

## Sodium Sulfate Reactivity Test of Carbon Anodes in Aluminium Production

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### Abstract

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Prebaked carbon anode is the primary consumable material in the aluminum reduction cell. Its quality directly affects the durability of carbon anodes and the costs associated with the Hall-Héroult aluminum production process. The conditions of traditional anode quality control tests, such as CO<sub>2</sub> and air reactivity tests, differ from those of industrial electrolytic cells. This study presents an alternative Sodium Sulfate Reactivity (SSR) test, which could better simulate real electrolysis conditions by incorporating in-situ CO<sub>2</sub> generation and liquid-solid interactions in the molten sodium sulfate bath. An experimental setup was used to immerse carbon anode samples in a molten sodium sulfate bath. Initial tests showed the importance of optimizing test parameters, particularly test temperature and time, to achieve measurable mass loss results. At a test temperature of 990 °C and a test time of 30 min, measurable mass losses were obtained for samples extracted from industrial baked anodes. Multiple linear regression analysis showed that both centered apparent density ( $p = 0.0007$ ) and anode-to-anode variability ( $p = 0.0387$ ) have a significant correlation to the mass loss, with a global  $R^2$  of 0.870.

**Keywords:** Aluminium electrolysis, Carbon anode, Carbon consumption, CO<sub>2</sub> reactivity, Sodium sulphate reactivity.

### 1. Introduction

Aluminium is produced from its alumina (Al<sub>2</sub>O<sub>3</sub>) ore through the Hall-Héroult process. In this process, Al<sub>2</sub>O<sub>3</sub> is reduced in the electrolytic cell. The electrolytic cell is composed of a carbon cathode, carbon anodes, and molten cryolite (Na<sub>3</sub>AlF<sub>6</sub>) as electrolyte. The cells typically operate at 940–980 °C [1]. The prebaked carbon anode is the primary consumable material in the reduction cell, which, in addition to conducting electric current, acts as the reducing agent in the electrochemical reaction:



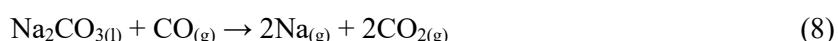
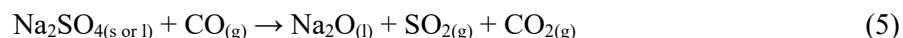
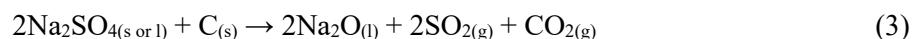
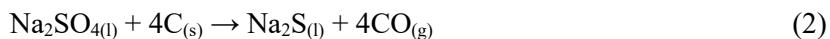
Based on this reaction, the theoretical consumption of anodes is 333 kg per ton of aluminium produced. However, additional consumption is observed due to side reactions such as air oxidation, the Boudouard reaction, and preferential binder oxidation (dusting) [2–4]. Excessive carbon consumption increases Al production costs and CO<sub>2</sub> emissions [4, 5]. This excessive carbon consumption is influenced by a number of material and processing factors. Processing parameters, i.e., mixing and compaction of anode paste and baking temperature (BT), and anode

properties, i.e., baked density, pore size distribution, and chemical composition, may affect anode reactivity [6].

Carbon anode reactivity is conventionally assessed through ISO standard tests. In these tests, the carbon anode is exposed to the flow of reactive gases (CO<sub>2</sub> or air) in a furnace, and the mass loss of the samples is measured [7, 8]. However, the conditions of these indirect methods differ from those of real electrolysis conditions, limiting their ability to fully represent industrial anode performance in the reduction cell. Specifically, these tests do not consider the effect of molten electrolyte environment, in-situ CO<sub>2</sub> generation, or temperature gradients present in operational reduction cells.

Given these limitations, we propose revisiting a complementary tool to assess anode reactivity under conditions closer to those of real electrolysis. This approach is based on sodium sulfate reactivity (SSR), and we believe that it will potentially enable the refinement of the anode reactivity tests and provide a detailed understanding of the effect of anode properties on carbon anode reactivity and consumption in the cell.

The SSR test was used in the industry between the 1950s and 1990s to evaluate anode reactivity. This test assesses the reactivity of an anode sample immersed in molten sodium sulfate. Therefore, it provides a reactive liquid environment and, consequently, liquid-solid interaction. At temperatures above 884 °C and in the presence of carbon, Na<sub>2</sub>SO<sub>4</sub> is reduced to Na<sub>2</sub>S, and carbon is oxidized to CO and CO<sub>2</sub>. According to the literature, the following chemical reactions are possible in this system [9, 10]:



Reactions (3) and (9) generate CO<sub>2</sub> directly, whereas reaction (2) generates CO, which can be transformed to CO<sub>2</sub> via the Boudouard reaction (4). CO<sub>2</sub> can also be generated via secondary reactions (5) or (8). Although the specific contribution of each reaction is undetermined, several in-situ CO<sub>2</sub> generation mechanisms are identified. The generated CO<sub>2</sub> can subsequently react with the carbon anode at the solid/liquid interphase, similar to the carbon/cryolite system.

Anode structural characteristics, including porosity and apparent density, could influence mass transport of CO<sub>2</sub> from the solid/liquid interface into the anode and consequently affect the mass

anode structural differences and suggest its use as a complementary method for anode reactivity evolution.

## 7. Future Work

For the next steps of this work, it is essential to evaluate the repeatability of the SSR test to establish the reliability and robustness of the method. For this purpose, cathode samples will be used instead of carbon anodes. The use of cathode materials is motivated by their more homogenous structure, which minimizes the influence of microstructural variability and allows a more accurate assessment of test repeatability.

Future experimental work will focus on elucidating the effect of the time to reach  $T_{\text{test}}$  on anode mass loss. Additional investigations will explore the influence of other test parameters, including larger sample sizes and larger amounts of sodium sulfate. Furthermore, the effect of anode properties, including porosity, crystallite size ( $L_c$ ), chemical composition, and BT, on the SSR test results will be studied, and results will be compared to those of the air and  $\text{CO}_2$  reactivity standard tests.

A thermodynamic approach will also be used to investigate the equilibrium state of the system. Several chain reactions are proposed in the literature to describe the overall reaction of sodium sulfate with carbon. Identifying the most prominent reaction may help better understand the possible correlations between test results and anode characteristics and evaluate the effects of factors such as temperature variations, phase changes, and the formation of secondary compounds on the SSR test results. In addition, kinetic study of the reactions and off-gas analysis can help to link the rate of different reaction pathways to the mass loss of the carbon anode samples.

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