

Recovery of Aluminium from Metal Pads in Shutdown Aluminium Electrolysis Cells

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<https://doi.org/10.71659/icsoba2024-al065>

Abstract

Remaining aluminium mixed with cryolite from shutdown electrolysis cells, commonly called metal pads, have been collected from two aluminium smelters in Norway for process developments to recover the aluminium metal. Two samples of metal pads were collected from the smelters. One sample was pre-processed via mechanical cleaning to reduce the cryolite content. Both pre-processed and non-pre-processed metal pads were heated to temperatures of 750 °C and 830 °C in a crucible placed in an electric furnace. A Fourier-transform infrared spectroscopy, FTIR, gas measurement instrument was used to characterise the off gases. Results from the aluminium recovery tests showed a higher productivity and lower HF emissions for the pre-processed metal pads relative to the non-pre-processed metal pads. Furthermore, the importance of water vapour to the formation of HF during the heat treatment was investigated using a humidifier.

Keywords: Metal pads, Pre-processing, FTIR, Shutdown, Aluminium, Cryolite.

1. Introduction

The global aluminium industry produced ca. 70.6 Mt of primary aluminium using the Hall-Héroult (HH) technology in 2023 [1]. The HH technology is based on an electrochemical reduction in an electrolysis cell at about 960 °C to produce aluminium. The electrolysis cell consists of carbon anodes that conduct electricity and are consumed during the production process, a molten cryolitic based electrolyte that conducts electricity and dissolves alumina, a molten aluminium metal pad that acts as the electrochemical cathode, a cathode lining consisting of carbon cathode blocks (with different degrees of graphitization) rodded with current collector bars for conducting electricity, refractories and insulation materials, and a side wall material. The carbon cathode blocks together with the current collector bars, refractories, insulations, side wall materials are usually arranged in a rectangular steel shell that vary from 9 to 18 m long, 3 to 5 m wide and 1 to 1.5 m deep. The operating cavity depth after installation of all lining materials is about 0.4 to 0.5 m [2]. The molten electrolyte and aluminium metal pad are usually kept at a height of 15-20 cm and 10-20 cm, respectively, during the electrolysis process [2, 3]. Two types of anode technologies exist in the industry; Söderberg technology, where the carbon anodes are baked in the reduction cell during electrolysis, and prebaked technology, where the carbon anodes are baked at a separate unit and transported to the electrolysis cell [2, 4]. Figure 1 is a sketch of the electrochemical reduction cell using the prebaked anode technology.

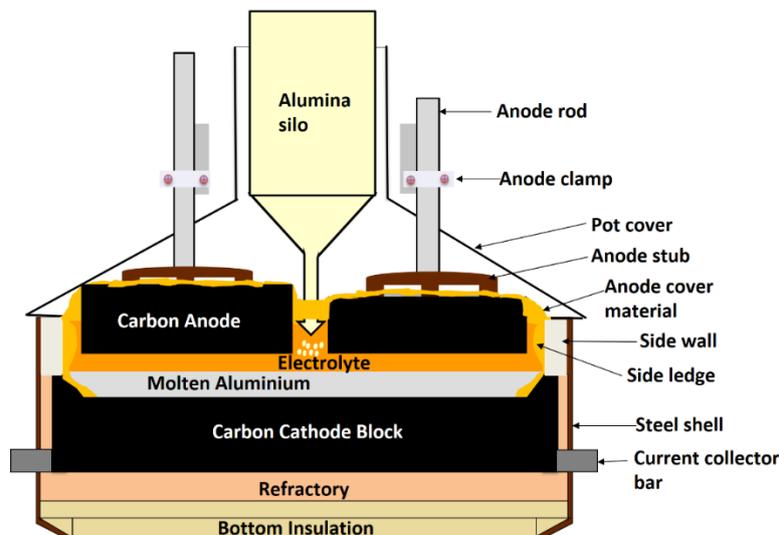


Figure 1. Electrochemical reduction cell using prebaked anode technology [5].

