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):

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

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

$$6NaF + 9SiO_2 + 2Al_2O_3 = 3NaAlSi_3O_8\,(\text{albite}) + Na_3AlF_6 \tag{2}$$

The barrier materials are typically laid above the thermal insulation layer, replacing the original refractory brick layer and alumina layer, with the cathode blocks directly placed on the rammed and levelled barrier materials. The barrier materials react with the infiltrated electrolyte and sodium vapor to form a nepheline or albite layer, which effectively blocks further electrolyte infiltration and provides excellent protection to the thermal insulation layer. The barrier materials are paved in a non-rigid integrated way, which can absorb partial vertical stress from cathode expansion and mitigate vertical uplift of the cathode [8, 9]. In recent years, as the cell voltage has decreased, the thermal insulation requirements for the cell bottom have become more stringent. Since the thermal insulation of barrier materials is greater than refractory bricks, the cell bottom thermal insulation and thermal balance stability can be improved by replacing refractory bricks with barrier materials.

The thickness of the rammed barrier materials currently used in the cells is generally around 18 cm. If the barrier material used has good seepage performance, only a thin layer of the material beneath the cathode reacts with the electrolyte after the cell is shut down, forming a hard barrier layer (with a thickness of about 5–15 mm) of nepheline or albite. The properties of the barrier material below this barrier layer remain largely unchanged [2]. However, for cells with exceptionally long service life, the thickness of the barrier layer formed by the reaction between the infiltrated electrolyte and the barrier material can far exceed 15 mm.

3. Test Method

3.1 Test Materials

Spent barrier materials: After the cell in a smelter was shut down, multi-point sampling was made on the barrier materials in the cells. Based on their positions in the cells, the spent barrier materials were sequentially classified into the upper layer, which was just below the cathode block, the middle layer, which is after the upper layer and the lower layer, which comes after the middle layer. The barrier materials were prepared according to the established procedure.

3.2 Experimental Procedure

First, the morphology and composition distribution of spent barrier materials at different locations in the cell were obtained to identify which parts are suitable for recycling. Tests were carried out by mixing the preferred spent barrier materials and fresh barrier materials in specific proportions. The mixed barrier material samples were dried at 110 ±5 °C for 2 hours, then cooled to room temperature in a desiccator. Then the physico-chemical properties of the samples were studied, including chemical composition (XRF), apparent density, stamped density, thermal conductivity, and permeability. The overall performance of each barrier material mixture was evaluated. Ultimately, the formula meeting all standard requirements was selected for the recycling and reuse test in the cell.

3.3 Test Method

3.3.1 Determination of Chemical Composition of Spent Barrier Materials

Three types of typical spent barrier materials were selected, ground separately using a vibrating mill, and sieved through a 200-mesh sieve for sampling. The samples were dried at 110 ± 5 °C for 2 hours, and the chemical composition of the samples were analysed using an X-ray diffractometer (XRD), model: X'Pert PRO, manufactured by PANalytical B.V., Netherlands, equipped with an X'Celerator ultra-fast detector, Cu Kα radiation, at a scanning speed of

2θ = 0.016°/min, step width of 0.002°, divergence slit (DS) of 1°, scattering slit (SS) of 1°, receiving slit (RS) of 0.5 mm, tube voltage of 45 kV, and tube current of 30 mA.

3.3.2 Determination of Apparent Density

A calibrated stainless-steel cylinder with known mass (inner diameter: 50 mm, height: 190 mm) was placed on the platform. The sample was poured steadily into its centre from approximately 40 mm above the cylinder, ensuring no vibration of the cylinder or platform during the process. When the sample formed a cone at the top of the stainless-steel cylinder and began to overflow, the sample dosing was stopped. Then, a straight steel ruler was used to gently scrape off the excess sample along the edge of the stainless-steel cylinder, and the total mass of the cylinder was weighed. The apparent density of the barrier material was calculated using Equation (1).

$$\rho = \frac{m_2 - m_1}{V} \tag{1}$$

where:

ρ	Apparent density of the tested barrier material, g/cm^3
m_2	Total mass of the stainless-steel cylinder and the sample, g
m_1	Mass of the stainless-steel cylinder, g
V	Volume of the stainless-steel cylinder, cm^3

3.3.3 Determination of Stamped Density

A 650 g sample was poured into a stainless-steel cylinder (inner diameter: 50 mm, height: 190 mm) in batches. After each addition of the test material, the materials were rammed by allowing the rammer (a stainless-steel rammer with a diameter of 49.5 mm and a height of 200 mm; the upper end could be weighted to achieve a total mass of 4.0 kg) to fall freely no fewer than 50 times. The drop height of the rammer was adjusted so that its lower edge was level with the upper edge of the stainless-steel cylinder. Then the remaining length at the upper part of the stainless-steel cylinder was measured by using a vernier calliper. The stamped density of the barrier material was calculated according to Equation (2):

$$\rho_T = \frac{m}{\pi \left(D/2 \right)^2 (H - H_1)} \tag{2}$$

where:

ρ_T	Stamped density of the tested barrier material, g/cm^3;
m	Mass of the sample = 650 g
D	Diameter of the cylinder = 5 cm
H	Height of the cylinder = 19 cm
H_1	Remaining height of the upper part of the cylinder, cm.

