluminum waste. This study provides a theoretical basis for commercialization.

Keywords: co-combustion, mixing ratio, flue gas analysis, solid waste treatment

1. INTRODUCTION

Aluminum is the second largest metal after iron. China is the largest producer of primary aluminum, with a production capacity of 410,000 tons and an output of 320,000 tons in 2016[1]. Electrolytic aluminum waste is a collective term for the waste generated during the electrolytic aluminum production process, including waste cathode carbon block, waste anode material. Generally, electrolytic aluminum production enterprises will overhaul the electrolytic cell every five years, with a large amount of waste generated in this process. Electrolytic aluminum scrap mainly contains NaF, Na_3AlF_6, CaF_2, SiO_2, Al_2O_3 and a small amount of complex fluoride, and NaF and Na_3AlF_6 account for the majority of the electrolyte quality[2].

In 1988, the U.S. Environmental Protection Agency issued a decree to classify electrolytic aluminum waste tank linings as hazardous waste. In 1996, the direct landfill or open storage of waste tank linings was explicitly prohibited, requiring all electrolytic aluminum plants in service to properly dispose of them. Since the F^- content in the waste tank lining and waste electrodes produced by the electrolytic aluminum industry is as high as 2000 mg/L and CN^- is about 15 mg/L, the National Development and Reform Commission of China stipulated in the "Law of the People's Republic of China on the Prevention and Control of Environmental Pollution by Solid Waste" in 2008. These wastes were listed in the "National Hazardous Waste List"[3] on August 1, 2008, Electrolytic aluminum scrap is a kind of toxic solid waste, any electrolytic aluminum manufacturing enterprise is not allowed to discard. Therefore, studying the co-combustion mechanism of electrolytic aluminum electrode waste and coal powder is of great significance for further research on the green and harmless treatment of electrolytic aluminum waste.

According to previous studies on the treatment of electrolytic aluminum waste at domestic and abroad, the requirements are large processing volume per unit time [4], simple operating conditions and easy control, low costs and quick results. However, the utilization process may cause secondary pollution to the environment. For example, there are problems such as large capital investment, long investment recovery period, and the project is likely to cause secondary water pollution [5]. With the continuous improvement of people's awareness of resource crisis, the treatment of solid waste has gradually changed from the initial extensive treatment to the refined recycling method. In order to effectively solve some of the contradictions in the harmless treatment of electrolytic aluminum waste, it is necessary to propose a new recycling model. By studying the mixed combustion of electrolytic aluminum waste and pulverized coal, a truly harmless treatment method for electrolytic aluminum waste is proposed. This mode is to pulverize the electrolytic aluminum waste, and then mix the crushed electrolytic aluminum waste with the raw coal of the circulating fluidized bed boiler [6], then send it to the circulating fluidized bed boiler for combustion.

In this study, a mixed combustion experiment of electrolytic aluminum electrode waste and pulverized coal was carried out in a fixed-bed burner system, which was established to simulate the combustion environment with a combustion temperature of 900 °C-1050 °C. Based on the total pollutant emissions of different blending ratios of electrolytic aluminum electrode waste and pulverized coal at different combustion temperatures, the composition transformation of the combustion products of electrolytic aluminum waste at different combustion temperatures was studied through SEM and XRD analysis. With the structure of ash and slag, as well as the product after adding limestone, it is theoretically feasible for the circulating fluidized bed boiler to burn electrolytic aluminum waste on a large scale.

2. MATERIALS AND METHODS

2.1 Materials and methods

2.1.1 Material

This study collected electrolytic aluminum waste cathodes, anodes, limestone and other materials. After grinding the materials with an electric mill, 50 grams of electrolytic aluminum waste samples were sieved to 0.075 mm. The sample was then dried for 2 hours at a temperature of 110 °C in the dryer, then stored in a drying container for later use. Use the same method to grind and store pulverized coal and limestone. During the experiment, a balance is used to weigh the samples in a certain proportion for the experiment. The mixing ratio of the experimental materials is in accordance with the four working conditions in Table 1. The total amount of each sample is the mass is 10g, and the mass of limestone is added separately.

2.1.2 Test system

The experimental system is mainly composed of three parts: gas supply system, combustion system, flue gas analysis and processing system. The tube furnace (GSL-1600X) is used as the combustion equipment. As shown in Fig 1, the composition of flue gas is analyzed with the GASMET DX4000 infrared flue gas analyzer. The environment is simulated by adjusting the gas volume of the nitrogen and oxygen cylinders.

