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 CO_2 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, CF_4 and C_2F_6.

The standard potentials required for the decomposition of cryolite and discharge of CF_4 and C_2F_6 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 CO_2 according to Welch [1] as shown in Table 1. However, the changeover from solely oxide ion discharge (forming CO or CO_2) to co-discharge of the fluoride intermediate, COF_2 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	$Al_2O_3 + 3C = 2Al + 3CO(g)$	1.074
2	$Al_2O_3 + 1.5C = 2Al + 1.5CO_2(g)$	1.191
3	$Al_2O_3 + 2AlF_3 + 3C = 4Al + 3COF_2(g)$	1.685
4	$Al_2O_3 + 2Na_3AlF6(l) + 3C = 4Al + 3COF_2(g) + 6NaF(l)$	1.863
5	$1.33AlF_3 + C = 1.33Al + CF_4(g)$	2.175
6	$2AlF_3 + 2C = 2Al + C_2F_6(g)$	3.394

The change-over from aluminum cells typically producing 90 % CO_2, (70 % CO_2 just prior to AEs) and 10 % CO_2, (30 % CO prior to AEs) to the co-evolution of 20 % CO_2, 70 % CO, 20 % CF_4 and 1 % C_2F_6 during the AE as shown in Figure 1 was reported by Tabereaux, et.al [2].

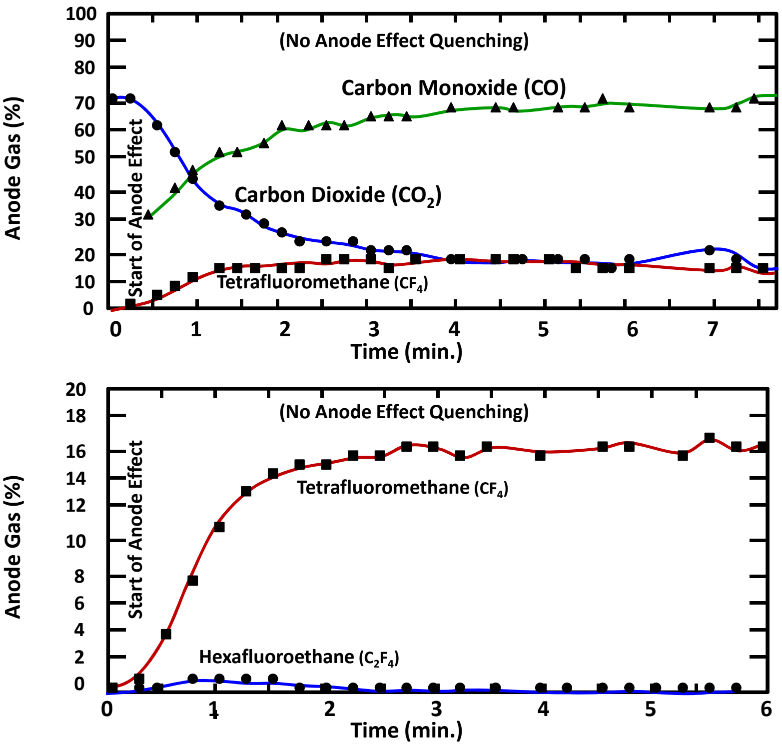

Figure 1. Anode gas products before and during an anode effect.

Prior to the onset of anode effect one more of the anodes begins to under-load (lower current) with respect to the rest of the group as shown in Figure 2 due to the initial production of a film of PFCs on anode surfaces as reported by Tarcy and Tabereaux [3]. This shifts the amperage that the under-loading was carrying to the other anodes in the circuit increasing the current density as well as increasing the polarization potential and the rate of alumina consumption under those anodes. Navarro et al. [4] provided data that showed that one or more prebake anodes go on anode effect ~ 60 seconds prior to the sudden increase in pot voltage when the entire cell reaches anode effect.

