# Latest Progress in IPCC Methodology for Estimating the Extent of PFC Greenhouse Gases Co-evolved in the Aluminium Reduction Cell and Challenges in Reducing these Emissions

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## Abstract

In recent years, the primary aluminium industry has increasingly found that perfluorocarbon (PFC) greenhouse gases can be co-evolved in reduction cells during normal operation, i.e. without an anode effect (AE) that is typically defined as when cell voltage exceeds 8 V. Other than during an AE, PFC co-evolution rates are invariably low. However, because of the long duration of these ‘low voltage’ emissions they can contribute as much than 90 % of a smelter’s total PFC output, depending on cell technology, practices and operating conditions. These emissions help explain some of the discrepancy between ‘top-down’ global atmospheric estimates of PFCs vs. ‘bottom-up’ industry estimates via the International Aluminium Institute (IAI). To provide a more complete estimate of total greenhouse gas emissions, the Intergovernmental Panel for Climate Change (IPCC) is updating its PFC accounting guidelines for the aluminium industry, covering both anode effect and low voltage emissions – respectively termed ‘high voltage anode effect’ (HVAE) and ‘low voltage anode effect’ (LVAE) emissions in the guidelines. The following paper summarises some of the latest progress in this. While the updated 2019 IPCC Refinements provides an important first step in estimating all PFCs co-evolved in the aluminium reduction cell, this paper also explores some of the challenges that remain – firstly in finding a more scientific basis to estimate low voltage PFCs for future IPCC methodologies; and secondly but more importantly, for smelters to determine strategies to detect and mitigate low voltage emissions when they occur.

**Keywords:** Perfluorocarbons, greenhouse gas emissions, IPCC methodology, anode effect PFCs, low voltage PFCs.

## 1. Introduction

This article discusses the latest progress and challenges in the global effort to account for PFCs from aluminium smelting, particularly with the inclusion of low voltage PFCs (termed ‘low-voltage anode effects’ or LVAEs) in updated greenhouse gas (GHG) accounting guidelines from the Intergovernmental Panel for Climate Change (IPCC). It follows on from a detailed investigation of the fundamental mechanisms and underlying causes of all PFC coevolution – from anode effects (AEs) and during ‘normal’ cell operations (low voltage PFCs) in two ICSOBA articles by Welch et al. (“Part 1” and “Part 2”) [1 - 2]. Part 2 in particular describes the impact of changes in cell design that have resulted in low-voltage PFCs becoming more prevalent in modern aluminium reduction cells.

Perfluorocarbons (PFC) – in particular tetrafluoromethane ($CF_4$) and hexafluoroethane ($C_2F_6$) – are potent GHGs with extremely long lifetimes in the atmosphere (50 000 and 10 000 years, respectively) and with high global warming potentials (GWP over a 100-year period) at 6 630 and 11 100 times the equivalent of $CO_2$, respectively [3]. While very low trace levels of PFC do occur naturally (in the range of ~ 0.1 - 10 t $CF_4$/y), anthropogenic sources of emissions are 3 to 5 orders of magnitude greater (~ 11 000 t $CF_4$/y) [4].

The two major anthropogenic sources of PFCs are primary production of aluminium and manufacture of semi-conductors/electronics; other sources include industrial rare-earth metal smelting (with a similar fluoride-salt electrochemical process to aluminium smelting), production of fluorochemicals (e.g., HFC, HCFC), waterproofing of circuit-boards and textiles [5].

### 1.1. PFCs from Aluminium Smelting

In the aluminium reduction cell, PFCs occur when the electrical potential across the anode $E_{anode}$ exceeds the threshold that enables PFC co-evolution, i.e. the reversible potential $E_{reversible}$ for reactions that generate PFCs. Typical anode reactions are summarised below (gas products in bold) – for more details, refer to [1 - 2]:

- Reactions in normal aluminium reduction (equations 1 and 2) are enabled when $E_{anode}$ exceeds 1.07 - 1.19 V
- Reactions for PFC co-evolution (producing $COF_2$, or CO and $CF_4$) enabled once $E_{anode}$ exceeds 1.83 - 1.89 V (equations 3 and 4)
- Reactions for direct or independent PFC co-evolution are enabled at much higher anode potentials, at $E_{anode}$ > 2.59 V (equations 5 and 6).

| *Typical reactions in normal aluminium electrolysis:* | $E_{reversible}$(V) | Eqn. |
|---|---|---|
| $Al_2O_3(s) + 3C = 3\mathbf{CO}(g) + 2Al(l)$ | 1.07 | (1) |
| $Al_2O_3(s) + 1.5C = 1.5\mathbf{CO_2}(g) + 2Al(l)$ | 1.19 | (2) |
| *Reactions with PFCs co-evolved*: | | |
| $Al_2O_3 + 3C + 2Na_3AlF_6 = 3\mathbf{COF_2}(g) + 4Al(l) + 6NaF(l)$ | 1.89 | (3) |
| $Al_2O_3 + 4.5C + 2Na_3AlF_6 = 3\mathbf{CO}(g) + 1.5\mathbf{CF_4}(g) + 4Al(l) + 6NaF(l)$ | 1.83 | (4) |
| *Reactions with directly PFCs co-evolved, at higher potentials*: | | |
| $3C + 4Na_3AlF_6 = 3\mathbf{CF_4}(g) + 4Al(l) + 12NaF(l)$ | 2.59 | (5) |
| $2C + 2Na_3AlF_6(l) = \mathbf{C_2F_6}(g) + 2Al(l) + 6NaF(l)$ | 2.75 | (6) |

Note that the $COF_2$ in equation (3) *spontaneously* reacts with anode carbon to form $CF_4$ gas:

$2COF_2(g) + C = 2CO(g) + CF_4(g) \quad G_{1233\,K} = -45.77$ kJ (7)

To enable each reaction, extra entropic energy TΔS is required in addition to the $E_{reversible}$ to *complete* the formation of gas products at the anode – this can be supplied either electrically by anode overpotential or through joule heating. This is discussed in further depth by Welch et al. [1-2].

### 1.2. PFCs from Anode Effects

Historically the aluminium industry considered that ‘anode effects’ were good for the cells as they helped “clean up the sludge/muck” in the cell, which tended to accumulate through centre- or side-breaking and feeding a mass of alumina in excess of that able to dissolve it. Until approaching the turn of the century, operating control logic scheduled regular anode effects – such as once per week – to bring about this benefit. In the absence of sensitive gas analysis equipment, PFCs were only detected in measurable quantities during an anode effect and therefore the concept developed that generation of PFCs from aluminium smelting only occurred during 'anode effects' (AE), but during 'normal' cell operation they were considered non-existent [6].

With the ability of the DC electrical energy in the early 19th century, numerous chemists explored the opportunity of electrowinning metals from molten salts since they were stable in aqueous solutions. Typically, their experimental procedure involved using a DC voltage supply, such as a battery, plus a variable rheostat/resistance in either parallel or series connected to the electrodes so that they could explore reactions when applying various voltages or currents. When using a carbon anode, a phenomenon named an "anode effect" was observed [7] with characteristics being:

- Cells under *voltage control* would experience a very sudden drop in current to virtually zero.
- Cells under *current control* would experience a sudden and substantial increase in cell voltage to maintain the current.

