Recycling and Utilization of Used Dry Barrier Materials of Aluminium Electrolysis Cells

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Abstract

Dry barrier materials for aluminium electrolysis cells play an important role in preventing the penetration of electrolyte into the potlining. After the cells are shut down, the dry barrier materials have a certain value for recycling and reuse. However, at present, during the de-lining process, the dry barrier materials and other lining materials are disposed of together as solid hazardous waste. This not only increases the disposal cost but also causes waste of resources. This paper introduces the seepage prevention principle of the dry barrier materials and the methods for determining the physical and chemical properties of the dry barrier materials, and the composition of the waste dry barrier materials in different layers below the cathode block: upper, middle and lower layers in the cell. Based on the analysis of the composition of the waste dry barrier materials in different layers, the waste dry barrier materials in the lower layer were selected to carry out the experimental research on recycling and reuse. The physical and chemical performance indicators and anti-penetration ability of the electrolyte of three mixing formulas between spent and new barrier materials were studied. Overall, the third mixing formula, which consisted of spent barrier material and fresh barrier material with a ratio of 3:7, respectively, was found to be the best. Using the optimal mixing formula, 25 tonnes of dry barrier materials were prepared and tested on a 400 kA aluminium electrolysis cell. The test cell operation was stable, and the performance indicators reached the potline averages.

Key words: Aluminium electrolysis cell, Dry barrier material, Recycling and utilization, Barrier test.

1. Introduction

The current production method for aluminium is the cryolite-alumina molten salt electrolysis in the aluminium reduction cell. The cell lining consists of cathode blocks, refractories, and thermal insulation materials. In the early stages, the refractories used below the cathode blocks were primarily refractory bricks and alumina. During cell operation, these refractories are subjected to the combined effects of penetrating electrolyte and sodium vapor, leading to gradual degradation and eventual loss of their protective function for the underlying thermal insulation materials. This results in deteriorating the thermal insulation of the cell, worsening production performance, and even causing metal and electrolyte tap-out incidents that force the cell to shut down. Since 1995, dry barrier materials (hereinafter referred to as barrier materials) have been used domestically, which resolved the critical issue of electrolyte infiltration and significantly extended the cell service life. Barrier material, also known as a chemical baffle, can chemically react with the infiltrating electrolyte to form a solidified baffle, thereby preventing further electrolyte infiltration [1]. The primary function of the barrier material is to prevent electrolyte penetration and provide thermal insulation. In the cells using high-performance barrier materials, only a thin layer of the barrier material under the cathode block (hereinafter referred to as spent barrier material) reacts with the electrolyte after the cell is shut down, and a hard nepheline or albite layer is formed. The underlying barrier material below this nepheline or albite layer shows no visually discernible difference from fresh barrier material, with no significant changes in its properties [2]. During cell de-lining, the unchanged barrier materials and other lining materials are typically managed as cell lining hazardous waste specified in the *National Hazardous Waste Inventory* (Code: 321-023-48, Hazardous Characteristics: T) [3].

China has introduced relevant policies strictly prohibiting the open-air stacking, illegal discharge, and unauthorized transfer of aluminium electrolysis spent pot lining (SPL). Smelters must engage third-party vendors with hazardous waste treatment qualifications for their disposal. The disposal cost of cell linings is approximately 4 000 RMB/t (555 USD/t approx.) [4], which not only increases the expenses for smelters but also results in significant waste of resources. China's aluminium industry has maintained rapid development, with its primary aluminium production consistently ranking first in the world since 2000. In 2024, China's primary aluminium output reached 44.005 million tonnes, marking a 4.6 % year-on-year increase and accounting for approximately 60.12 % of the world's total primary aluminium production [5]. With the implementation of China's policies on total capacity control and capacity replacement in the electrolytic aluminium industry, a significant amount of spent barrier materials generated during the shutdown or major repair of the cells has become an issue that cannot be ignored. Improper handling of these spent barrier materials not only wastes resources but also causes environmental hazards.

In early 2022, China's *Implementation Plan for Accelerating the Comprehensive Utilization of Industrial Resources* [6] explicitly set a target to strive for a 57 % comprehensive utilization rate of bulk industrial solid waste by 2025. Therefore, the recycling and reuse of cell barrier materials are of particular importance. This paper investigates the state and composition of spent barrier materials, with focus on experiments for the recycling and reuse of recoverable spent barrier materials from the lower layer. In addition, the preferred method was applied by mixing the recycled materials with fresh barrier materials in a 400 kA aluminium reduction cell, which demonstrated satisfactory operational performance.

2. Barrier Mechanism of Barrier Materials

The amount of barrier material used in aluminium reduction cell cathode is related to the cell size. For example, a 400 kA cell requires approximately 25 tonnes per cathode, while a 500 kA cell uses about 33 tonnes per cathode.

The barrier material is an unshaped refractory prepared by mixing various refractory particles of different size fractions in specific proportions, which have functions of anti-penetration, fire-resistance and thermal insulation. The ratios of SiO_2 % to Al_2O_3 % in the barrier material vary, leading to differences in the reaction mechanisms with the infiltrated electrolytes [7].

At low SiO_2 % / Al_2O_3 % ratios, the primary product of chemical reaction is nepheline, as shown in Equation (1):

$$6NaF + 3SiO_2 + 2Al_2O_3 = 3NaAlSiO_4\,(\text{nepheline}) + Na_3AlF_6 \qquad (1)$$

Meanwhile, at high SiO2 % / Al2O3 % ratios (SiO2 > 72 %), the primary product is albite, as shown in Equation (2):

6. References

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