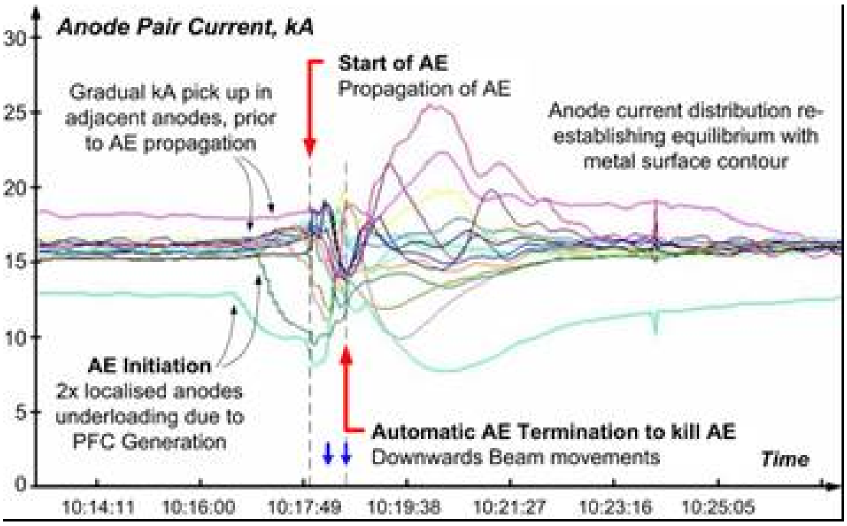

Figure 2. Anode current distribution before, during and after an anode effect.

The overall low alumina concentration in the pot then leads to more anodes reaching the anode potential required for generation of PFCs. In the end the anode effect eventually spreads in a cascading series phenomenon as the current is transferred to the remaining anodes and the polarization potential increases significantly until all anodes in the cell are on anode effect. The highly irregular current distribution after the anode effect is due to the after effect oscillations in the metal pad surface.

3. Rate of PFC Emissions

The rate of PFC emission, (kg CF_4 per minute) during anode effects has been established for different cell technologies based on actual PFC emission measurements from industrial cells in aluminium potlines for the duration over which cells have their anode effect as reported by Marks and Bayliss [5].

$$\frac{kgCF_4}{tAl} = S \times AEF \times AED \tag{1}$$

where:

AEF	Average anode effect frequency (AE/potday)
AED	Average anode effect duration (minutes)
S	Technology specific factor for the emission rate in kg CF_4 per AE minute.

4. Terminating Anode Effects

Anode effects are typically terminated in prebake cells using automatic anode effect termination programs by the potline computer process control system. First, a large quantity of alumina is rapidly added to the bath by the point feeders to increase the alumina content uniformly in the bulk bath all around the cell; secondly, the anode beam (with all anodes) is then moved down in several sequences to decrease the anode-to-cathode distance (ACD) until electrical short-circuits are formed between anodes and aluminium waves. Anode effects can often be terminated quickly, 5 to 15 seconds, using this practice. Due to the low ACD in low energy cells operating at low cell voltages, ~ 3.8 V, very small anode down moves are required until MHD instability occurs and a self-sustained wave develops that causes instant short-circuits with anodes.

In addition to the ultra-rapid feed of alumina to bath by point feeders during the anode effect, the increase in anode immersion and the intense bath circulation produced by the metal wave causes the liquid bath to come into contact with the anode cover which is a source of alumina all around the pot. Another source of alumina is by some sludge dissolution that is removed by the metal waves from the cathode surface. The intense bath circulation due to metal waves and high bath temperature (> 1000 °C) quickly increases the alumina concentration overall in the cell bath and importantly makes it more homogeneous throughout the cell thus diminishes any localized alumina depleted regions of the cell.

5. Anode Effect Detection and Accounting of PFC Emissions

Through the industry’s own voluntary efforts in the past three decades, smelters globally have been very active in targeting PFC emissions, by addressing both the frequency and duration of AEs. The aluminum industry has made great strides in reducing AEF and AED from conventional AEs. PFC generation from AEs has traditionally been associated with a rapid, exponential increase in total voltage measured across a reduction cell. AEs are typically detected by computer control systems when cell voltage exceeds a predefined voltage threshold, for more than a specified time interval. For example, a common definition of AE is when cell voltage exceeds 8 V threshold cell voltage for more than 3 consecutive seconds.