This phenomenon was observed in carbon anode systems with both pure molten halides and mixed molten halides including those that were oxide free. Simple early observations included:

- If you electrolysed pure molten NaCl, you evolved $Cl_2$ (g) from the anode ($E^\circ_{950C} = 3.14$ V), but if you tried to increase the current beyond a "critical current density" an anode effect occurred, dropping the current (or increasing the voltage) depending on the circuitry used. $CCl_4$(g) ($E^\circ_{950C} = 3.33$ V) became a second anode product during an anode effect.
- If you tried to do the same experiment with pure NaF, you could not produce $F_2$(g) ($E^\circ_{950C} = 4.65$ V) but if under current control the cell went immediately to an anode effect, requiring a high voltage and the product formed was $CF_4$(g) ($E^\circ_{950C} = 2.72$ V).

In aluminium smelters, the cells are connected in series with a high voltage power supply which gives *almost* a constant current. The primary difference with the second scenario described here above is the presence of dissolved oxide anions ($O^{2-}$) as well as fluoride anions ($F^-$) in the molten salt, and the oxide anions require a significantly lower voltage to initiate ($E^\circ_{950C} < 1.2$ V) evolution of $CO_x$ gases. It is therefore no surprise that anode effects are observed when the oxide becomes depleted and the process disturbance is associated with a rapid increase in the voltage of a cell from normal operating levels – between 3.85 and 6 V depending on the technology. Figure 1 shows an example where voltage initially rises slowly from normal operating levels ~ 4.5 V, and then above 5 V the rate of voltage (dV/dt) exponentially increases to an anode effect.

However, the smelter operating voltages include not only the reversible potential but also added electrode potential (over-potential / polarisation) and the voltage associated with the ohmic resistance of the electrolyte and cell-to-cell circuitry. When the industry became concerned about the environmental impact of PFC co-evolution through AEs and attempted to account for and monitor its contribution, the range of operating voltages across different cell designs and operating conditions presented a challenge since voltage rise and resulting steady state value is the primary indicator of the initiation of an AE. The question arises – *to what level can you be sure the cell is having an AE, and when you are terminating it at what level does the PFC co-evolution stop?* Subsequently the industry introduced an arbitrary threshold voltage of > 8 V (Figure 1, with variations from 6 – 10 V) to classify when a cell is on AE and used the *frequency* and *duration* of these AEs to correlate with the emission of PFC gases. (This definition can also encompass newly started cells that are temporarily held at higher voltages than for normal operation).

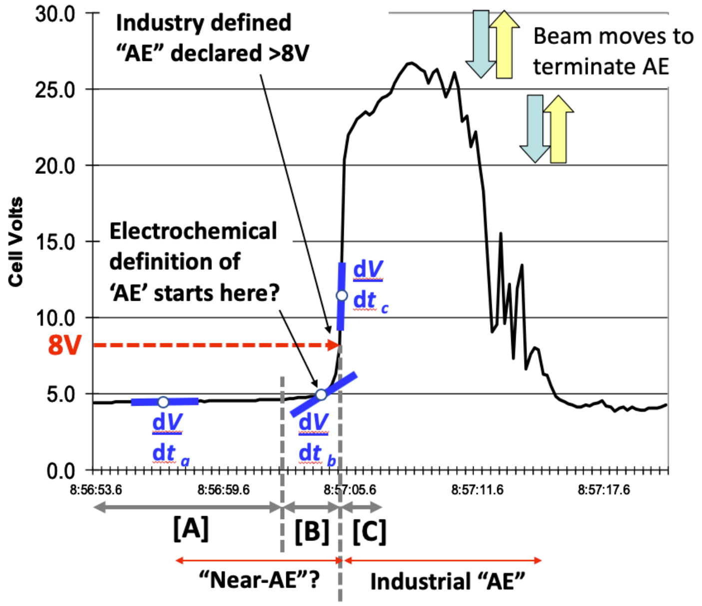

**Figure 1. Voltage signature of an anode effect on a 220-kA cell (Courtesy of Alton Tabereaux)**

*This, however, remains an assumption and is not a true definition of an anode effect. It is purely an empirical formula to encompass cells evolving PFCs at a rate where gas composition is similar to that measured during actual anode effects.* It is a definition of a condition whereby all smelting cells are having an "aluminium industry-defined AE" and it forms a reasonable approach for quantitative calculations of the emission rate of PFCs. Importantly, it also presents a means to track emissions performance.

Since the 1990s, the aluminium industry has made significant progress – largely through voluntary efforts – to reduce PFCs from AEs. Between 1990 to 2017, the industry has achieved ~ 90 % reduction in the intensity of emissions (kg PFC/t Al) or a 63 % reduction in absolute emissions per year from AEs [8].

Initially, as a consequence of the performance of the improved technology and control there was an acceptance of the fact that regular anode effects were not necessary, and the 'scheduled anode effect' logic was phased out in the control systems of smelters. More recent progress has been through better cell voltage monitoring and signal processing in the control systems and logic for adding the alumina. These changes have led to significant reductions in both anode effect *frequencies* (AEF) and *durations* (AED) across the global industry, as shown in Table 1.

**Table 1. Global median, 10th percentile and benchmark performance values for AEF and AED from reporting aluminium producers in 1990 and 2016 (data courtesy of the IAI).**

| | **AE Frequency (AEF)** (AE/pot-day) | | **AE Duration (AED)** (minutes) | |
|---|---|---|---|---|
| Year | 1990 | 2016 | 1990 | 2016 |
| Median | 1.07 | 0.15 | 2.41 | 1.14 |
| 10th percentile | 0.19 | 0.06 | 1.33 | 0.50 |
| Benchmark* | 0.03 | 0.03 | 0.67 | 0.14 |

*Benchmark statistics for AEF and AED are not necessarily correlated to the same facility.

AEs are always associated with a depletion of alumina concentrations, but the transition is accelerated by high anode current densities and other conditions that impact the anode potential $E_{anode}$ to the point where PFCs can be coevolved. As discussed by Welch et al. [1-2], spatial variations in alumina concentrations and current density occur frequently in aluminium reduction cells, particularly in today's modern, large and high-amperage cells. As illustrated in Figure 2, the phenomenon initiated when PFC generation on a localised anode results in passivation, due to the highly resistive C-F intermediate film formed on the anode surface. Thereafter, PFC generation and subsequent passivation of anode surfaces rapidly propagate from one anode to another as current is quickly redistributed to other anodes in the cell; the passivation and propagation of PFC coevolution on multiple anodes results in the high cell voltage observed in an anode effect.

