

## Arguments for Keeping Uniform Alumina Concentration and Anode-Cathode Distance in Aluminium Electrolysis Cells

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### Abstract

Four main topics related to non-uniformity in aluminium electrolysis cells are treated in this paper. i) The alumina concentration can vary by 2 wt% throughout the bath, which is the root cause of the low voltage anode effect (LVAE). By using a statistical method, a general chart separating the fields for LVAE and high voltage anode effect (HVAE) could be derived. Both types of AE occur at higher average alumina concentration when the concentration is less uniform. ii) Anodic current distribution can be used as a rough measure of the standard deviation in the anode-cathode distance (ACD); e.g., 12 % standard deviation for the current distribution corresponds to 5 mm standard deviation for the ACD. It is suggested that variation in ACD is caused by perturbation of the metal pool surface each time anodes are replaced due to Lorentz forces and bath density variations. iii) A simple formula for the effect on local ACDs by local bath density variations due to non-uniform alumina concentration was derived. It was shown that the time for equalisation of individual ACDs by current dependent anode wear is longer than the time between anode shifts. This entails that the ACD always varies with time and position. iv) Non-uniform ACD may be detrimental to the current efficiency (CE) because gas bubbles and metal waves can contact each other underneath anodes with low ACD. The effect is more severe when the average ACD is low.

**Keywords:** Alumina, Anode-cathode distance, Anode effect, Current efficiency.

### 1. Introduction

The alumina concentration in the electrolysis bath varies significantly with time and position. The concentration in samples taken simultaneously at different locations can vary by at least 2 wt% [1-3]. The variation affects the onset of anode effect, the individual anode-cathode distances (local ACD), the anodic current distribution, and the current efficiency (CE). These items are all related to the alumina distribution.

During anode effect perfluorocarbons (PFCs) evolve (tetrafluoromethane, CF<sub>4</sub> and hexafluoroethane, C<sub>2</sub>F<sub>6</sub>). The PFC generation due to the "classic" high voltage anode effect (HVAE) has been significantly reduced during the last three decades [4]. The first news about PFC evolution during apparently normal electrolysis stems from a report by the Research Institute of Chalco in 2009 [5]. It turned out that this was caused by a "new" class of AE, today termed LVAE. The LVAE is strongly linked to the alumina distribution. Methods for calculation and consistent reporting of PFC from LVAE are still being developed [6].

It has been substantiated [7, 8] that changes in local bath density due to variable alumina concentration affect the local bath depth, and thereby the local ACD. While it is generally accepted that the metal-bath interface is curved due to magnetic forces, the present author has experienced that many are sceptical about a similar effect of density variations – perhaps because it feels intuitively wrong that a liquid-liquid interface should be non-horizontal in absence of external forces. Moreover, the effect of variable density in a system of two immiscible liquids is

not treated in common textbooks. The effect is the same as when the sea level increases locally due to low atmospheric pressure.

It was suggested that the CE may become low due to direct contact between metal waves and gas bubbles at low ACD [9]. Too large variation in ACD will then be detrimental to the CE because several anodes will be below the critical limit where the metal loss becomes significant. The present paper does not contain radical or new thoughts, and most of the contents has been published earlier [7-10]. Still, it may be useful to take a step back and contemplate several pieces in the puzzle to see the entire picture. The main purpose is to demonstrate how non-uniformity brings about several adverse effects, which can be estimated by statistical methods.

## 2. A Statistical View on Anode Effects

### 2.1 Theoretical Treatment

A statistical analysis of the anode effect was recently published [10]. The idea was that the regions of LVAE and HVAE could be estimated from the mean alumina concentration and the standard deviation. A summary of the calculations and results is given in the following.

The anode effect starts when the alumina concentration at the anode surface becomes virtually zero, resulting in the formation of a non-conducting  $CF_x$  film blocking of the current at a part of the anode. If the rest of the anode can handle the increased current density, the AE will remain local (LVAE). If not, the AE will spread rapidly to the entire anode (HVAE) as explained by Thonstad et al. [11]. An LVAE can take place not only at entire single anodes, but also locally on a part of a single anode block. If the LVAE affects a significant part of an anode, it can be detected in prebake cells equipped with individual anode current measurement [12]. However, it will be difficult to discover if only a minor area is affected. Söderberg cells probably also have LVAEs, due to their highly irregular surface on the bottom of the anode, but they are even harder to reveal.

Alumina is transported to the anode by diffusion (ordinary mass transfer). The "critical" alumina concentration ( $c_c$ ) is the bulk concentration when the surface concentration becomes zero. When the current is blocked at an area fraction of the anode ( $a_{AE}$ ),  $c_c$  increases at other parts of the anode:

$$c_c = \frac{c_c^0}{1 - a_{AE}} \quad (1)$$

If there is enough alumina elsewhere, only the passivated part of the anode will be affected. The possible spreading of the AE depends on the concentration distribution, and the problem therefore lends itself to statistical treatment.

The alumina concentration ( $c$ ) has a mean value ( $c_m$ ), a standard deviation ( $\sigma$ ), and a certain probability distribution ( $p$ ) around the mean value. The familiar Gaussian "bell curve" was used, which has the probability distribution formula:

$$p = \frac{1}{\sigma\sqrt{2\pi}} \cdot \exp\left\{-\frac{1}{2}\left(\frac{c - c_m}{\sigma\sqrt{2}}\right)^2\right\} \quad (2)$$

The cumulative distribution ( $a$ ) represents the area underneath the probability distribution curve at a certain  $c$ , in our case the fraction of the anode that is at AE (erf is the error function):

Putting an end to anode replacements would largely eliminate ACD variation caused by Lorentz forces as well as changes in bath density, but variation related to sludge or bottom ledge may not be eliminated. Several patents concerning continuous prebaked anodes have been filed in the past (e.g., see refs. [21-23]). Even though the use of continuous anodes in modern cells has not been considered successful, it should be mentioned that such anodes were operated for more than 20 years at Rheinwerk, Germany [24], indicating that the technology is not entirely impracticable. Maybe it's time to wipe off the dust from the concept of continuous prebaked anodes?

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