6. Categories of Anode Effects

Conventional anode effects (by definition voltage > 8 V) are typically initiated under 1 - 2 individual anodes when their anode potential exceeds *threshold potential* for co-generation of CF_4 and C_2F_6 gases. Current load transfers to adjacent anodes, which increased polarization potential and results in very rapid propagation of AE to rest of anodes. The cell voltage rises exponentially upon AE propagation reaching 18 - 50V. CF_4 emissions rapidly increase to about 20 % and remain nearly constant if there are no short circuits. When the AE is terminated, CF_4 emissions decreases to 0 % and the cell voltage rapidly drops back to normal levels.

There is a growing awareness in Al industry of unaccounted PFCs generated outside conventional AE definition as described by Wong, et al [6, 7]. These AEs are non-detected low voltage AEs that occur below the 8 V threshold. PFCs generated in such scenarios are not declared by smelter control systems as anode effects as they are either:

- Low-Voltage Propagating Anode Effects (LVP-AE): anode effects that have discrete small PFC emission signatures very similar to conventional AEs, but exhibit peak overall cell voltages that fall below the threshold cell voltage (e.g., < 8 V) used by control systems.
- Non-Propagating Anode Effects (NP-AE): Continuous background level of PFC emissions below the 8 V threshold voltage; they do not appear to have the same discrete voltage or PFC emission characteristics as low-voltage propagating AEs.

Modern high amperage cells have a greater propensity for low voltage AEs due to spatial alumina concentration gradients in long cells with a high number of anodes per cell especially when operating at low voltage (~ 3.8 V) and low ACD.

7. Evolutionary Changes in Cell Technology in Higher Amperage Cells

LVP-AEs & NP-AEs are more prevalent for large, high amperage (300 to 500 kA) prebake cells which have the common features: very long (18 m) with high number of anodes (40 - 48) and operated with lower bath volumes and increased alumina per point feeder than smaller, low amperage cells. These high amperage cells have very stable magnetic designs with low metal velocity and minimum surface curative and are currently operating at a low energy consumption ~ 12.5 kWh/kg Al and low cell voltage ~ 3.85 V.

Lavoie et al. [8] indicate that the drive to increase productivity resulted in the need to feed and dissolve more alumina in less electrolyte. There is mounting evidence that these two trends are pushing the electrolysis cells above their capability to maintain alumina concentration, through time and space, at levels preventing both conventional and non-propagating anode effects. These modern cell characteristics tends to restricts local Al_2O_3 transport, thus promote large Al_2O_3 concentration gradients. This helps limit AE propagation to all anodes in the entire cell as it is less likely for anodes to reach threshold potential for C-F generation and it reduces impact of anodes on AE on adjacent anodes.

The Pechiney AP cell technology has evolved from the AP18 low current density 0.75 $A.cm^2$ cell technology developed in the 1970's to the AP30-AP60 high productivity technology designed to operate at higher current density. Aluminium production is proportional to their operating amperage, which has increased over decades with each design iterations and done in conjunction with lengthening of cells.

- AP18 cell operates at 180 kA with 18 anodes and is 9 meters in length
- AP30 cell operates at 300 - 400 kA with 40 anodes and is 14 meters in length
- AP60 cell operates at 600 kA with 48 anodes and is 18 meters in length.

Forté et al. [9] pointed out that these evolutionary changes in AP cell dimensions from 180 kA to 600 kA shown in Figure 3 have resulted in some fundamental changes in cell operations with the lower bath mass and higher alumina throughput per alumina point feeder. The mass of molten bath in cells decreased threefold from 30 kg bath per kA for AP18 cells to 12 kg bath per kA for 600 kA cells due to the decrease in available cathode cavity volume as a result of increases in anode dimensions necessary at higher amperage operations. The amperage per point feeder (and thus the quantity of alumina) increased in cells twofold from 60 kA per point feeder for 180kA cells to 120 kA per point feeder for AP60 cells.