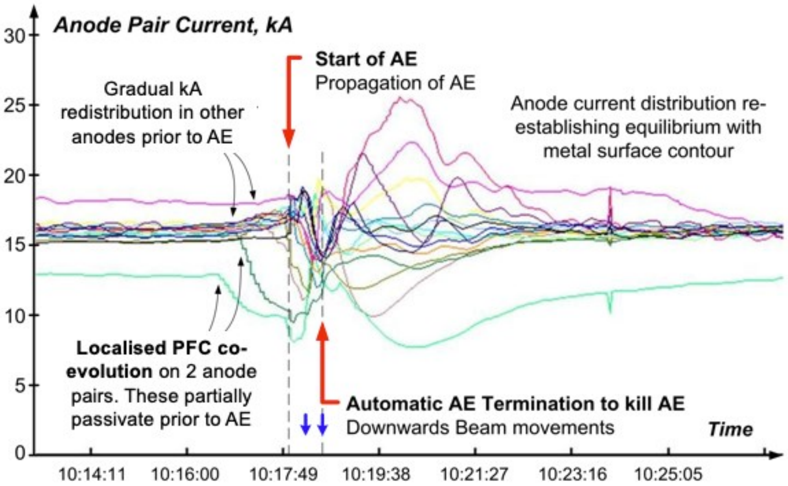

**Figure 2. Individual anode currents before, during and after an anode effect (Courtesy of Alton Tabereaux)**

### 1.3. PFC Co-evolution during Normal Cell Operation

In the past decade the industry has established that PFCs (particularly $CF_4$) can be emitted in the *absence* of an anode effect – even during 'normal' cell operations and operating voltages. As covered in Parts 1 and 2 by Welch et al. [1, 2], this has been made much more prevalent by the changes in cell design, pot operation and raw materials in many of today's modern smelting cells and in existing cells after they become retrofitted towards greater productivity. Such factors include:

- A significantly reduced volume of liquid electrolyte per kA
- A reduction in the driving forces for electrolyte mixing – via lower anode-cathode distances (ACD) to achieve low energy operation
- An uptake of anode slots, and lower metal pad velocities through better MHD compensation;
- Longer durations to heat new anodes to operating temperature as a direct result of increase in the size of anodes or where multiple anode changes are adopted, but posing a barrier to electrolyte flow, combined with
- Greater pressure for each point feeder to deliver more alumina per kA to cover all anode reaction surfaces, as amps are increased.

These changes drive greater opportunities for spatial variation and localised conditions to enable PFC generation on individual anodes for long periods of time (where anode potentials $E_{anode}$ exceed levels that enable PFC coevolution). This is without the propagation to further anodes that would lead to a full anode effect.

It is important to note that these PFCs are generated below the ~ 8 V detection thresholds for anode effects and hence are referred to in this work as 'low voltage PFCs' (LV-PFC). Another industry term for these are 'low voltage anode effects' (LVAE) which is a terminology which has been adopted by the IPCC in the latest PFC accounting guidelines. A 2012 survey of 13 Chinese and 17 non-Chinese aluminium smelters [9] found that low voltage PFCs contributed a median of 70 % and 22 % of total emissions, respectively; in another study, Li et al. [10] found that LV-PFCs could contribute as much as 93 % of total emissions in a smelter. These and many others [11 - 12] have established that low voltage emissions are now are significant component of the industry's real total PFC output.

### 1.4. Addressing the 'Gap' between Atmospheric vs. Industry Accounting of PFCs

Atmospheric ('top-down') measurements of PFCs attributed to the aluminium industry can be used to cross-check the industry's own estimates ('bottom-up) of annual emissions. Industry estimates are regularly collated by the International Aluminium Institute (IAI) and are largely based on methods in the IPCC's 2006 Guidelines for PFC accounting with the only exception being smelters in China, where the IAI uses a separate emissions factor of 0.80 kg $CO_2$e/t Al for *total* PFCs (both AE and low voltage emissions). This is based on a 2008-2013 survey of 27 PFPB Chinese smelters [8]. Figure 3 shows that from 1990 to 2002 both industry and atmospheric approaches were roughly consistent and showed a reduction in PFCs – a testament of the industry's focused efforts to reduce anode effects. However, from approximately 2003 onwards, a growing discrepancy was observed by Kim et al. [13]. This can be partly attributed to the non-accounting of PFCs generated in the absence of anode effects – something that is being addressed in the IPCC's latest methods for estimating PFCs.

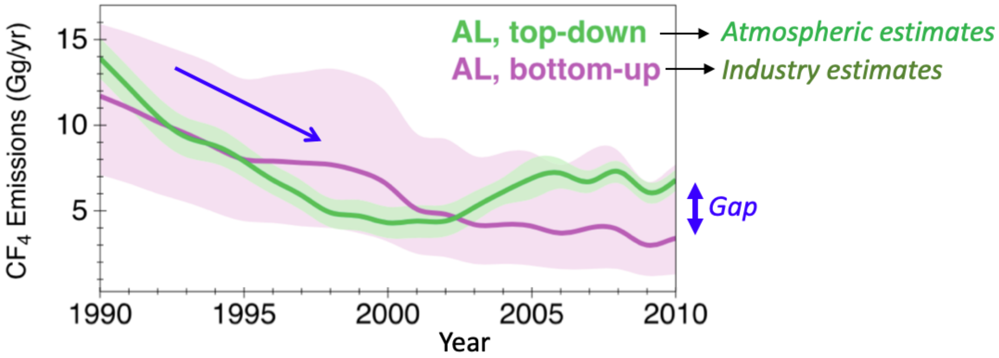

**Figure 3. Comparing atmospheric (green) and industry (blue) estimates of global $CF_4$ emissions annually from aluminium production [13].**

## 2. IPCC Guidelines for Accounting PFCs from Aluminium Smelting

Since the 1990s, the IPCC has been tasked with providing methodology reports for countries to account for greenhouse gases (GHGs) and to report these to the UN Framework Convention on Climate Change (UNFCCC). To maintain the accuracy and completeness of global emissions inventories, the guidelines are periodically updated with the latest science.

The most relevant guidance for accounting of PFCs from aluminium production include:

a. The '2006 IPCC Guidelines for National Greenhouse Gas Inventories' (*2006 Guidelines*) – these are the currently active guidelines.
b. The '2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories' (*2019 Refinements*), which are the most recent updates to the *2006 Guidelines*. While these new updates have been adopted / accepted by the IPCC in its 49th

Session in May 2019, they have yet to be adopted (at the time of writing) by the UNFCCC for implementation and use for national emissions inventories.

For industrial GHG emissions, the IPCC methods are generally structured on a '3-Tier' basis, with better accuracy and completeness at higher tiers, but with increasing complexity and requiring more plant-specific data and/or emission factors (EFs). In the *2006 Guidelines* [14], AE-related PFCs from aluminium production are estimated as follows:

- The *'Tier 1'* approach is the simplest and emissions are estimated by multiplying metal production (*MP*) by a default emission factor ($EF_{CF4}$ or $EF_{C2F6}$) for that technology class.
- The *'Tier 2'* approach takes into account average AE performance at a smelter. The most common 'Slope' method estimates emissions by multiplying average AE minutes per cellday (*AEM*), by a default Slope coefficient ($S_{CF4}$ and $S_{C2F6}$) for that technology class and metal production (*MP*). This assumes that emissions correlate *linearly* with AE duration. A less commonly used alternative is the 'Overvoltage' method.
- The 'Tier 3' approach is identical to Tier 2, but uses a facility-specific coefficient, i.e. one obtained from PFC measurements at that smelter and correlating these to AEs. While the most accurate method, it comes at a cost as it requires direct measurements.

## 3. Updated PFC Methodology in the 2019 IPCC Refinements

For the aluminium industry, the *2019 Refinement* methodology for PFCs [15] sets out to address some of the gaps in accounting and to provide updated emission factors given the improvements in AE performance across the industry since 2006. The *2006 Guidelines* [14] did not account for low voltage PFC emissions since at the time these were not known, were not measurable or if measured, found to be insignificant compared to AE-related PFC emissions.

