TRAVAUX 48, Proceedings of the 37th International ICSOBA Conference and
XXV Conference «Aluminium of Siberia», Krasnoyarsk, Russia, 16 – 20 September, 2019

Linking Electrochemistry, Modern Aluminium Cell Design and Operating Conditions, for a Better Understanding of Anode Reactions and Various Levels of PFC Co-evolution

Part 1: Changes in Cell Reactions as Raw Materials and Cell Designs have Evolved.

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Abstract

Aluminium smelting has always been an evolving process. As a consequence of environmental concerns, control automation, and growth in cell size, there have been changes in the quality of raw materials used as well as changes to the physics of mass transfer within the cell. The alumina shifted from being well calcined "sandy" or "floury" mix of alpha and gamma phases, to one that includes approximately 5 % boehmite (AlOOH), a more stable soluble hydroxide in the electrolyte. Simultaneously there have been increases in sulfur and other impurity levels in the baked anodes. Meanwhile, the volume of the electrolyte in modern cells (per kA) is less than 30 % of what it was, and the area over which the alumina is distributed for dissolution in the cell is reduced also. Better magnetic compensation coupled with the advent of slots in the anodes have also dramatically reduced the driving force for electrolyte mixing introducing spatial variations in cell conditions. The situation is made worse by the longer anodes increasing the travel path for its distribution. Consequently, spatial variations in cell conditions have become more prevalent and with the traditional methods of operation and control of the cells there is an increase in the ease with which PFC co-evolution can occur.

This paper looks at the scientific and practical background of all anodic reactions that can occur and the conditions that contribute to variations in the proportion of each reaction. It simultaneously raises questions on how applicable the past mechanistic interpretations of the anodic processes are, since they have ignored the need to provide the entropic energy of each reaction. With the increase in size of cells, changed cell conditions and work practices, spatial variations can occur more readily and these can have adverse effects on the greenhouse gas footprint. In order to discuss the options to minimise this trend, the understanding of all factors contributing is presented here.

Keywords: Aluminium reduction, anode reactions, gas products, PFC co-evolution, spatial variation.

1. Introduction

The cell design, control, performance and operating conditions of aluminium smelting cells are continuously evolving in order to reduce production costs, minimise the environmental impact, and use the energy more efficiently. Each change brings about a consequential impact, which can affect the basis of the models on which the design and predictions have been based, but at times some of the impacts are overlooked when models are updated. Therefore, the purpose of this paper is to present a better understanding of what happens within the cell so that models can move from simplifications of the past as the margins of gain have become narrower.

The essential ingredients for aluminium smelting are alumina, a suitable fluoride-based solvent for it, anode carbon and electrical energy. The final stage of the Bayer process for producing smelter grade alumina involves a calcination step to convert the aluminium trihydrate ($Al_2O_3{\cdot}3H_2O$) to the smelter grade product. Originally this was performed by rotary kilns, which have a long residence time, leaving a moisture-free product described as either 'sandy' or 'floury'.

The cell design and operating practices enabled the solvent electrolyte to come in contact with moist air and hydrolyse according to the overall reaction:

$$2Na_3AlF_6(l) + 3H_2O(g) = 6NaF + 6HF(g) + Al_2O_3 \tag{1}$$

which becomes thermodynamically favoured once the temperature exceeds 900 °C. The reacting water could also come from a limited amount absorbed by the non-alpha alumina phases.

The introduction of fluid-bed calcination for aluminas increased the rate of emission of gaseous (HF) and particulate ($NaAlF_4$) fluorides, and the combination of these emissions often upset the ecosystem surrounding smelters and adversely impacting both vegetation and animals. Consequently, hooded cell design modifications were introduced and these were subsequently coupled with dry scrubbing technology. However, coupled with optimising the capture efficiency of the HF, the level of calcination of the trihydrate in the fluid-bed process was reduced in order to provide adequate surface area for efficient HF capture. This resulted in a significant fraction of the Bayer alumina feedstock (~ 5 %) being in the hydroxy-oxide form $Al_2O_3{\cdot}H_2O$, which gives rise to a stable hydroxyl anion in the smelter's electrolyte.

Furthermore, the available raw materials and production of anodes have changed over time; anodes today typically have in excess of 2 wt.% S, which can be electrochemically oxidised[1].

With the various changes in smelting cells design, raw materials, work practices and control, new electrochemical reactions are introduced, and these are reviewed here to form a basis for developing better operational and control paths in the future.

1.1. Electrochemical Laws Controlling Parallel Reactions

In electrochemistry the rate of any reaction (i_i) is given by the current carried by that individual reaction and the stoichiometry involved. Where multiple parallel reactions are occurring, the cell current (I_{cell}) is given by:

$$I_{cell} = \sum i_i \tag{2}$$

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[1] While there is significant sulfur impurities in the anodes, discussion of reactions involving sulfur are not included in this paper. Practically, it has been shown [1] that it is electrochemically oxidized and released from the anode as COS(g). As it cools and permeates through the crust, it decomposes, giving rise to a range of products including carbon dust, CS_2(g) and elemental sulfur. The proportion that leaves with the anode gas burns to sulfur dioxide in the flame. Analysis of the secondary sulfur reactions shows that they only have a minor impact on the energy balance.

the superheat, which influences the resulting transfer between the electrolyte and active anode surface.

2. Critical for environmental performance there is a need to ensure the interfacial anode potential is kept significantly below 1.8 V for all anodes. In order to achieve this:
   a. Conditions need to ensure fast alumina dissolution with good mixing of the electrolyte from the feeders to all the zones of the cell.
   b. The current density of individual anodes is constrained (see below). This is especially so following anode set and the current redistribution.
   c. To minimise the imbalance after anode set, slow anode current pickup to target value needs to be avoided.

3. PFC co-evolution is not confined to anode effects as cells and individual electrodes can continue emitting low levels of CF_4 without any signs of what classically design defines an anode effect.
   a. As a consequence, the present industry definition of an anode effect is too conservative and will result in more significant underreporting of PFC emissions from smelters. Current estimation methods are being updated.

To close, the theoretical development for cell operation and control have been on the assumption that all anodes are behaving the same. Cells operate at constant total current, and under a constrained voltage, which is influenced by the current distribution between anodes and the electrochemical processes occurring at each. While we can get a measure of voltage, we cannot have any measure of the interfacial anode potential, which is one of the two determining factors causing swings in anode reactions and energy efficiency. Spatial variations therefore need to be minimized and then compensated for in some appropriate way in order to optimise the cell's environmental and energy performance.

6. Acknowledgements

The contents of this paper has been generated by an extensive team of co-workers over many years that the authors have been proud to be associated with. Thanks to their efforts we are getting close to completing the jigsaw puzzle. The special thanks to Rod Farr-Wharton, Richard Haverkamp, Edwin Patterson, Alton Tabereaux and Sheryl Hume. And thanks to Halvor Kvande for critical editing and comments.

7. References

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