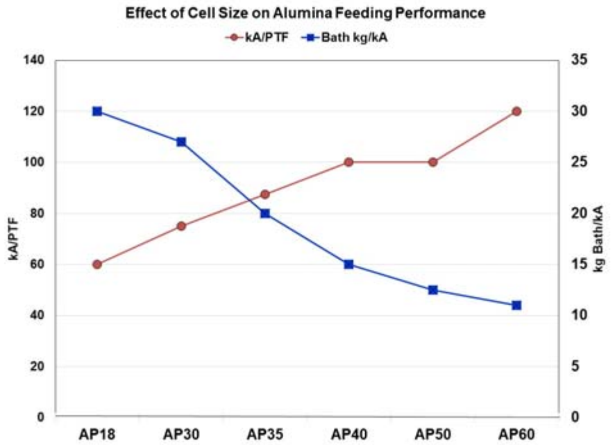

Figure 3. Impact of increased AP cell size on decreasing the bath volume and increasing alumina throughput per point feeder.

8. Calculation of Anode Current Density vs. Number of Anodes on AE.

Wong et al. [6] suggested that large cells with a higher number of anodes are less likely to have conventional AEs compared with small cells, but instead are more likely to have LVP-AE or NP-AEs. The increase in anode current density for a 200 kA Cell with six of the 24 total anodes on AE is compared in Figure 4 with a 400 kA cell six of its 48 anodes on AE.

- With six anodes on AE, the current density (> 1.0 A/cm^2) and polarization potential increases with a rapid cascading effect on the remaining 18 anodes of the 200 kA cells causing propagation of the AE to all other anodes in the entire cell.
- With six anodes on AE, the increase in current density (0.85 A/cm^2) and polarization potential is much lower on the remaining 42 anodes on the 400 kA cell; thus the AE is not propagated and is limited within local area of the cell.

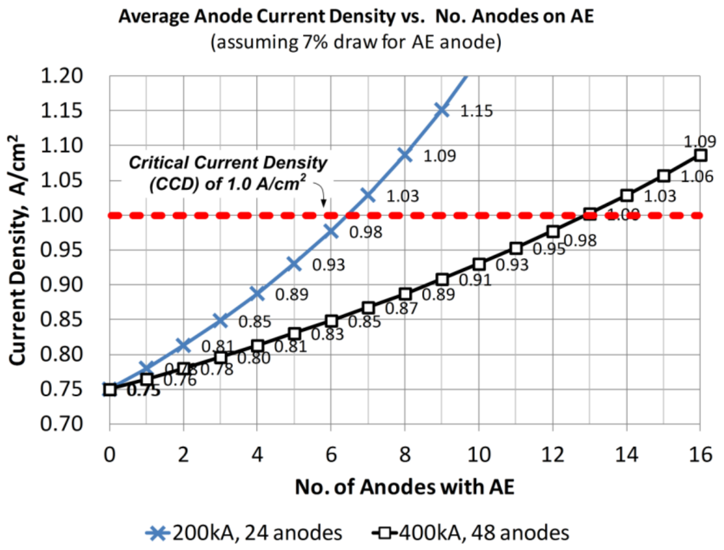

Figure 4. Comparative difference in the increase in anode current density for a 200 kA and 400 kA cell with six anodes on AE.

9. Calculation of Cell Volt vs. Number of Anodes on AE

Calculations by Wong et al. [6] indicate that the 200 kA cell has a much greater increase in Cell V vs. 400 kA due to same number of anodes on AE. Results explain why large kA cell with many anodes can have limited section of anodes on AE but remain < 8 V trigger (LVP-AE) and they can have 1 - 2 anodes on AE, but still not display a significant difference in Cell V (NP-AE).