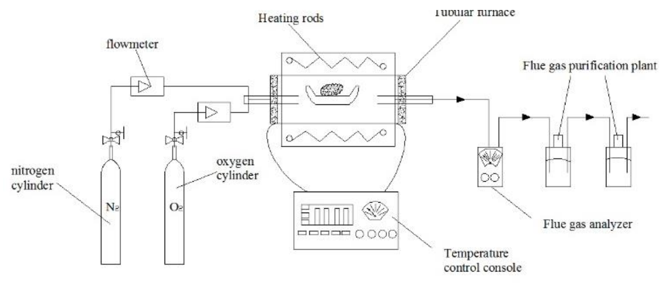

Fig. 1. Test system

2.1.3 Blending ratio chart

There are four blending ratios for pulverized coal and electrolytic aluminum scrap, as follows:

Table 1. Comparison table of four experimental conditions

	Blending ratio	Calcium carbonate/g
Condition 1	5:5	0
Condition 2	7:3	0
Condition 3	3:7	0
Condition 4	7:3	5

2.2 Experiment method

The above-mentioned pulverized coal and electrolytic aluminum scrap are proportioned according to the three ratios of 7:3, 5:5, and 3:7. Then separately loaded into three volumetric flasks. Finally the mixed combustion experiment is carried out according to the following experimental steps:

The first step: in the air, the temperature is set to 900 °C, 7:3, 5:5, 3:7 samples are mixed and burned, respectively. Pollutant emission data are recorded, while the products after combustion are sampled and retained.

The second step: in the air, add limestone, set the temperature to 900°C, take 7:3 samples for mixed combustion. Pollutant emission data are recorded, while the products after combustion are sampled and retained.

The third step: in the air, the temperature is set to 980°C, and 7:3 samples are taken for mixed combustion. Pollutant emission data are recorded, while the products after combustion are sampled and retained.

The fourth step: in the air, the temperature is set to 1050 °C, 7:3 samples are taken for mixed combustion.

Pollutant emission data are recorded, while the products after combustion are sampled and retained.

Step 5: XRD and SEM analysis are performed on the combustion products under the above-mentioned different working conditions.

3. RESULTS AND DISCUSSION

3.1 Pollutant Emission

Through the analysis of Fig 2, working condition 1 has the highest total amount of pollutants, while working condition 4 has the lowest total emissions. It can be seen that when pulverized coal and electrolytic aluminum scrap are mixed and burned in a ratio of 5:5, the pollutant emission is the highest. The pollutant emission value is the lowest when mixed in 7:3 ratio (with limestone) [7]. Based on this, it can be inferred that when a circulating fluidized bed boiler is used to treat electrolytic aluminum waste, 30% mixing is the best process Situation point.

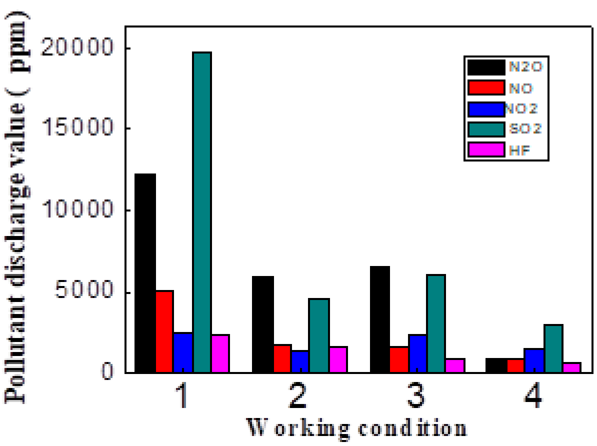

Fig. 2 Total emissions of pollutants under various combustion conditions at 900°C

3.2 Ash Properties

In order to facilitate the study of the mixed combustion of electrolytic aluminum waste and pulverized coal, the physical properties of the ash are the best. In the experiment, three combustion temperatures of 900 °C, 980 °C and 1050 °C were selected, and the mixture of electrolytic aluminum waste and pulverized coal The ratio is 7:3. The physical photos of the combustion products and the SEM results of the combustion products are shown in Fig.3:

From Fig 3(d)-(f), it is concluded that at a combustion temperature of 900 °C, the internal structure of the combustion product (d) is loose, composed of more granular and micro-droplet-like structures. Because when burning at 900 °C, the internal crystal lattice changes, and some soluble substances containing potassium and sodium are melted out of the surface, while minerals composed of iron and aluminum form skeletons at high temperatures. These molten skeletons adsorb part of potassium and sodium. Other substances show a loose structure at 980 °C. Part of the combustion product (e) minerals form a eutectic with the influence of high temperature. At the same time, under the action of water vapor generated inside, the combustion products have a bubble-like appearance. At 1050 °C, the entire combustion product (f) begins to gradually take on a glassy appearance, which is similar with the study of Wang et al. [8]. The internal space gradually becomes tighter during the melting process. Due to the high temperature, the volatilized water inside bursts. Some larger holes are formed on the surface of the object.

