

Low Voltage Anode Effects and Unreported PFC Emissions

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Abstract



It has been established in a number of industrial plant measurements that low voltage anode effects (LVAE) occur in primary aluminum electrolysis cells with the emission of perfluorocarbons (PFCs), CF_4 and C_2F_6 . These LVAE are more common in modern high amperage cells that have twice the number of anodes, e.g., 40 - 48 anodes compared with about 24 anodes in small 100 to 250 kA prebake cells. The emission of PFCs during LVAE is not currently reported by plant computer process control systems because they occur below the usual 6 to 8 V detection limit. The causes for the propagation of anode effects on individual anodes during high voltage anode effects versus the non-propagation of anode effects on individual anodes during LVAE is discussed. The trend to reduce the specific energy consumption by reducing the anode-cathode distance has been shown to have an impact on reducing the maximum voltage as well as the duration of LVAE in cells due to electrical shorting between anodes and aluminum metal waves.

Keywords: Low voltage anode effects; anode effects on individual anodes; PFC emissions; reporting of PFC emissions.

1. Introduction

Aluminum is produced industrially by electrolytic reduction of alumina (Al_2O_3) dissolved as ions in a cryolite based molten salt electrolyte, or bath. Alumina is added to cells by multiple point break feeders in cells that break holes in the top alumina crust of bath between two adjacent rows of anodes. The point feeders add 1 to 2 kg of alumina per feeder into the liquid electrolyte at each discharge. The dissolved alumina concentration in bath is regulated from about 1.5 to 3 % by a series of underfeed and overfeed alumina operations with the point feeders using state-of-the-art computer alumina feed control algorithms.

Failure to replenish or uniformly distribute dissolved alumina throughout the electrolysis cell results in an anode effect (AE), a phenomenon where ionic fluoride species are electrolyzed instead of alumina when polarization increases the anode potential above the decomposition potential of other dissolved ionic species. Anode effects typically occur when the concentration of alumina dissolved in the bath becomes too low, typically below 1.5 %.

Aluminum electrolysis cells operate at constant current, thus the formation of a highly electrical resistive carbon-fluoride intermediate film on the bottom surface of carbon anodes causes the cell voltage to increase very rapidly from about 4.2 V up to anywhere as high as > 30 V, causing the electrolyte temperature to increase to > 1000 °C. Additional heating occurs due to localized electrical arcing of the resistive film.

It is clear that anode effect starts at a localized location probably due to a local low alumina concentration under some anodes. This can be caused by a combination of a insufficient transport of alumina underneath the anode, low bath immersion, low superheat or carbon dust blocking the surface of the anode. The bath flow underneath anodes can be constrained by reducing the ACD resulting in greater extremes of alumina concentration under anodes.

2. Initiation of Anode Effects

Anode effects are known to be caused by the depletion of alumina in electrolyte at which point anode polarization increases the local potential above other ionic species decomposition potentials and the cell then goes into anode effect.

- Anodes become more de-wetted, (less anode surface area in contact with molten bath) as the alumina content in bath becomes lower thus increasing the anode polarization potential due to the higher current density.
- Different anodes start to draw different amounts of current and the alumina concentration becomes more non-uniform in the cell as the pot gets closer to anode effect. Anodes with higher current consume alumina at a faster rate.
- An anode effect is usually initialized at a single anode and then propagated to the rest of the anodes. The anode effect eventually spreads in a cascading series phenomenon as the current density and potential increases significantly on the remaining anodes until all anodes in the cell are on “full” anode effect.
- The electrolysis reactions change from being a predominately CO₂ producing reaction to a more CO (60 – 70 %) producing reaction.
- Fluorine ion discharged at the anode reacts with the carbon forming the PFC by-product gases, CF₄ and C₂F₆.