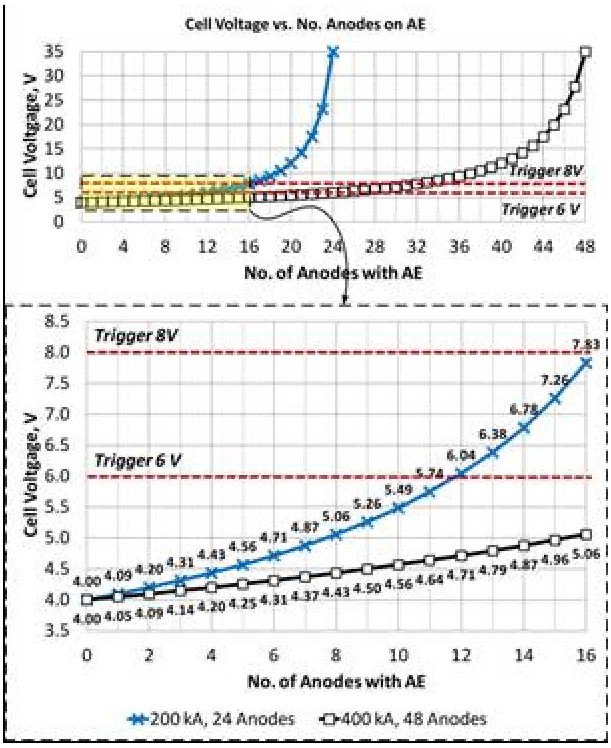

Figure 5. Comparative difference in the increase in cell voltage for 200 kA and 400 kA cell with increasing number of anodes on AE.

The increase in cell voltage for a 200 kA cell is compared in Figure 5 with a 400 kA cell with increasing number of anodes on AE. The 200 kA cell requires 12 anodes to be on AE to increase cell voltage by 4.0 V to 6.0 V and 15 anodes to be on AE for an increase from 4.0 V to 8.0 V. Comparatively, in the 400 kA cell, > 12 anodes to be on AE to increase cell voltage from 4.0 V to 6.0 V.

The analysis explains why large 400 kA cells with high # of anodes can have limited section of anodes on AE but remain < 8 V trigger (LVP-AE) as well as have 1 - 2 anodes on AE, but still not display a significant difference in Cell V (NP-AE).

10. PFC Emission Signatures for Conventional Anode Effect Emissions and Voltage Peaks

Typical PFC emission signature peaks for conventional AEs are characterized by Tabereaux [10] as a rapid rise in PFC emissions together with a simultaneous sudden rise in cell voltage above 8 volts followed by a quick decrease in PFCs and cell voltage. However, the PFC emission peak profiles can vary greatly depending on the anode effect kill strategy employed.

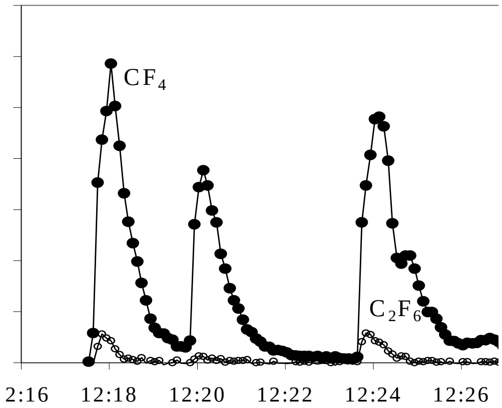

Figure 6. Typical short CF_4 and C_2F_6 emission peak profiles of conventional anode effects.

The major difference in PFC emission between individual prebake smelters especially those using the same technology is largely due to differences in the anode effect termination strategy. The emission of PFC gases stops, or are greatly reduced, each time anodes are short-circuited with metal. Thus the manner and timing in which the anodes are lowered to cause short-circuit with the metal pad waves in order to terminate the anode effects has a great influence on the rate of PFC generation in prebake cells.

“Anode pumping” uses sequential slow multiple cycles of reducing and increasing the ac-distance until short-circuits occur with metal waves that terminates the AE, usually in 3 to 4 minutes. Slow pumping of anodes characteristically results in several emission peaks of PFC gases during the same anode effect. Modified “anode pumping” utilizes faster, deeper anode down moves until short-circuits occur with metal waves that terminates the AE usually in 1 to 2 minutes. Faster “anode pumping” usually results in lower emission peaks of PFC gases during anode effects.