Key updates proposed in the *2019 Refinement* include:

1. *Updates to Cell Technology* divisions for estimating PFCs.
2. *Updated methods for estimating AE-related (> 8 V) PFC emissions* (reclassified as 'high voltage anode effects' or HVAEs). This included updated default emission factors for Tier 1 and default Slope coefficients for Tier 2; also new alternative 'non-linear' Tier 2 methods based on the duration of *individual* AEs for each cell.
3. *New methods for estimating low voltage (< 8 V) PFC emissions* that are classified as 'low voltage anode effects' or LVAEs – new Tier 1 and Tier 3 methods, based on metal production or as a ratio of AE-emissions. Note that only low voltage *$CF_4$ emissions* are accounted for; low voltage emissions of $C_2F_6$ are not considered significant (either not detectable or up to two orders of magnitude lower) and for this reason are not included in the *2019 Refinements*.
4. *More explicit guidance for accounting emissions during cell start-up* (CSU).
5. *New Tier 3 direct gas measurement method* – one where total PFCs are directly measured and reported, rather than estimating emissions from process data.

Note that for completeness and accuracy, readers should always refer directly to the final *2019 IPCC Refinements*, available on the IPCC website [15].

### 3.1. Challenges and Insights during Updating of PFC Guidelines

A number of challenges were experienced and interesting insights gained in the updating of PFC guidelines for the aluminium industry. Firstly, IPCC guidelines were to be primarily based on the latest science to provide the most representative or accurate assessment of emissions rather than having an undue consideration of policy ramifications (e.g. the impact on smelters regulated by regional GHG cap-and-trade schemes, through the introduction of a previously unknown category of low voltage PFCs). It is also acknowledged that the guidelines are always a snapshot in time of the current state of knowledge and reflect the industry's current emissions profile and there is no guarantee that they will be representative in the future, especially with industries such as aluminium that evolve with economic and technological pressures.

Secondly, guidelines were primarily targeted for use by government-based inventory compilers for the purpose of tracking national/regional GHG emissions. On that basis:

- Default emission factors and coefficients (Tier 1 and 2 methods) were intended to be broadly representative of national or regional inventory circumstances, sometimes at the expense of being necessarily representative for individual facilities / smelters. For example, *average* emission factors were adopted to provide a better estimate of global / national emissions, rather than *median* values which exclude the extremities but can be more representative of a typical smelter's emissions performance [16].
- Guidelines needed to be framed for the non-expert user, using data that might easily be gained from individual smelters or industry bodies (e.g. the IAI). At the same time, the guidelines had to provide sufficient flexibility for industry (and individual smelter) users, who often are the ones submitting data for those building these GHG inventories.
- Inclusion of novel and promising, but as yet unproven methods to estimate PFCs (e.g. use of individual anode current measurements and models for estimating LV-PFCs – discussed in Section 4) could not be justified.

Some specific challenges included determining an appropriate time-frame to start including LV-emissions in PFC accounting, as well as when to apply updated AE-emission factors. For the former, the approach adopted is not to account for LV emissions prior to 2006 – since emissions were considered immaterial, or not significant vs. AE-emissions prior to this. For the latter, the approach is to adopt updated AE emission factors at the 'median point in time' within which emissions data for each technology class was gathered.

### 3.2. Updates to Reduction Cell Technology Classes

In the previous *2006 Guidelines* [14], default emission factors and coefficients for estimating PFCs were defined for the four cell technology classes at the time:

- CWPB – Centre-Worked Prebake, which also incorporated Point-Fed Prebake (PFPB)
- SWPB – Side-Worked Prebake
- HSS – Horizontal Stud Søderberg
- VSS – Vertical Stud Søderberg.

Clearly the technological landscape has changed considerably across the industry since 2006, with PFPB now representing more than 90 % of global production. As such, the previous CWPB technology class has been expanded into three further categories in the 2019 Refinements [15]:

- $PFPB_L$ – Legacy PFPB, i.e. older technology with amperage < 350 kA
- $PFPB_M$ – Modern PFPB, i.e. modern technology cells with amperage > 350 kA
- $PFPB_{MW}$ – Modern PFPB technologies (typically >350 kA) *without* fully automated AE intervention strategies, and/or employ *non*-standard AE definitions (particularly in China [17]). Today, most other PFPB potlines employ fully automated intervention strategies to terminate AEs and typically define AEs as when cell voltage exceeds ~ 8 V for ~ 1 – 3 s.

Note that the '350 kA' amperage threshold adopted for legacy vs. newer, large modern cell technologies could be argued as somewhat arbitrary and is based more on the statistical distribution of current technology and their emission factors. However, it is acknowledged that the factors discussed in Parts 1 and 2 by Welch et al. [1, 2] that make PFC coevolution more likely apply not only to smelters upgrading to the most recent, modern cell technologies, but also those retrofitting existing technologies towards lower energy, high productivity operations, beyond the original nameplate capacity and design. Suggestions towards other divisions / process factors that might have a closer relationship to emissions intensity (vs. just amperage) are discussed in Section 4 of this paper.

### 3.3. Summary of Updated Accounting Methods in 2019 Refinements

Table 2 summarises the new PFC accounting methods available in the *2019 Refinements*, in comparison to those in the *2006 Guidelines*, with divisions for Tiers 1, 2 and 3 and separate methods defined for each of the denoted PFC sources, i.e.:

- AE = anode effect PFCs (or 'HVAE' in the *2019 Refinements*)
- LV = low voltage PFCs (or 'LVAE' in the *2019 Refinements*), i.e. $CF_4$ only.
- CSU = PFC emissions during cell start-up (only if not already accounted for in AE and low voltage emissions)

**Table 13. Comparison of PFC accounting methods in the 2006 [14] vs. 2019 IPCC [15] methodologies.**

| **2006 IPCC Guidelines** | | | | | **2019 IPCC Refinements** | | | |
|---|---|---|---|---|---|---|---|---|
| **Tier** | **PFC Source** | **PFC Gas** | **Method** | **Basis** | **Tier** | **PFC Source** | **PFC Gas** | **Method** |
| 1 | AE | $CF_4$, $C_2F_6$ | Production-based emission factors (EFs) | Default EFs by *Cell Technology* | $1_{HVAE}$ | AE | $CF_4$, $C_2F_6$ | Production-based EFs |
| | | | | | $1_{LVAE}$ | LV | $CF_4$ | Production-based EFs |
| 2 | AE | $CF_4$, $C_2F_6$ | Slope | Default Coefficients by *Cell Technology* | $2a_{HVAE}$ | AE | $CF_4$, $C_2F_6$ | Slope |
| | | | Over-voltage | | $2b_{HVAE}$ | AE | | Non-Linear, using individual AE durations |
| 3 | AE | $CF_4$, $C_2F_6$ | Slope | *Facility-Specific* Coefficients | $3a_{HVAE}$ | AE | $CF_4$, $C_2F_6$ | Slope or Overvoltage |
| | | | | | $3b_{HVAE}$ | AE | | Non-Linear, using individual AE durations |
| | | | Over-voltage | | $3_{LVAE}$ | LV | $CF_4$ | Ratio or production-based EF |
| | | | | | $3_{CSU}$ | CSU | $CF_4$, $C_2F_6$ | Cell start-up factor |
| | | | | | $3_{DM}$ | Total | $CF_4$, $C_2F_6$ | Direct measurement for total PFCs |