3.3.4 Measurement of Thermal Conductivity

The thermal conductivity of the test sample was measured using a plate thermal conductivity apparatus in accordance with the test method specified in the *Refractory materials–Determination of thermal conductivity (calorimeter)* (YB/T 4130). The test sample was placed into a refractory ring (inner diameter 180 mm, outer diameter 210 mm, height 20 mm) and rammed until level with the ring's top surface, then the sample loading and testing were carried out according to the equipment operating procedures.

3.3.5 Determination of Electrolyte Infiltration Resistance

A refractory brick with a diameter of 60 mm and a height of 50 mm was placed at the bottom of a covered graphite crucible (inner diameter: 60 mm, inner height: 200 mm). The samples were loaded into the crucible in batches, and each batch was rammed with a stainless-steel round rod (diameter: 49.5 mm, height: 200 mm) until the sample thickness reached 25 mm. 270 g of electrolyte with a molecular ratio of 2.70, alumina content of 4 % and calcium fluoride content of 4 % was weighed out and placed on the rammed sample, with the graphite crucible covered properly. The graphite crucible was protected with other materials to prevent oxidation, then placed in a crucible furnace and maintained at 950 ± 5 °C for 96 hours, followed by natural cooling to room temperature. After taking out the graphite crucible, the material was poured into a ceramic tray to measure the thickness of the formed dense barrier layer, and to observe whether the electrolyte had infiltrated into the refractory brick under the sample. If the electrolyte did not infiltrate into the refractory brick and the thickness of the dense barrier layer was less than 7 mm, the sample would meet the requirement for electrolyte infiltration resistance. If the electrolyte infiltrated into the refractory brick or the thickness of the dense barrier layer exceeded 7 mm, the sample would fail to meet the requirement for electrolyte infiltration resistance.

4. Results and Discussion

4.1 Study on Chemical Composition of Spent Barrier Materials

The chemical composition of the three samples is shown in Table 1.

Table 1. Chemical composition of spent barrier material samples from the cells (%).

Category	Upper layer spent barrier materials	Middle layer spent barrier materials	Lower layer spent barrier materials
Sample photographs			
Chemical composition (%)			
NaF	47	18	
LiF	8	6	
$Na_3K(Si_{0.56}Al_{l0.44})_8\ O_{16}$	17	19	
Mg_2SiO_4	15		
$Na_5Al_3F_{14}$	12	10	
$(K, H_3O)\ Al_2Si_3\ AlO_{10}$		10	
$Na\ (AlSi_3O_8)$		37	8
$Al_{4.59}Si_{1.41}O_{9.7}$			52
SiO_2			27
$K(AlSi_3O_8)$			14

According to Table 1, the upper layer of barrier material near the cathode had a significant reaction with the electrolyte, appearing as white blocks with a similar appearance to the electrolyte. Electrolyte components (NaF, LiF, and $Na_5Al_3F_{14}$), along with minor amounts of nepheline-series minerals ($Na_3K\ (Si_{0.56}Al_{0.44})_8O_{16}$) and magnesium silicate (Mg_2SiO_4), were the main chemical components in the upper layer spent barrier material.

The middle layer spent barrier material was sintered into a hard spinel form, appearing as gray or black, with the primary chemical components comprising of albite (Na $(AlSi_3O_8)$), illite ((K, H_3O) $Al_2Si_3AlO_{10}$), nepheline-series minerals (Na_3K $(Si_{0.56}Al_{0.44})_8O_{16}$), and electrolytes (NaF, LiF, and $Na_5Al_3F_{14}$).

The appearance of the lower layer spent barrier material resembled that of fresh barrier material, presenting as bulk materials. The results indicated that the chemical composition of the spent barrier material samples were mainly mullite ($Al_{4.59}Si_{1.41}O_{9.7}$), silica ($SiO_2$), albite (Na $(AlSi_3O_8)$), and potassium feldspar ($K(AlSi_3O_8)$). These major components of the spent barrier material were similar to those of fresh barrier material.