Fast AE termination strategy utilizes fast aggressive anode down moves and makes contact with MHD self-sustained waves that causes short circuits with anodes and terminate the AE in less than 1 minute. Deep fast anode down move of anodes generally results in only one small emission peak of PFC gases during anode effects. Very small anode down moves are required in low energy cells operating at low cell voltages (~ 3.8 V) due to the low ACD between anodes and the metal waves.

11. PFC Emission Signatures and Voltage Profiles for Unaccounted Low-voltage Propagating and Low-voltage Non-propagating Anode Effects

Wong and Marks [11] measured the PFC emissions in 400 kA cells with 48 anodes and operating at 3.8 V. They confirmed the difference in emissions signatures of low voltage conventional type anode effects and low voltage continuous emission.

The sharp PFC emission peak illustrated in Figure 7 is less than then 8 V “trigger” voltage and thus it is a non-detected low voltage AE. The low voltage indicates that the AE was not propagated to other anodes in the cell. The shortness of the AE and voltage peaks indicate that the AE was probably “self-terminated” due to localized shorting caused by increased metal waves instability current imbalances during the AE; additionally, the anodes were at a shortened ACD with the cell operating at 3.8 V. An anode effect was confirmed by measurements of two under-loading anodes followed by partial propagation to other anodes in the cell.

A non-detectable low voltage CF_4 emission peak was measured to have occurred about 16:45 hour as the cell voltage was less than 8 volts. After the cell voltage returned to normal, a continuous “back ground” emission of low voltage PFC persisted in the cell. The continuous emission of PFCs is an indication of localized AE.

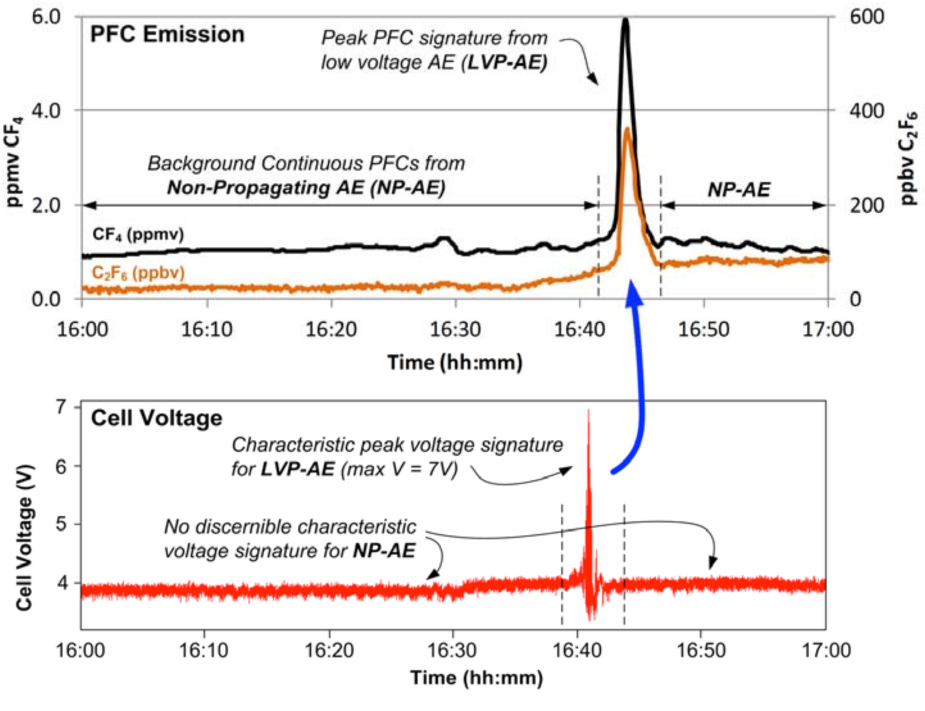

Figure 7. Typical PFC emissions and cell voltage profile during a low voltage AE.

Jassim et al. [12] indicated that low voltage CF_4 emissions frequently occur in high amperage cells after changing anodes due to spatial changes in anode current density and/or alumina concentration as shown in Figure 8. Increasing current density at localized locations increases the alumina depletion rate causing the formation of spatial alumina concentration gradient condition while at the same time lowering the wettability of anodes and increases the current density and ultimately increases polarization of anodes beyond the enabling limits of PFC formation. The co-evolution of PFCs was found to be sensitive to imbalances in anode current 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.

