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A STUDY OF LOW VOLTAGE PFC EMISSIONS AT DUBAL

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Abstract

Perfluorocarbon (PFC) emissions are the result of a phenomenon called anode effect (AE), when normal electrolysis is discontinued due to lack of alumina and another reaction takes place leading to generation of PFC gases. Anode effects have been characterized in the industry by measuring their frequency and duration when the cell voltage is above 8 volts. Efforts have been made by the Aluminium Industry to reduce AE frequency and duration leading to considerable reductions in PFC emissions. However, recent independent measurements reported sources of PFC emissions that are “non AE related”. Measurements have been carried out on all DUBAL cell technologies in 2010/2011 and similar occurrences have been observed. DUBAL has initiated a program to identify the possible mechanism of the “non AE related” PFC emissions and to develop new logics for treating it. In this paper, a study of low voltage PFC emissions at DUBAL will be presented.

Introduction

AE occurs when the alumina concentration in the electrolyte becomes depleted and instead of the normal electrolysis reaction, other competing reactions start taking place [1] along with a simultaneous rise in voltage and evolution of PFC's. PFC's evolved during AE, such as CF_4 and C_2F_6 , have a several thousand times stronger Global Warming Potential (GWP) than CO_2 and hence are undesirable [2]. Most pot control systems are programmed to declare AE when the cell voltage reaches a level of 7 - 8 volts. Currently accepted methods for estimation of PFC emissions are Tier 2 or Tier 3, described by International Aluminium Institute (IAI), which use the Anode Effect Frequency (AEF) and the Anode Effect Duration (AED) as inputs in this calculation and report the emissions in terms of CO_2 equivalent per unit weight of aluminium produced [3]. These estimates are used in place of actual measurements, because the latter require complex and expensive analytical instrumentation and hence impractical for day to day operations.

Due to the nature of the empirical methods used in estimating PFC emissions, those emissions during periods when there are no anode effects declared by the control system are ignored. The terminology “non AE PFC emission” will be used in this paper to discuss these excluded emissions, even though it is recognised that local low voltage anode effects are probably taking place when PFC emissions occur. Non AE PFC emissions are currently not reported by the potlines. However, due to the steep decrease in the AEF, AED and very low estimated PFC emissions at DUBAL this phenomenon is being discussed in this paper. These type of non AE PFC emissions have been noticed only after 2007 [4] since prior to this the instrumentation was not sensitive enough to detect PFC's at very low concentrations. In addition, the non AE related emissions are more visible in modern cells operating with efficient AE control systems and achieving long periods without AE. Modern cells tend to have a large number of anodes which

increases the probability to have local depletion of alumina below specific anodes.

For example, the aluminium industry global PFC emissions due to anode effect was 580 kg eq. CO_2 / t Al in 2011[5]. DUBAL, which reported a very low emission of 9 kg CO_2 eq./t Al during 2010 for its DX potline, had started investigating this phenomenon [6]. The current paper describes this investigation in more detail with an emphasis to quantify the “non AE PFC emissions” as a first step to reduce or eliminate these emissions.

Results of PFC measurements at DUBAL

DUBAL has periodically commissioned studies to survey the PFC measurements for the different cell technologies and estimated design specific factors for the more accurate Tier 3 method to report to IAI [7]. The most recent survey by Dr. Jerry Marks involved measurements for potlines using D18, D20, CD20 and DX cell technologies as well as the five DX+ demonstration cells during 22nd November, 2010 to 4th January 2011 [8]. As per definition in [3], used for PFC emission calculations by Tier 2 method, all DUBAL cells are Centre Worked Prebake (CWPB) type. These comprise the D18 potlines which use both bar breaking and a retrofit of the same, called Poor Man's Point Feed (PMPF) as well as the rest of the potlines with Point Fed Prebake (PFPB) cell technology.

The PFC measurements utilised Fourier Transform Infrared (FTIR) spectroscopy, as per USEPA protocol [9,10]. Real time FTIR monitoring of PFC components was carried out using Temet DX4000 FTIR spectrometer in the sample gas stream. The concentrations of CF_4 and C_2F_6 were recorded continuously throughout the test period at each sampling location and values corrected for fugitive emissions. AE data was captured from the control system. Sampling durations are described in Table I.