In general, total PFC emissions ($E_{CF4}$ and $E_{C2F6}$, for $CF_4$ and $C_2F_6$ emissions respectively) are calculated as the sum of estimated AE, low voltage (LV) and cell start-up (CSU) emissions, i.e. $E_{CF4\_AE}$, $E_{CF4\_LV}$ and $E_{CF4\_CSU}$, respectively for $CF_4$, and $E_{C24F6\_AE}$ and $E_{C2F6\_CSU}$ respectively for $C_2F_6$:

$$E_{CF4} = E_{CF4\_AE} + E_{CF4\_LV} + E_{CF4\_CSU} \tag{8}$$

$$E_{C2F6} = E_{C24F6\_AE} + E_{C2F6\_CSU} \tag{9}$$

### 3.4. PFCs from Anode Effects – Updated Emission Factors and Coefficients

Updates have been made to the *Tier 1* default emission factors (based on metal production) for AE-related PFC are presented in Table 3 for each technology. The calculation of emissions remains the same, i.e.:

$$E_{CF4\_AE} = EF_{CF4\_AE} \bullet MP \tag{10}$$

$$E_{C2F6\_AE} = EF_{C2F6\_AE} \bullet MP \tag{11}$$

where $EF_{CF4\_AE}$ and $EF_{C2F6\_AE}$ are the default emission factors for $CF_4$ and $C_2F_6$ respectively, and MP is metal production.

**Table 14. Tier 1-PFC emission factors in the 2019 Refinements [15] by technology.**

|  | **2019 Tier 1 PFC Emission Factors#** |  |  |  | **Contribution towards Total $CF_4$** |  |
|---|---|---|---|---|---|---|
|  | **$CF_4$ Emissions kg $CF_4$/t Al** |  |  | **$C_2F_6$ Emissions kg $C_2F_6$/t Al** |  |  |
| **Cell Technology** | **AE: $EF_{CF4\_AE}$** | **LV: $EF_{CF4\_LV}$** | **Total** | **$EF_{C2F6\_AE}$ AE** | **% AE** | **% LV** |
| $PFPB_L$ | 0.016 | 0.009 | 0.025 | 0.001 | 64 | **36** |
| $PFPB_M$ | 0.011 | 0.018 | 0.029 | 0.001 | 38 | **62** |
| $PFPB_{MW}$* | - | - | 0.161 | 0.013 | ~ 30* | **~ 70*** |
| SWPB | 0.354 | 0.010 | 0.364 | 0.093 | 97 | 3 |
| VSS | 0.159 | 0.001 | 0.16 | 0.009 | 99 | 1 |
| HSS | 0.477 | 0.026 | 0.503 | 0.033 | 95 | 5 |

*For $PFPB_{MW}$, separate accounting of LV and AE-emissions is not possible and only a Tier 1 total emission factor is available for this technology class. However, an estimation of % contributions by AE vs. LV emissions is based on the IAI study by Marks & Bayliss [9].
#Note: uncertainties for emission factors not shown – refer to the 2019 Refinements [15].

As shown in Figure 4, the updated emission factors reflect the significant reductions in AE emissions intensity over time across almost all cell technologies apart from perhaps HSS (with only a very few smelters remaining). The left figure compares the 2006 CWPB emission factor vs. the new 2019 values for legacy PFPB, modern PFPB and $PFPB_{MW}$ technology classes, and shows a 96 – 97 % reduction in AE-related $CF_4$ emissions intensity for the legacy and modern PFPB classes. The contribution of LV-emissions vs. AE-emissions can also be observed in this figure and in Table 3 for each PFPB technology which is further discussed in Section 3.6.

At *Tier 2*, AE-related emissions can be calculated via two methods – the linear ‘Slope Method’ that is identical to that from the 2006 Guidelines (now relabelled ‘Tier 2a $_{HVAE}$’), and via the ‘Non-Linear Method’(Tier 2b $_{HVAE}$). The classical Slope Method (Tier 2a) calculates emissions via the equations:

$$E_{CF4\_AE} = S_{CF4} \bullet AEM \bullet MP \tag{12}$$

$$E_{C2F6\_AE} = E_{CF4\_AE} \bullet F_{C2F6/CF4} \tag{13}$$

where $S_{CF4}$ is the default Slope coefficient for $CF_4$ emissions for that technology, AEM is the AE minutes (where AEM = average AEF x average AED for the facility) and $F_{C2F6/CF4}$ is the weight ratio of $C_2F_6$ to $CF_4$ emissions. Updated coefficients in the *2019 Refinements* are shown in Table 4 – for uncertainties, refer to the actual guidelines [15].

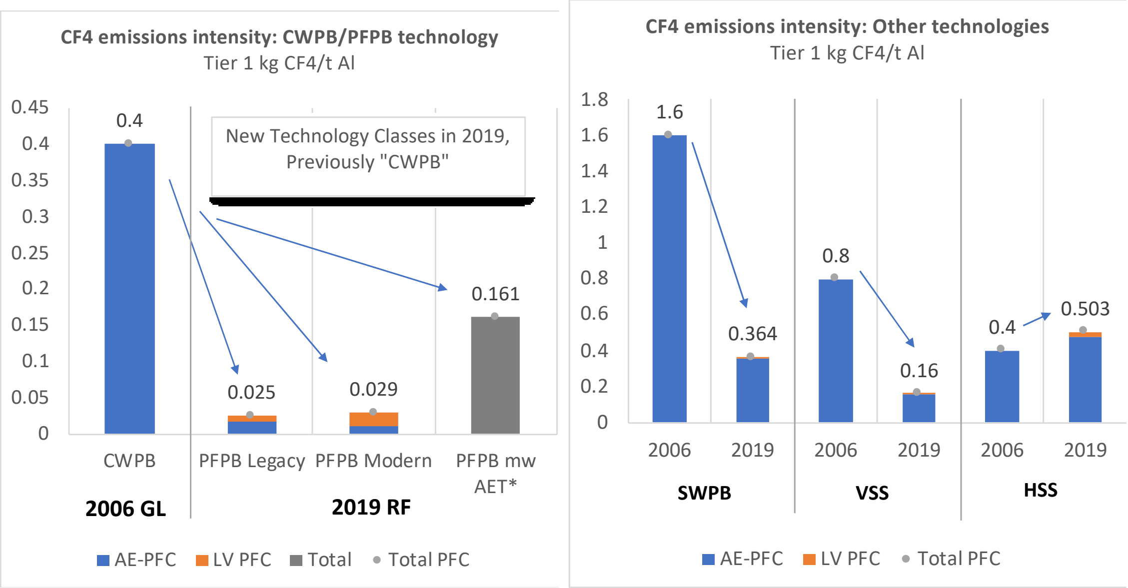

**Figure 4. Changes in 2006 [14] vs. 2019 [15] Tier 1 CF4 emission factors for CWPB and PFPB technology (left) and SWPB, VSS and HSS technologies (right).**

**Table 4. Updated 2019 coefficients for the Tier 2a 'Slope Method' for AE-emissions [15].**

| **Cell Technology** | **Slope Coefficient, $S_{CF4}$** (kg $CF_4$/t Al) / (AE-min/cell-day) | **Weight fraction $F_{C2F6/CF4}$** |
|---|---|---|
| $PFPB_L$ Legacy | 0.122 | 0.097 |
| $PFPB_M$ Modern | 0.104 | 0.057 |
| $PFPB_{MW}$* | - | - |
| SWPB | 0.233 | 0.28 |
| VSS | 0.058 | 0.086 |
| HSS | 0.165 | 0.077 |

*Tier 2 methods cannot be used for $PFPB_{MW}$ as they do not use consistent AE definitions.