The lining materials within the electrolysis cell will over time degrade or in some extreme conditions fail leading to the shutdown of the cell [6]. The time from which an electrolysis cell is started to when it must be decommissioned is referred to as the pot age. The pot age varies a lot and can be from a few hundred days to over 3000 days [7, 8]. Prior to shutting down an electrolysis cell due to lining degradation or failure, operators at smelters attempt to tap as much molten aluminium metal out of the pot as possible. However, the amount of metal tapped varies a lot based on the experience of the operators and other factors such as potholes and other deformations on the cathode lining. Thus, quite a considerable amount of metal is sometimes left in shutdown cells. Considering the number of electrolysis cells that are shut down daily at the different smelters across the industry, this translates into many tonnes of aluminium left untapped. A few days after shut down, the electrolysis cell cools down causing all remaining electrolyte (mostly cryolite) and aluminium metal to freeze [6, 9]. The densities of molten aluminium and molten cryolite at the operation conditions are ca. 2.3 g/cm^3 and 2.1 g/cm^3 , respectively [2]. The small density difference between the two liquids and the close contact with each other results in the frozen metal being partly mixed with frozen cryolite after the cooling preceding shutdown. Thus, the frozen metal pad is always observed together with frozen cryolite and can in some cases be mixed with but in most cases found only on the surface of the metal. This paper describes the recovery of aluminium from the metal pads collected from two smelters in Norway.

2. Experimental

Metal pads were collected at two different aluminium smelters in Norway, denoted as Smelter 1 and Smelter 2. Figure 2a shows the metal pads from Smelter 1, which were used “as collected”. The metal pads from Smelter 2, shown in Figure 2b, were pre-processed by mechanical cleaning using pneumatic hammers to remove most of the frozen cryolite. Additionally, the metal pads from smelter 2 contained alumina balls which had been used to seal a hole created in the cathode lining during operation to prolong the lifetime of the cell.

A resistance heated furnace was used to heat the crucible employed in all the melting tests. In the first melting test using batch 1 from smelter 1, the metal pads were added to an empty crucible inside the furnace before the pre-heating started. The furnace was then pre-heated and held at a temperature of ca. $830 \text{ }^\circ\text{C}$.

moisture was detected. It was after about 3 hours of heating when the temperature reached ca. 450 °C that one could observe HF emission. This is shown in Figure 5. This observation is consistent with the laboratory experiments by Patterson [12] which showed hydrolysis of the fluoride particulates to be only significant at temperatures above 400 °C. Once the right temperature for hydrolysis is reached, HF emission is then dependent on the moisture and fluoride sources. The influence of moisture on HF emission was investigated by using the humidifier to vary the content of moisture and monitoring the corresponding HF emissions during test 1. The results, as can be seen by Figure 6 from ca. 26 hours to 30 hours, confirm the importance of moisture on HF emissions. Also, it was observed that the concentration of HF emitted varied between the non-pre-processed and pre-processed metal pads. The tests using the pre-processed metal pads had the lowest HF emissions relative to the tests with non-pre-processed metal pads which had ca. 5 times higher emissions of HF.

As mentioned above, the HF emissions were higher for the non-pre-processed metal pads probably due to the high frozen cryolite (fluoride) content. However, a difference in HF emission was also observed for the two tests that used the pre-processed metal pads. The HF emission was lowest for the test where the metal pads were immersed in molten aluminium. This is assumed to be due to the reduced exposure to moisture from the environment when the metal pads are immersed.

5. Conclusions

The melting tests have shown that pre-processing of metal pads to reduce the frozen cryolite content has positive effect on both the output and HF emissions. Furthermore, melting the pre-processed metal pads in pre-melted aluminium helps to further reduce the HF emission, however, at the cost of dross formation.

6. Acknowledgement

The present work was financed by the Research Council of Norway (NFR-nr 327564) and done in cooperation with Alcoa Norway, Hydro Aluminium, and Speira. The industry partners also provided materials for the tests. Permission to publish the results is gratefully acknowledged.

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