Table I: PFC Sampling details

| Potline design | Number of cells represented | Duration of measurement (hours) |
|----------------|-----------------------------|---------------------------------|
| Line 3 (D18) | 124 | 64 |
| Line 5 (CD20) | 120 | 68 |
| Line 7 (D20) | 120 | 71 |
| Line 8 (DX) | 40 | 140 |
| DX+ | 5 | 480 |

AE data and PFC emissions attributed to the AE as well as non AE events during the period of measurements are summarised in Table II. It is obvious from the table that the contribution of non AE PFC emissions varies with the levels of AE frequency and duration. These contributions are lower for cells with higher values of AE frequency and duration whereas for cells with very

low AE frequency and duration these contributions are much higher relative to the total emissions.

Table II: Results from PFC measurements

| Design | Avg. AEF (no/pd). | Avg. AED (min) | % of AE and non AE PFC Emission | |
|--------|-------------------|----------------|---------------------------------|--------|
| | | | AE | Non AE |
| D18 | 0.47 | 0.55 | 90 | 10 |
| CD20 | 0.34 | 0.37 | 96 | 4 |
| D20 | 0.12 | 0.47 | 67 | 33 |
| DX | 0.077 | 0.25 | 38 | 63 |
| DX+ | 0.20 | 0.13 | 28 | 72 |

Anode effect detection and treatment logic and its relation to PFC emissions

One of the main reasons for high PFC emission, due both to AE and non AE events, is the way AE detection and treatment was designed at DUBAL at the time of measurements and possibly many other smelters. This is illustrated in Figure 1.

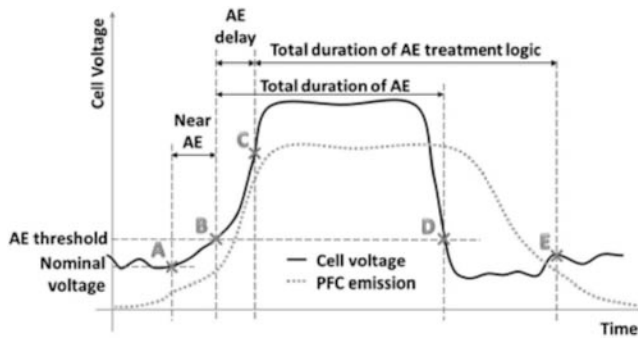


Figure 1. Typical design of AE detection and treatment logic.

The different events are labelled A to E, where point A-B represents the beginning of PFC emission which happens before the threshold voltage (marked by point B) is reached. DUBAL has termed this phenomenon as “Near AE” event [6]. It was the practice in the industry to have a waiting period to confirm AE (typically 8-10 seconds at DUBAL). Points B-C represents the “AE delay” period in Figure 1.

If the pot voltage does not remain continuously above the threshold voltage B during the waiting period, then the control system does not declare AE and hence takes no special action. Because of this, Tier 2 and Tier 3 methods will not take the associated PFC emissions into account. If the pot voltage remained continuously above B during the waiting period, then at point C the control system acts to quench the AE by anode movements and alumina feeding. Once the cell voltage drops below the threshold voltage at point D, the AE is declared as ‘off’ from which point onwards the quenching actions are discontinued and the control system brings the cell to target operating voltage gradually. However, PFC emissions may continue even after point D, till such time the cell reaches normal operations, say at point E and beyond. In the same figure, the AE duration is shown as the distance between B and D, this being inclusive of the waiting period. The time period between C and E is the total duration of

the treatment period by the control logic. However, it can be seen that PFC emissions may occur even before point A and after point D.

Subsequent to these investigations, DUBAL has implemented the reduction of the AE delay almost to zero for all the potlines, in order to capture anode effect events that may occur and disappear during this period. Prior to this change, it is obvious that these anode effects would not have been declared and treated. Hence, the corresponding PFC emissions would not have been accounted for.

In addition, DUBAL has introduced new logic to treat the “near AE” events and hence reduce the contribution to PFC emissions for these as shown in Figure 2. However, there are still some PFC emissions before point A and after point D that are unaccounted for.

It should be noted that at DUBAL since these measurements were performed in 2010/11, the values of AEF and AED for the DX and DX+ technologies have decreased significantly leading to very low PFC emissions < 10 kg eq. CO₂ / t Al. The improvements have been cascaded to other DUBAL potlines with similar decreasing trends achieved [7].