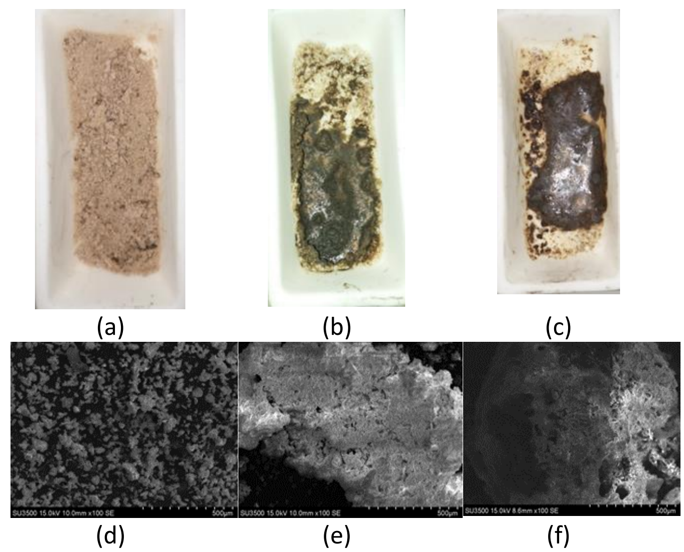

Fig.3 Pictures of combustion products and SEM image

Comparing the three physical diagrams of combustion products at different temperatures (Fig.3 (a)-(c)), it is obvious that in Fig.3 (a), the combustion products are in the form of fine sand particles with a certain degree of fluidity. (B) is in a molten state. In Figure (c), you can see obvious light reflection, indicating that as the temperature rises, the combustion products gradually appear in a molten state. The higher the temperature, the more obvious the glass state.

3.3 XRD Analysis

By analyzing the XRD patterns of the combustion products before and after adding limestone (Fig 4), we can see that when limestone is not added, the combustion products are mainly potassium sulfate. After limestone is added, calcium carbonate is heated and decomposed to form calcium oxide, and calcium oxide encounters water. Calcium hydroxide is produced.

Calcium hydroxide absorbs the hydrogen fluoride gas generated at high temperature from sodium fluoride and potassium fluoride in the electrolytic aluminum waste. The product is solid calcium fluoride, thus confirming that the addition of limestone can effectively reduce the emission of hydrogen fluoride. Comparing Fig.4 and Fig. 5, it can be seen that the content of potassium sulfate and calcium silicate is reduced after limestone is added. The main products carbonate and silicate.

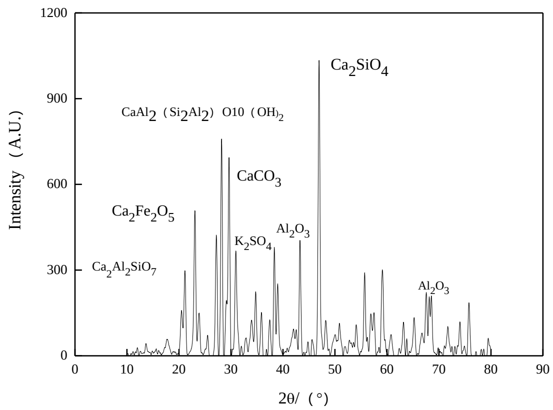

Fig.4 XRD diffraction pattern of combustion products under working condition 4

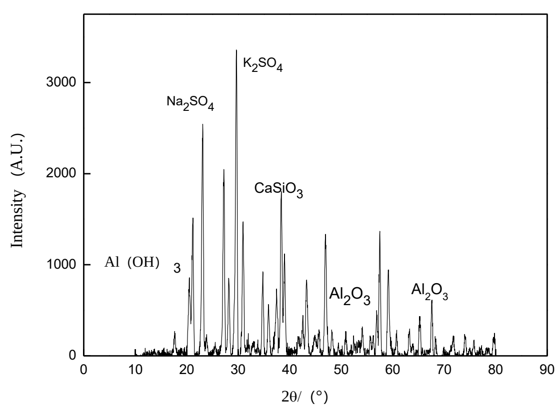

Fig.5 XRD diffraction pattern of combustion products under working condition 2

4. CONCLUSIONS

The article uses electrolytic aluminum waste as the experimental raw material. The mixed combustion experiment of raw materials and pulverized coal is carried out by using a fixed-bed burner combustion method. The conclusions can be drawn as follows:

The mixed combustion after adding limestone in a proportion is the best combustion condition. Limestone can effectively reduce the pollutant emission.

The physical properties of ash at this combustion temperature point are better. It is theoretically feasible for a fluidized bed boiler to mix and burn electrolytic aluminum waste on a large scale.

Through the analysis of XRD spectrum, it can be seen that the products after adding limestone are basically calcium silicate and other salts, and the combustion products can be further used to realize the transformation of waste into treasure [9], with the environmental protection equipment of the circulating fluidized bed boiler body, it is fully capable of removing the pollutants released by the electrolytic aluminum waste during the combustion process.

ACKNOWLEDGEMENT

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