The standard potentials required for the decomposition of cryolite and discharge of CF₄ and C₂F₆ are 2.175 V and 3.394 V respectively, which are much higher than the -1.191 V potential necessary for the formation of CO or CO₂ according to Welch [1] as shown in Table 1. However, the changeover from solely oxide ion discharge (forming CO or CO₂) to co-discharge of the fluoride intermediate, COF₂ occurs at a much lower anode potential, 1.685 V, which is achievable due to the increase in polarization potentials on anodes. The low alumina concentration and corresponding higher polarization potential in the cell is the cause for the shift in reactions. Although under most circumstances it is more difficult to break the carbon-carbon bonds the increasing lack of oxygen bearing anions leads to the competing reaction becoming more favourable.

Table 1. Standard potentials for overall reactions in aluminum electrolysis cells [1].

#	Reaction	E°(V) at 960 °C
1	$\text{Al}_2\text{O}_3 + 3\text{C} = 2\text{Al} + 3\text{CO}(\text{g})$	1.074
2	$\text{Al}_2\text{O}_3 + 1.5\text{C} = 2\text{Al} + 1.5\text{CO}_2(\text{g})$	1.191
3	$\text{Al}_2\text{O}_3 + 2\text{AlF}_3 + 3\text{C} = 4\text{Al} + 3\text{COF}_2(\text{g})$	1.685
4	$\text{Al}_2\text{O}_3 + 2\text{Na}_3\text{AlF}_6(\text{l}) + 3\text{C} = 4\text{Al} + 3\text{COF}_2(\text{g}) + 6\text{NaF}(\text{l})$	1.863
5	$1.33\text{AlF}_3 + \text{C} = 1.33\text{Al} + \text{CF}_4(\text{g})$	2.175
6	$2\text{AlF}_3 + 2\text{C} = 2\text{Al} + \text{C}_2\text{F}_6(\text{g})$	3.394

The change-over from aluminum cells typically producing 90 % CO₂, (70 % CO₂ just prior to AEs) and 10 % CO, (30 % CO prior to AEs) to the co-evolution of 20 % CO₂, 70 % CO, 20 % CF₄ and 1 % C₂F₆ during the AE as shown in Figure 1 was reported by Tabereaux, et.al [2].

distribution as they occur more often after anode setting at specific anode locations, e.g., corner anodes.

In the future, to eliminate or significantly reduce PFC emissions during low voltage anode effects in high amperage cells, requires development of affordable individual anode current monitoring sensors that are robust in potroom environment and innovative computer algorithms that can rapidly recognize current imbalances in anodes and take the necessary corrective actions such as moving the anode beam up/down to prevent low voltage PFC emissions.

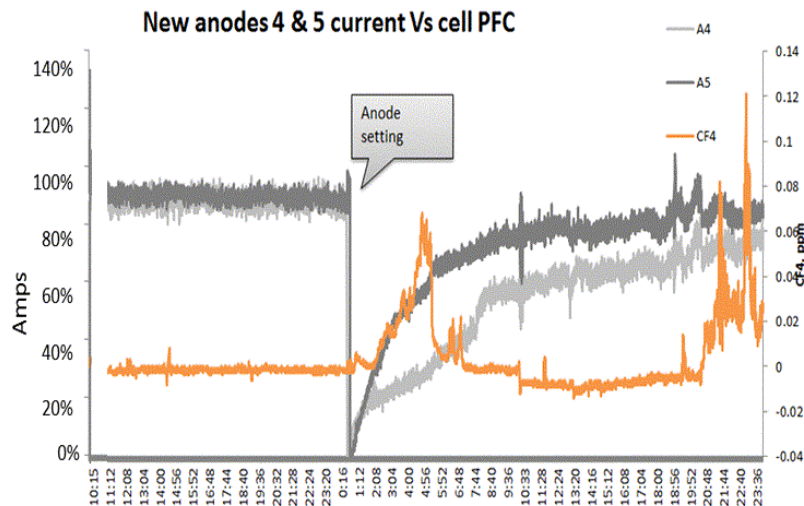


Figure 8. CF4 emissions during a low voltage AE following an anode set operation, Jassim [9].

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