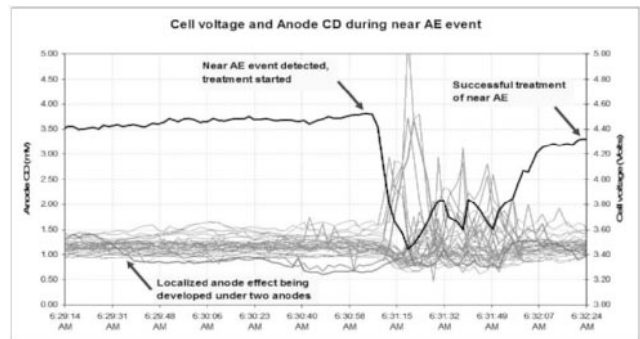


Figure 2. Anode current distribution showing polarization of two anodes along with Near AE event.

Quantification of PFC emissions for different events

Since “non-AE” related PFC emissions are not covered in the Tier 2 and Tier 3 methods and are becoming a significant part of the total PFC emissions as shown in Table II, DUBAL has taken the initiative to investigate these further.

The PFC emissions during the period of analysis carried out on a group of five cells are shown in Figure 3 and Figure 4. During this period there were only two anode effect events as indicated. All other emissions are during “non-AE” events where cells remained at voltages below 5 volts.

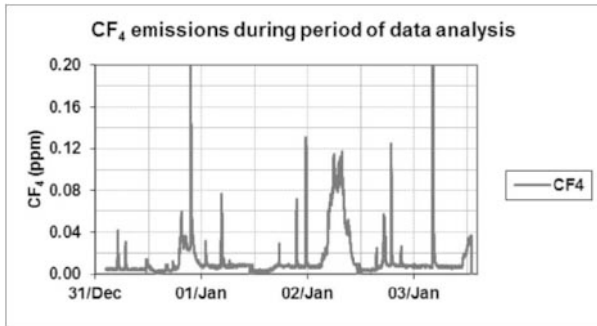


Figure 3. CF_4 emissions during period of data analysis.

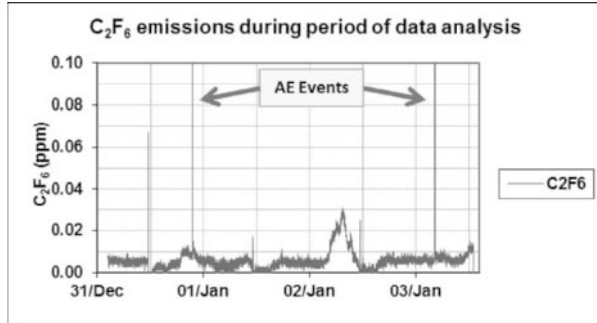


Figure 4. C_2F_6 emissions during period of data analysis.

Further investigation of these emissions has been carried out in relation to the operational activities as well as alumina feeding cycles. In this study it was observed that there are two clear events leading to PFC emissions increase, these being anode change and end of some underfeeding periods respectively.

Study of PFC emissions related to anode change

The increase in PFC emissions was noticed to take place during and immediately after anode change. In Figure 5, the increasing levels of CF_4 and C_2F_6 are linked to the five anode changes performed in the group of five pots. The anode change operations for the five pots took around 4 hours, each change involving a pair of anodes in each pot. However, increased emissions continued for a further 4-5 hours. The initial increase in the emissions can be attributed to the increase in the current density in the other anodes following the removal of the old anodes leading to localized polarization of some anodes [11]. In addition, the localised cooling of the bath due to setting of new cold anodes will make alumina dissolution more difficult. The subsequent decrease of PFC emissions can be attributed to either one of the following phenomena or a combination of both:

- Progressive increase of current pick up by the new anode, decreasing the current density in the other anodes,
- Covering of new anodes supplying some alumina which helps restoring alumina content in the bath, stopping anode polarization.