4.2 Study on Formulas for Recycling and Reusing Spent Barrier Material

The stamped density and apparent density of barrier materials are important performance indicators for their application. Barrier materials with higher stamped density have better resistance to electrolyte infiltration. Both apparent density and stamped density are mainly used to calculate the compression ratio during construction, providing essential references for construction organizations [10]. In July 2024, China implemented the latest standard for dry barrier materials, *Dry Impervious Material for Aluminium Electrolysis Cell* (YS/T 456-2023), with its key indicators listed in Table 2.

Table 2. Chemical composition and performance indicators of dry barrier materials.

Chemical composition (%)			Physical properties			Electrolyte infiltration resistance (mm)	
SiO_2 % + Al_2O_3 %	SiO_2	LOI	Apparent density (g/cm^3)	Stamped density (g/cm^3)	Thermal conductivity (W/(m·K)) 800 °C	Thickness of barrier layer	Electrolyte infiltration depth
≥ 85	50–60	≤ 2.0	≥ 1.48	≥ 1.93	≤ 0.55	≤ 7	≤ 25

The recycled spent barrier materials and fresh barrier materials were mixed in specific ratios to obtain three formulas for recycled barrier material. Following the test methods, the apparent density, stamped density, thermal conductivity, and electrolyte infiltration resistance of the three formulas were investigated. Comparative tests were also conducted on fresh barrier materials.

The test results are shown in Table 3, where it can be observed that the three formulas of recycling lower layer spent barrier materials all met the standard requirements of YS/T 456-2023 in terms of thermal conductivity at different temperatures, barrier layer thickness, and electrolyte infiltration depth. However, regarding the combined SiO_2 % and Al_2O_3 % content, formula 1 and formula 2 both complied with the standard, while formula 3 failed to meet the standard. Additionally, the stamped density of formula 2 and formula 3 were 1.91 g/cm^3 and 1.88 g/cm^3, respectively, both substandard. Among the three formulas, only formula 1 fully met all the specified requirements in the standard. After a 96-hour anti-infiltration test, the three formulas formed an electrolyte infiltration barrier layer with a thickness of 2–5 mm, meeting the standard requirements for barrier layer thickness of anti-infiltration materials. However, as the dosage of fresh barrier material decreased, the electrolyte infiltration depth gradually increased. In the three formulas, the electrolyte infiltration depth was all less than 25 mm after the anti-infiltration test. The barrier layer thickness of formula 1 was 2.9 mm, its electrolyte infiltration depth was 6 mm, with the best barrier effect, and other physical and chemical performance indicators were all up to standard. Therefore, formula 1 was selected for industrial cell tests.

Table 3. Test results of three formulas using fresh barrier material and recycled spent barrier material from the lower layer.

Formula	Barrier material	SiO_2 +Al_2O_3 (%)	Apparent density (g/cm^3)	Stamped density (g/cm^3)	Thermal conductivity (W/(m·K))				Thick-ness of barrier layer (mm)	Electrolyte infiltration depth (mm)
					200 °C	420 °C	650 °C	800 °C		
	100 % fresh barrier material	91	1.61	1.99	0.18	0.23	0.28	0.31	1.8	4.8
1	Spent barrier material (30 %) + fresh barrier material (70 %)	88	1.57	1.94	0.22	0.25	0.31	0.34	2.9	6.2
2	Spent barrier material (40 %) + fresh barrier material (60 %)	86	1.54	1.91	0.24	0.27	0.33	0.37	3.5	10.1
3	Spent barrier material (50 %) + fresh barrier material (50 %)	83	1.52	1.88	0.27	0.30	0.35	0.39	4.7	16.6

4.3 Cell Tests

Based on the test results of the formulas for recycling spent barrier materials, the optimal ratio of 3:7 (spent barrier material from the bottom layer to fresh barrier material) was selected for the industrial-scale cell tests. The test was conducted on a 400 kA cell. During de-lining of the cell, the barrier material was stripped layer by layer. From the spent barrier material, the lower layer spent barrier material showing no visible signs of reaction was selected. 7.5 tonnes of such spent barrier materials were prepared and crushed into particles of 0–10 mm. Samples were taken for analysis to ensure that the combined content of alumina and silica was no less than 75 %. Additionally, 17.5 tonnes of fresh barrier material were prepared. The spent and fresh barrier materials, totalling 25 tonnes, were blended to serve as the barrier material for the cell tests. During the cathode building of the test cell, the uniformly blended barrier materials were paved in two layers on the thermal insulation bricks, and rammed and tamped layer by layer. The furnace bottom temperature and technical-economic indicators of the test cell were monitored during the first 12 months of operation after the cell start-up, as shown in Figure 1.

