

Carbon Dusting Mechanisms and Countermeasures

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Abstract

Carbon anodes are an integral component of the molten salt electrolysis for primary aluminium production. Raw materials for anode production are suffering a reduction in quality and the aluminium world faces competition from lithium-ion batteries. The knowledge and improved process control in anode manufacturing has increased, where now anodes are manufactured to a better quality than 40 years ago. Despite the improved quality of the anodes, the problem of carbon particles mixed into the electrolyte (also known as carbon dust) is still prevalent. The usual recommendation in operations in smelters is: "Get better anodes and the problem will take care of itself". This summary of PhD thesis aims to investigate carbon particles and their distribution in industrial electrolyte taken from cells in the TRIMET Hamburg smelter.

An electrolyte sample containing carbon particles was analysed using STEM-EDS. The particles have an increased sodium content on the surface, which indicates sodium intercalation. Analysing the results of the industrial sampling at 600 positions, cells did not reveal fundamental patterns of carbon distribution. Modelling using PCR was able to explain a maximum of 19.1 % variance in the average carbon concentration. No mechanism was found to be acting on the distribution – in contrasts to other components in the electrolyte.

The analysis of frozen electrolyte samples taken under newly changed anodes within eight hours shows layered structures of the frozen bath. Many of the samples contained carbon particles. The size of the particles depended on whether the anode change was carried out using a scoop to clean the surface of the open electrolyte. Fine carbon particles remained in most cases. The formation of spikes, which damage the process, could not be detected in any of the anode changes observed within the first eight hours.

Overall, the methods and analysis conducted in this study did not show common particle patterns. The carbon particle distribution can be random.

Keywords: Carbon dust, Microstructure, Carbon distribution in bath, PCR, STEM-EDS.

1. Introduction

The use of carbon anodes in the primary production of aluminium has been the status quo since the inception of the process itself. While the overall demand for aluminium is growing, the primary production is hampered by its direct and indirect CO₂ emissions, which are contrasting the use in the green transformation. While today the CO₂ scope 2 footprint of aluminium ranges between four and 16.5 t CO₂-e/t Al [1-3], the reduction with green energy will only go so far. In the end, the process of carbon oxidation in the production is still relevant, until the inert anode is successfully integrated on a large scale, or an alternative process has been industrialized. However, the oxidation and consumption of carbon is both intentional and - due to side reactions - unintentional.

1.1 Carbon Reactivity in Electrolysis Cells

Carbon particles can be found in the electrolyte. The definition of carbon dust was published by the author elsewhere [4]:

“Carbon dust refers to small carbon particles, which are located in the electrolyte of an aluminium reduction cell [5-7]. Older sources refer to carbon slough [8] or carbon foam [9], which refers to a mixture of carbon particles of various sizes within the electrolyte in an aluminium reduction cell.”

Carbon dusting can be considered unintentional carbon consumption. It occurs due to various processes within the electrolysis process. The main ones are the reactivity of anodes with air or CO_2 . Figure 1 shows an anode with the temperature zones and the areas of air and CO_2 reactivity.

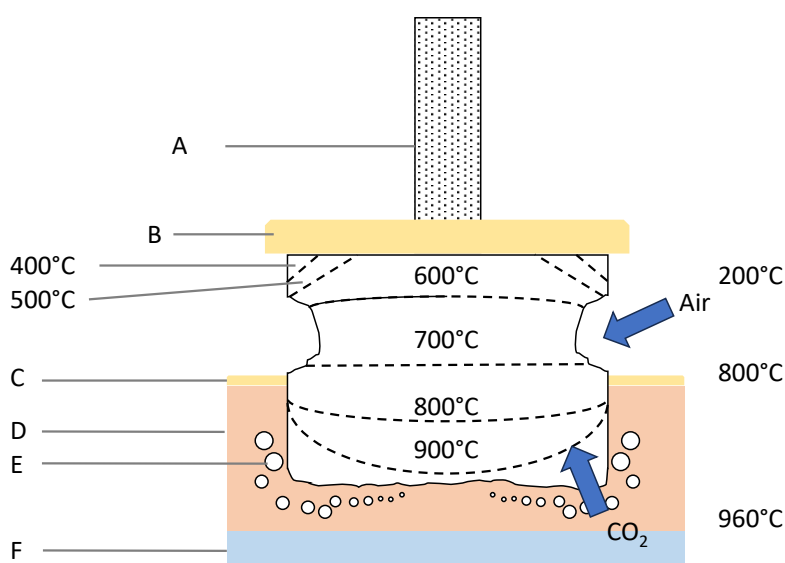


Figure 1. Anode sketch with zones of O_2 and CO_2 reactivity. The temperature scale shows the increasing temperature of the anode from top to bottom. Bottom surface profile of anode is exaggerated. With a temperature between 550 – 600 °C air reactivity starts, when air is available (arrow left of the word Air). This part can be, depending on the cell design, operation and time in the anode cycle, above anode cover material, which is supposed to seal the anode from air access. A: anode rod, B: Anode Cover Material, C: Bath Crust, D: Electrolyte, E: CO_2 bubbles, F: Aluminium. Recreated from Fischer and Perruchoud [10].

The rate and amount of CO_2 reactivity are temperature dependent and influenced by the anode properties [10-11]. Polished butts (used anodes) cores were investigated at 10x magnification. Sadler et al. showed a higher rate of sub-surface carboxy attack on the sides of anodes, when compared to the working surface [12]. Engvoll et al. supported the finding by analysing samples over the height of an anode after use [13]. Both groups stated that CO_2 can move through porosity for up to 50 mm and oxidize the binder phase of the anode. These “pre-reacted” parts are consumed on the working surface, as protruding particles are consumed preferential [12-13]. The importance of porosity as an indicator for anode quality was highlighted by Galisiu et al., who proposed the ratio of large porosity (pore diameter > 7.5 μm) by total porosity as a proxy for anode quality. There was a strong correlation between the porosity ratio and anode performance [14].

The cost of a carbon dusting crisis is estimated at 80 \$ per tonne aluminium [46]. At 14 MWh per tonne, the EBITDA per tonne could calculate to 140 – 800 \$ [88]. These numbers show the financial urgency to resolve a dusting crisis.

6. Summary

The presented work set out to investigate the origin and distribution of carbon particles in industrial aluminium reduction cells.

- The carbon particles found in the samples ranged from 2 µm to 30 mm, revealing the range of the problem. While larger particles can be removed with cavity cleaning, fine particles have to agglomerate before attempting removal.
- It was not possible to distinguish the origin of carbon particles (anode or cathode carbon) with the applied methods and the limited number of samples. However, it was possible to visualise carbon and alumina particles within a cryolite matrix.
- The fundamental transporting mechanism for the particles has not been found and no underlying distribution pattern could be found. The models could only explain up to 19.08 % of the variation.
- The theoretical mechanism of sodium intercalation and wettability were combined with the particle sizes found to identify particles, which float in the electrolyte or rise to the surface due to relative density.

With today's published knowledge, the use of carbon anodes will likely continue for at least 15 years, even if the inert anode research has been pushed by projects like ELYSIS or Arctus Aluminium [89-90]. Anode problems can still hinder progress and capacity creep, even in modern smelters [91-92]. Today, carbon consumption is the biggest contributor of direct carbon emissions from our industry. To fulfill prosperity and a green transition in the energy sector, demand for aluminium will only grow in the coming years [93-94].

Creating a common understanding for processes and materials instead of playing a blame game between carbon plants and electrolysis departments can help to mitigate the effects of non-optimal anodes in a smelter without heading into a crisis.

7. References

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