### 3.5. PFCs from Anode Effects –Non-Linear Methods

A limitation of the Slope Method is that it assumes that PFC coevolution occurs at a constant rate, i.e. emissions vary *linearly* with AE duration. However, this approximation does *not* hold up for longer duration AEs as the actual rate of emissions tends to reduce over time. For long AEs therefore, emissions are over-estimated as circled in red in Figure 5-A [18]. The *2019 Refinements* therefore provide two alternative *non-linear* approaches (Tier 2b) for estimating AE emissions for the general smelter: one proposed by Marks and Nunez [19] (Figure 5-B) and another proposed by Dion et al [20].

Both non-linear methods differ from the Slope method where they rather estimate AE-emissions based on *individual* AE durations (AED), as opposed to the *average* AE performance (AEM) over an accounting period. Total AE-emissions are then the *sum* of emissions from all individual AEs over the accounting period:

*Non-Linear Method (Tier 2b $_{HVAE}$)* – Marks & Nunez approach [19]:

$$E_{CF4\_AE} = \Sigma_i \left( K_1 \cdot AED_i^{K2} \cdot kA_i / 1000 \right) \qquad (14)$$

$$E_{C2F6\_AE} = E_{CF4\_AE} \cdot F_{C2F6/CF4} \qquad (15)$$

where AED is the duration of each AE, kA is the amperage, $K_1$ and $K_2$ are constants that vary in steps dependent on the AE duration.

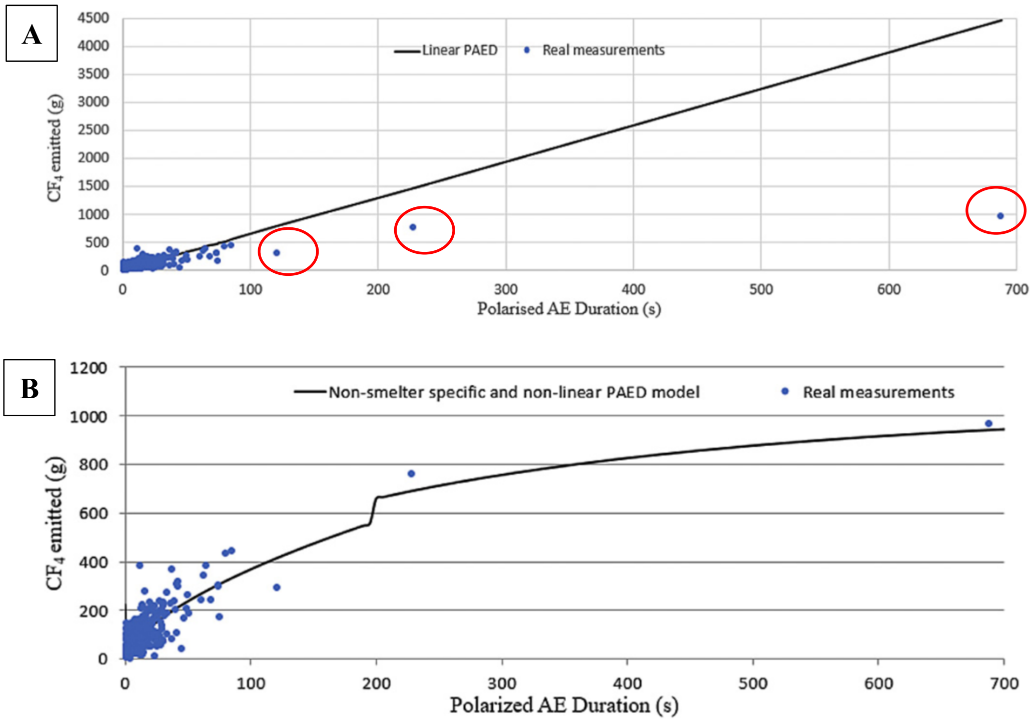

**Figure 5. PFCs against AE duration, comparing measured (dot) vs. estimated (line) emissions using the Slope Method (A) and Non-Linear (B) approach, from [18].**

*Non-Linear Method (Tier 2b $_{HVAE}$)* – Dion et al approach [20]:

$$E_{CF4\_AE} = \Sigma_i \,( C_1 \bullet AED_i^{C2} \bullet MP_{day} ) \quad (16)$$

$$E_{C2F6\_AE} = \Sigma_i \,( C_3 \bullet AED_i^{C4} \bullet MP_{day} ) \quad (17)$$

where $C_1$ and $C_2$ are coefficients for $CF_4$; and $C_3$ and $C_4$ are coefficients for $C_2F_6$; all four coefficients vary as a function of $MP_{day}$, the average daily metal production of a cell. For details of coefficients for both methods, refer to the *2019 Refinements* [15].

The Tier 2b Non-Linear Methods provide benefits in that they give more accurate emissions estimates than the Tier 2a Slope Method, but without the cost of upgrading to Tier 3 which requires elaborate gas measurements at each smelter to obtain facility-specific coefficients. These can be expensive (depending on the method used) and there may be practical challenges for high-performing smelters with very low AE frequencies as very long measurement campaigns may be required to capture a representative set of AE emissions.

## 3.6. Low Voltage PFCs – New Guidance, Emission Factors & Limitations

Low voltage (<8V) emissions are estimated in the *2019 Refinements* by Tier 1 or 3 methods. Default Tier 1 production-based emission factors $EF_{CF4\_LV}$ are shown in Table 3. As might be expected [1 - 2], LV emissions are on average more significant for the larger, modern $PFPB_M$ cells (0.018 kg $CF_4$/t Al) as they come with a greater risk of spatial variation in cells and therefore tend to experience more PFC coevolution when compared with smaller, legacy $PFPB_L$ cells (0.009 kg/t Al). Similarly, the bolded values in Table 3 shows that LV emissions makes up an average of 62 % and a median of 70 % total PFCs from modern PFPB and $PFPB_{MW}$ (China) cells, respectively. For $PFPB_{MW}$ technology this matches our observation that spatial variations are often a significant issue in Chinese smelting cells due to the extreme regional pressures to operate at low energy thereby often at the expense of cell conditions and other key performance indicators (KPIs).

The 36 % LV contribution to total PFCs in legacy PFPB cells is also worthy of noting as this highlights that legacy cells are not immune to LV emissions either, particularly cells that have been retrofitted for greater productivity and lower energy operations (which drive spatial variations in cells as discussed in Parts 1 and 2 by Welch et al. [1 - 2]). For much older SWPB and Søderberg (HSS and VSS) cells, LV emissions play an almost insignificant (1 – 5 %) role to total emissions when compared to the high AE-emissions profile; however, in terms of emissions intensity (up to 0.026 kg $CF_4$/t Al) they are on similar scales of magnitude to PFPB technologies.

The production-based approach to estimating LV emissions are to multiply Tier 1 default factors or Tier 3 *facility-specific* emission factors $EF_{CF4\_LV}$, by metal production MP:

$$E_{CF4\_LV} = EF_{CF4\_LV} \bullet MP \tag{18}$$

An alternative approach – at Tier 3 only – is to estimate LV emissions as a *ratio* of AE emissions performance, i.e.

$$E_{CF4\_LV} = E_{CF4\_AE} \bullet R_{LV\_CF4\,/\,AE\_CF4} \tag{19}$$

where $E_{CF4\_AE}$ are estimated AE-$CF_4$ emissions and $R_{LV\_CF4\,/\,AE\_CF4}$ is the facility-specific ratio of LV to AE-related $CF_4$ emissions.