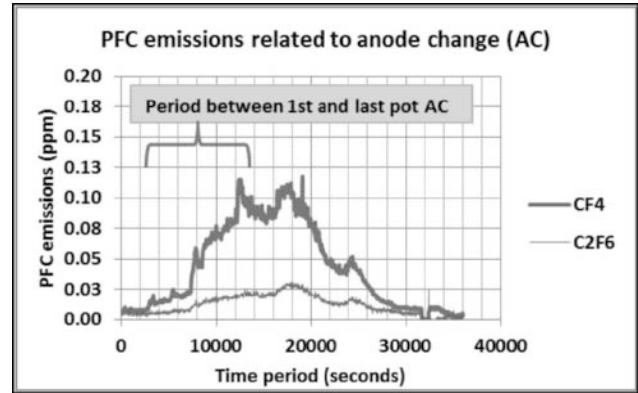


Figure 5. PFC emissions related to anode change (example 1).

Another example of the increase in PFC emissions due to anode changes in the same group of five pots on another day is illustrated in Figure 6. The sharp spike in PFC due to anode effect that occurred in one of the cells is also visible.

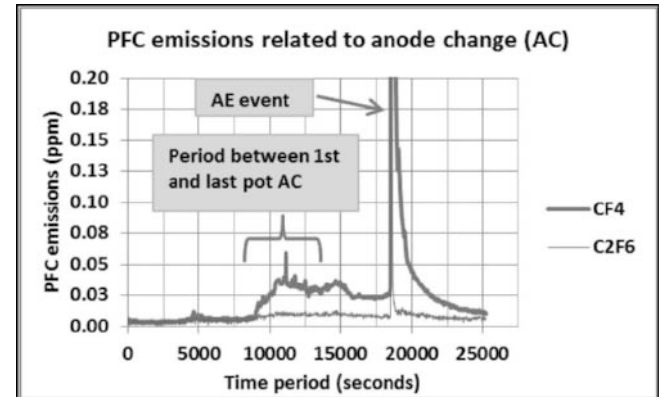


Figure 6. PFC emissions related to anode change (example 2).

Study of PFC emissions related to end of underfeeding periods

During the investigation it was also noticed that some PFC emissions occurred at times when there was no anode effect or anode change. Further analysis showed that these were linked to end of underfeeding. However, only about 10 % of end of underfeeding events triggered such increase in PFC emissions. It is interesting to note that in the examples studied so far only CF_4 emission seems to occur at significant levels as shown in Figure 7. It seems that when the slope of the resistance curve is much steeper than the usual trigger levels, this phenomenon occurs. Again, the emission can be attributed to localised anode polarisation due to depleted alumina content in the bath below specific anodes.

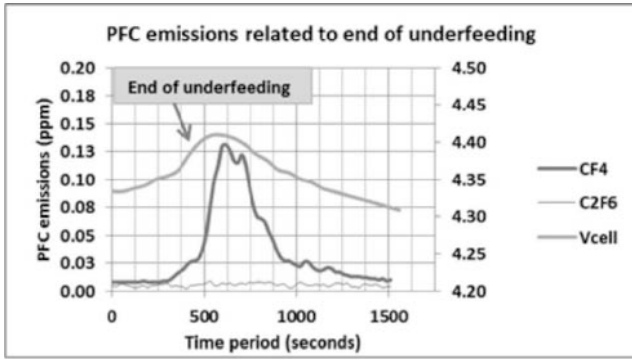


Figure 7. PFC emissions related to end of underfeeding for one cell.

Quantification of PFC emissions due to “non-AE” events

To obtain an order of magnitude of the levels of PFC emissions following “non-AE” events, this was estimated by computing the area under the curves for CF_4 and C_2F_6 concentrations respectively as a function of time. The area below two successive points was calculated using the trapezoidal method in MS Excel®, and then cumulated for the entire period as illustrated in Figure 8.

The area under the curve represents the PFC gas content in (ppm x seconds):

$$X_{PFC\ gas} = \sum_0^N A_n \quad (1)$$

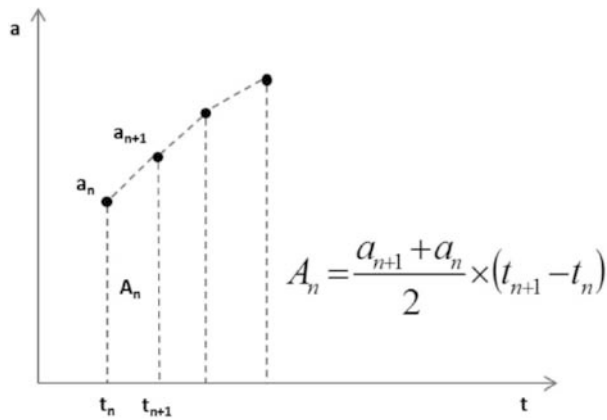


Figure 8. Illustration of calculation of area under the curve using trapezoidal method

where:

$X_{PFC\ gas}$ = Amount in ppm seconds,

A_n = Area under the curve calculated between successive points,

N = Total number of divisions.