The average cell voltage during the first 12 months of the test cell operation was 3.974 V, and the cell voltage gradually decreased after three months since start-up. The average cell voltage was 3.958 V in the last nine months, and the potline average value was 3.966 V. The average current efficiency of the test cell during the first 12 months after startup was 91.70 %, compared to the potline average of 91.46 %. During the 12-month test operation, the average temperature of the cathode bottom was 71.7 °C. In the first three months after startup, the temperature ranged 80–90 °C, then decreased and stabilized at 60–70 °C. The potline average was 68 °C. The cell was operating normally as a whole, with performance indicators meeting the potline average values.

The test cell underwent a major shutdown after 1379 days of operation due to the implementation of new technologies. The cell was autopsied. The cell barrier materials revealed that the electrolyte had stopped further infiltration after reaching a depth of 6.5 cm, forming a hardened barrier layer approximately 1.2 cm thick. In some areas, bulk barrier materials were found under the barrier layer. The results of the test cell demonstrate that spent barrier materials can be recycled and reused in the cells.

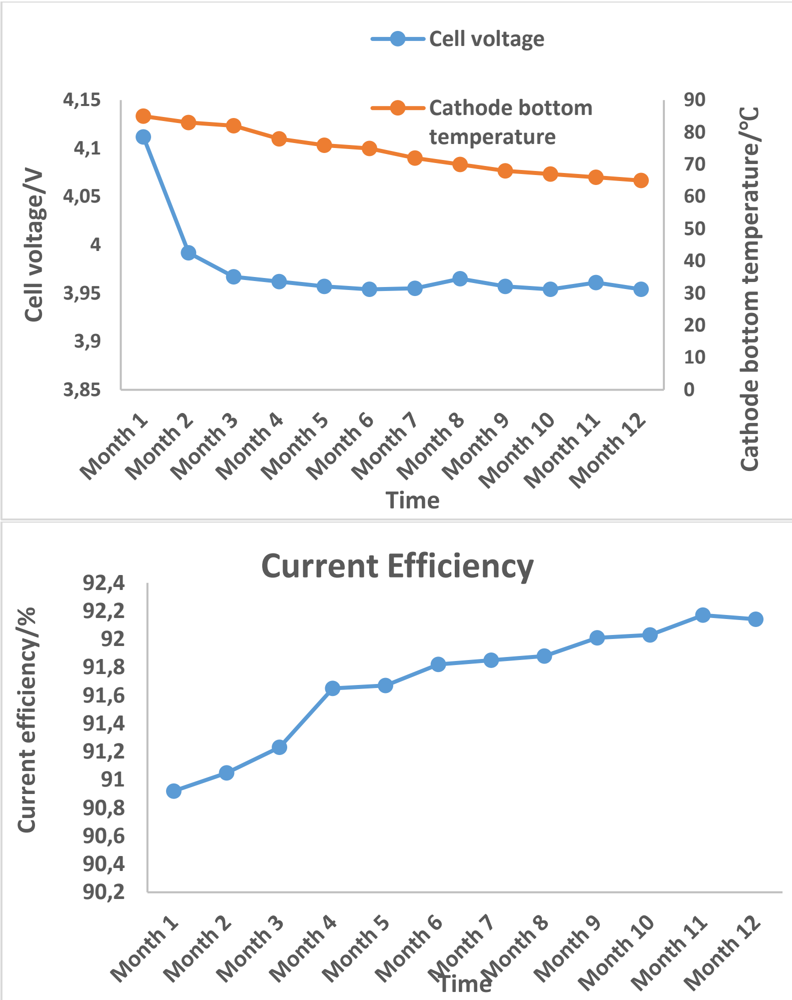

Figure 1. Cell voltage, cathode bottom temperature and current efficiency during the first 12 months after startup of the test cell. Top: Cell voltage represented by the blue line (left vertical axis) and cathode bottom temperature represented by the red line (right vertical axis), Bottom: Current efficiency.

5. Conclusions

1) The spent barrier materials were divided into the upper, middle, and lower layers of the cell. Each layer has a different appearance and chemical composition.
2) The different formulas of recycling and reuse of the lower layer of spent barrier materials were studied, and only the formula of the lower layer of spent barrier material and fresh barrier material with a ratio of 3:7 met the latest national standards in terms of physical and chemical properties, and had the best effect of blocking electrolyte infiltration.
3) The cell test was conducted to evaluate the recycling and reuse of spent barrier materials, using a blending ratio of 3:7 between spent and fresh barrier materials. During the test, the cell operation was stable, with the cell voltage, current efficiency, and cathode bottom temperature reaching the potline averages. Furthermore, upon shutdown of the cell, both the barrier materials and the barrier layer they formed remained in normal condition. This demonstrates that spent barrier materials can be effectively recycled and reused in electrolysis cells following an appropriate formulation.

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