A major challenge in drafting more accurate methods was that there were no clear technology divisions, industry-wide process performance factors (at least those readily available to the IAI and IPCC working group) that could be used to directly correlate with LV emissions – in the same way as AE-minutes/cell-day (AEF • AED) are used to model AE-emissions. Therefore, no good alternatives – apart from a Tier 1 production-based approach or relating back to AE-emissions (Tier 3) – could be found without excessive uncertainties.

The Tier 3 'ratio' method (equation 19), however, does have some limitations as it assumes that any reduction in AE-emissions at one facility must also result in lower LV-emissions. This may be a fair assumption within one facility *if* reductions are made via addressing the root causes of PFC co-evolution, e.g. optimizing feed control strategy and reducing spatial variations in cells [1-2], and *if* we were to expect a similar fraction of LV emissions to always progress to an AE. When comparing identical smelters over different years, the LV/AE ratio was found to remain reasonably within the same order of magnitude, justifying the Tier 3 'ratio' approach [16]. However, if AE-emissions are reduced merely by reducing AE durations – for instance, by more rapid quenching of AEs – and without reducing AE frequencies, then this would not address the root causes of PFC co-evolution and one might expect absolute LV emissions to be unchanged.

Use of the 'ratio' method was also considered at the Tier 2 level; however, there were large differences in the distribution of LV/AE emission ratios from one smelter to another within the same technology division and with sometimes up to 2 orders of magnitude of difference! Adoption of the 'ratio' method at Tier 2 (using *average* LV/AE ratios for each technology) in the *2019 Refinements* was therefore dropped as it would have resulted in *less accurate* estimates of LV-emissions for an individual smelter than taking the Tier 1 production-based approach.

Figure 6 compares LV vs. AE emission factors (units, kg $CF_4$/t Al) for a number of facilities (mostly legacy $PFPB_L$ technology, with some modern $PFPB_M$) showing that there is *no clear* correlation between absolute AE-emissions and LV-emissions. While some smelters exhibit both low levels of AE and LV-emissions, others with low AE emissions have comparatively high LV-emissions. This brings us to the need for better methods to estimate LV-emissions, using a smelter's process performance data and ideally based on technical factors in cell technology, operations or materials, rather than the statistical approach currently adopted – discussed in Section 4.

Finally, the obtaining of Tier 3 emission factors, specifically for low voltage PFCs will be an ongoing challenge for the industry given the very low detection limits (down to ppb levels) that are required (particularly if measurements of PFCs at taken in stacks of potline scrubbers). Updated PFC measurement protocols are in the process of being developed by the IAI since the existing protocols [21] focus only on AE-emissions.

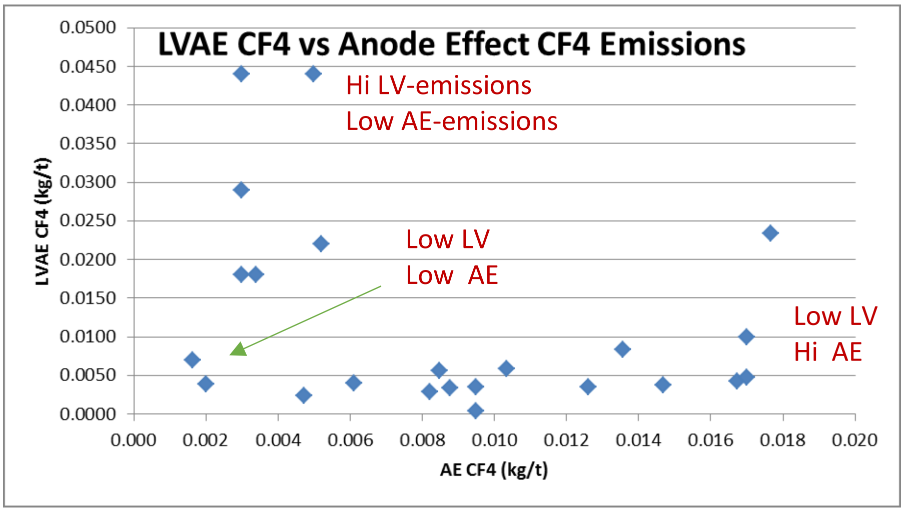

**Figure 6. Comparison of LV vs. AE-emissions intensity (kg $CF_4$/t Al) for multiple PFPB facilities. Data courtesy of the IAI.**

### 3.7. PFCs from Cell Startup – New Guidance

The *2019 Refinements* provides more explicit guidance on the accounting of PFCs (both AE and LV-emissions) during 'cell start-up' (CSU) to avoid underreporting of emissions in these periods. Cell start-up can be defined as from the point when the anode beam is raised and aluminium metal is first produced in the cell. As this is not the focus of this paper, the reader is referred to the *2019 Refinements* [15] for further detail.

### 3.8. Direct Total PFC Measurement – New Guidance

Given the substantial levels of uncertainty in estimating total PFCs – particularly LV emissions – with existing process data, the direct measurement of total PFCs at individual facilities is provided in the *2019 Refinements* as an alternative Tier 3 method. Total emissions could then be measured at potline stacks in a similar fashion to other smelter emissions (e.g. fluorides, dust, etc), through either continuous emission monitors (CEMs) or time-integrated sampling combined with offline lab-analysis. This would provide a simpler (at least for the GHG inventory compiler) and more accurate basis for emissions accounting whereby the measurement and sampling error are the only sources of uncertainty.

CEMs – particularly Fourier-Transform Infrared (FTIR) spectroscopy types – are a commonly used instrument as part of the method for establishing Tier 3 AE-emission factors; however, FTIR instruments often require highly trained staff or external consultants to operate and the high sensitivity (ppb-level) required for LV-emissions measurement are ongoing challenges. Development of simpler Tuneable Diode Laser (TDLAS) / Quantum Cascade Laser (QCL) technologies for $CF_4$ measurement – with a similar approach to 'plug-and-play' lasers for continuous HF measurement – appear promising and now being tested in smelters [22]. Recent advances in time-integrated sampling and offline-lab analysis for smelters – similar to the technology used for global atmospheric measurements of PFCs, as reported by CSIRO [23] – might also provide a highly accurate (down to *ppt* level sensitivity) and more economical alternative for emissions measurement.

As mentioned previously, the IAI's pending updates to the industry's PFC Measurement Protocol would be the best reference for measurement considerations and options, should smelters look to go down this pathway.

## 4. Pathways for Reducing All PFCs and More Accurate Accounting

### 4.1. Total PFCs as a Key Performance Indicator (KPI)

The aluminium industry has proven that great strides in emissions reduction can be achieved when it is a clear management KPI for smelter performance, shown by the past reductions in AE-related PFCs by focusing on AE *frequencies* and *durations*. Similarly – based on what we now know – it would be natural to consider extending these KPIs to *Total PFCs* (kg $CO_2$-equivalent/t Al), encompassing both AE and low voltage emissions. These could be reported on a monthly basis and progress tracked for reducing them.

Total PFCs could be considered as not only KPIs but as '*leading indicators*' for a smelter's overall process and environmental performance. On the process aspect, we have already demonstrated (through Parts 1 and 2 papers in this series [1 - 2]) that by addressing the root causes of PFC co-evolution one would address the factors that cause spatial differences across the aluminium reduction cell, resulting in overall better operational performance. Recent smelter studies [17, 24] have already demonstrated the potential to improve bottom-line smelter performance (e.g. noise, voltage, current efficiency and DC energy consumption) when reducing total PFCs, including low voltage emissions.