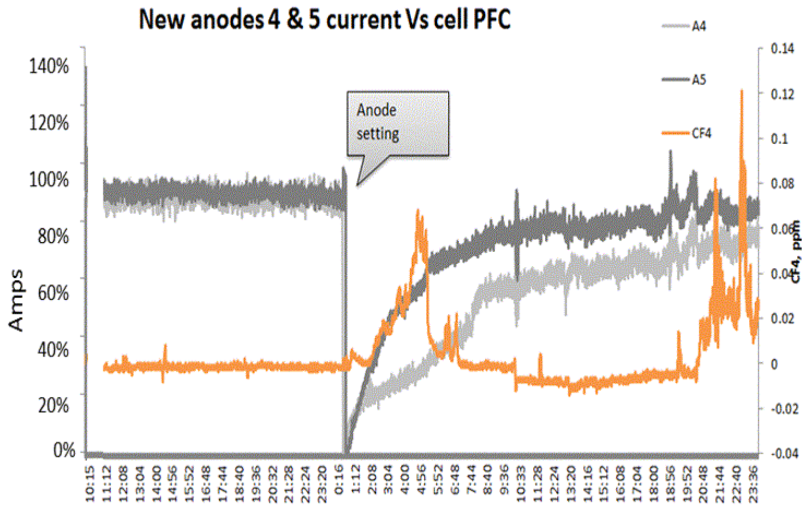

Figure 8. CF4 emissions during a low voltage AE following an anode set operation, Jassim [9].

12. References

1. Barry J. Welch, *10th Australasian Aluminium Smelting Technology Conference*, Launceston, Tasmania, 9–14 October 2011.
2. Alton T. Tabereaux, Nolan Richards and Charles Satchel, Composition of reduction cell anode gas during normal conditions and anode effects, *Light Metals* 1995, 325-333.
3. Gary Tarcy and Alton T. Tabereaux, The initiation and propagation of anode effects, *Light Metals* 2011, 329-332.
4. Pablo Navarro, Gustavo Gregoric, Osvaldo Cobo and Alfredo Calandra, A new anode effect quenching procedure, *Light Metals*, 2003, 479-485.
5. Jerry Marks and Chris Bayliss, 2008 Global anode effect survey results, *Light Metals* 2010, 259-263.
6. David S. Wong, Alton T. Tabereaux and Pascal Lavoie, Anode effect phenomena during AEs, low voltage propagating AEs & non-propagating AEs, *Light Metals* 2014, 529-534.
7. David S. Wong, P. Fraser, Pascal Lavoie and J. Kim, PFC emissions from detected versus non-detected anode effects in the aluminum Industry", *JOM* February 2015, Vol. 67, Issue 2, 342-353.
8. Pascal Lavoie and Mark P. Taylor, Alumina concentration gradients in aluminum reduction cells, *Advances in molten slags, fluxes, and salts: Proceedings of The 10th International Conference on Molten Slags, Fluxes and Salts (MOLTEN16), TMS (The Minerals, Metals & Materials Society)*, 2016, 791-797.
9. Martin Forté, Martin Robitaille, Nicolas Gros, René Gariepy, Isabelle Mantha1, Louis Lefrançois, Jean-Pierre Figue, Arvida Aluminum Smelter – AP60 Technology Center, start-up performance and development of the technology, *Light Metals* 2015, 495-498.

10. Alton T. Tabereaux, Impact of AE kill strategies on CF_4 emissions", 9th *Austalasian AASTC*, Terrigal, Australia, 4 – 9 November 2007.
11. David S. Wong and Jerry Marks, Continuous PFC emissions measured on Individual 400 kA cells, *Light Metals* 2013, 865-870.
12. Ali Jassim, Sergey Akhmetov, Barry J. Welch, Maria Skyllas-Kazacos, Jie Bao and Yuchen Yao, Studies on background PFC emission in Hall-Héroult reduction cells using online anode current signals, *Light Metals* 2015, 545-550.