In order to get the total mass of PFC gas, the calculated PFC gas content is multiplied by the total mass flow rate of the duct gases:

$$M_{PFC\ gas} = \frac{X_{PFC\ gas} \rho_{air} Q_v}{N} F \quad (2)$$

where:

$M_{PFC\ gas}$ = Amount of PFC gas in kg prorated per pot per day,

ρ_{air} = Density of air at 0 °C in kg/m^3 ,

Q_v = Gas flowrate in kg/s for the group of 5 pots,

N = Number of pots in the group = 5,

F = Frequency of the “non-AE” events.

In order to get the total mass of PFC per tonne of aluminium, the total mass per day is divided by the daily production of aluminium.

$$Y_{PFC\ gas} = \frac{M_{PFC\ gas}}{\text{Daily Al production per pot}} \quad (3)$$

where:

$Y_{PFC\ gas}$ = Mass of PFC gas in kg prorated to the daily aluminium production in tonnes.

This mass is converted to CO_2 equivalent as follows:

$$Y_{CO_2\ eq} = Y_{CF_4} GWP_{CF_4} + Y_{C_2F_6} GWP_{C_2F_6} \quad (4)$$

where:

$Y_{CO_2\ eq}$ = “Non-AE PFC emission” in eq. $kg\ CO_2 / t\ Al$,

Y_{CF_4} = Mass of CF_4 generated per tonne of aluminium,

$Y_{C_2F_6}$ = Mass of C_2F_6 generated per tonne of aluminium,

GWP_{CF_4} = Global warming potential of CF_4 ,

$GWP_{C_2F_6}$ = Global warming potential of C_2F_6 .

The GWP values are 6500 for CF_4 and 9200 for C_2F_6 , as per Second Assessment Report (SAR) of IPCC [2].

It was found that the PFC emissions linked to anode change were around 10 $kg\ CO_2\ eq. / t\ Al$ in example 1 and 4 $kg\ CO_2\ eq. / t\ Al$ in example 2. The PFC emissions linked to end of underfeeding (assuming 10% of such events leads to PFC emissions) was around 0.5 $kg\ CO_2\ eq. / t\ Al$.

Minimum Detection Limits (MDL)

The MDL for CF_4 and C_2F_6 are indicated in Table III below [8].

Table III. Analysis Method Parameters for Major Exhaust Gas Components and PFC Target Compounds

| Compound | Typical Concentration | Estimate of Minimum Detection Limit (MDL) |
|----------|-----------------------|---|
| CF_4 | 0.5 – 150 ppmv | 0.01 ppmv |
| C_2F_6 | 0.05 – 3.5 ppmv | 0.02 ppmv |

These values (in parts per million by volume, ppmv) represent the lowest possible detection limits that the measurement equipment used will allow.

It should be noted that although there is clear indication of increase in CF_4 and C_2F_6 emissions during the described events, some values measured are very close or below the MDL. However, in the calculation above, values below the MDL were not eliminated.

Conclusions

In its last campaign of PFC emissions measurements in all DUBAL potlines using state-of-the art equipment, clear evidence for PFC emissions at low cell voltage has been demonstrated.

DUBAL has investigated these “non-AE” or low voltage PFC emissions and identified possible sources for these. It is found that anode change and some of the end of underfeeding periods are contributing to these emissions.

A preliminary attempt has been made to quantify these emissions. Anode change seems to have an important share of these low voltage PFC emissions. End of underfeeding periods contribute to PFC emission only when the slope of the resistance is high. In the cases studied, the occurrence of such events with high slope was around 10%.

The recommendations of PFC measurement experts are required regarding the values measured below the MDL.

DUBAL has developed a logic called “Near AE Logic” which tackles the low voltage PFC emissions due to end of underfeeding events [6, 7].

As a way forward, DUBAL plans during its next campaign of PFC emission measurements to build upon this current study and refine the understanding and quantification in order to develop methodologies to reduce or eliminate these emissions.

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