On the environmental aspect, it is acknowledged that indirect GHG emissions from the supply of energy to smelters (highly dependent on whether the energy source is coal, gas or low-carbon footprint sources such as nuclear or hydro) can outweigh any contribution by direct GHG emissions from the smelting process. For smelters operating with hydro or other renewable energy sources, PFCs will still be a greater proportion of their total GHG emissions. Regardless of the energy source, the high atmospheric lifetime and potency of PFCs as a greenhouse gas and its impact on process performance – resulting from spatial differences in cells and process inefficiencies – is very clear.

Thoughts are provided in the next few sections on potential pathways to reduce total PFCs in the future, and on how industry-wide accounting of emissions could be further improved.

### 4.2. Attacking the Root Cause – Spatial Variations in Cells

In Parts 1-2 Welch et al. [1 - 2] presented some of the underlying factors why modern smelting cells have become more prone to PFC co-evolution. This is attributed to changes in cell design, operations and raw materials. To prevent all forms of PFC co-evolution, we must first attack the root cause which are mainly causes of spatial variation in aluminium cells so as to prevent anode potentials from getting to the point where PFC co-evolution is enabled.

The first question is – *can cells (and their control systems) be designed, retrofitted and operated in such a way that spatial variations in cells are minimised?* Rather than continuing down the same track for instance, can we consider:

- Strategies to increase or provide optimal electrolyte mixing and recirculation? e.g.: redesigning anode slots to enhances electrolyte circulation patterns, and balance their benefits against quality of operation?
- Maximising the volume of liquid electrolyte in cells per unit kA?
- Reducing the load on an individual point feeder per unit kA? e.g. more feeders, more equally distributed by anode surface or the time to transport alumina to that surface?
- Designing alumina feeding systems to ensure alumina is 'always' delivered to the electrolyte without physical obstructions? 'Smart' breakers/feeders [25] may be one way of detecting when this is not the case.
- A controllable alumina distribution system for feeding alumina to zones that better match the spatial consumption rate?
- Reducing the thermal impact (and duration of impact) of anode changes per operational cycle – e.g. anode preheating or designing anode flowsheets for 'just-in-time' delivery of 'hot' anodes straight after baking and rodding (also reducing total kWh burden) [26 - 27]? Or can extra thermal energy be provided post-anode change (or for specific anode locations)?
- Modifying the $AlF_3$ delivery system so that its distribution minimizes spatial variations in solvent electrolyte composition?

While some of these require a paradigm shift in way cells are designed or operated, the industry has benefitted considerably from previous changes in design philosophy (e.g. point-feeders, modern alumina feed control). Another paradigm shift would be – for further amperage increases – abandoning the philosophy of increasing cell length and thus changing to wider cell profiles. Such an approach not only has the benefits of reducing heat losses and kWh/kg, and increasing productivity/metre of potroom, but with multiple rows of anodes presents an opportunity to incorporate alumina feeding strategies to overcome the problems arising from spatial variability. Would such concepts be so 'far-fetched', as posed by Dupuis and Welch [28]? A hypothetical sketch of an 80-anode block (40 assemblies) ~ 830-kA cell is illustrated in Figure 7, with an anode/feeder ratio of 5.7 compared to 8 for today's modern 500-kA cells while simultaneously reducing the radius encompassed by each feeder.

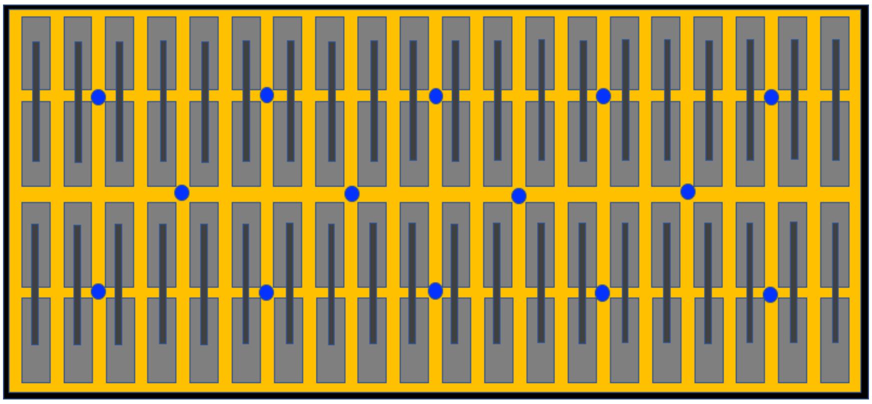

**Figure 7. Hypothetical 'wide' PFPB cell concept with multiple rows of anodes and greater ratios of electrolyte channels and feeders per anode, adapted from [27].**

Operational considerations are also key for reducing spatial variation in cells – for instance, can we consider:

- Better control of liquid electrolyte levels – ensuring all cells have sufficient electrolyte volume for good alumina dissolution?
- Improved anode change practices to reduce variations in ACD and therefore imbalances in current draw after each anode change?

- Addressing the causes of spike formation, which cause further spatial imbalances in current density and temperature (which could increase PFC co-evolution as the extra heat provides extra entropic energy to form C-F gases?)

Likewise, raw materials factors (as discussed in by Welch et al. in Parts 1 and 2 [1 - 2]) are an important consideration for minimising spatial variation:

Can alumina quality be optimised? For instance, many alumina impurities (e.g. Li, Mg, Ca – especially in Chinese smelters operating with up to 10 % LiF has been rumoured!) inhibit alumina solubility and therefore can impact dissolution kinetics [2]. Furthermore, can the properties of alumina be tailored to enhance alumina transport and dispersion once fed into the cell, e.g. with an 'optimal' level of $Al_2O_3•3H_2O$ that sometimes provide a 'volcano' effect in feeders?

Apart from systematically addressing the root causes of spatial variation in cells, the next best thing is for *earlier* detection or sensing of PFC coevolution – whether AE-related or LV emissions – and to respond to these quickly. The next two sections present some thoughts towards this.

### 4.3. Earlier Detection and Response for AEs – using Cell Voltage

In the past, the '8V' trigger definition of an AE in aluminium smelting cells introduced for PFC accounting purposes was a convenient threshold when older technologies operated at much higher voltages (e.g. HSS/VSS at ~5V or higher) and during cell start-up. This didn't matter previously, since in older technologies an increase in cell voltage ~ 150 mV above normal operating voltage would inevitably result in voltage rapidly exceeding 8 V, triggering control systems to flag an AE. However, in today's modern high-amperage cells the voltage does not need to exceed 8 V to co-evolve PFCs and exhibit characteristic 'pre-anode effect'-like behaviour (i.e. a sharp exponential rise in cell voltage above normal operating levels) and lead to a corresponding exponential rise or peak in measured $CF_4$ and $C_2F_6$ emissions from that cell [29]. This is the industrial equivalent to the electrochemical definition of an anode effect for fluoride-melt systems (with a single anode) where a sharp increase in voltage is observed under constant current control. Note that the definition is not solely for electrochemists, it is a scientific one fully supported by electrochemical engineers as well! Therefore, the '8 V' definition of an anode effect is no longer relevant.

Short of installing individual anode current monitors (discussed next), the next best solution would be for smelters to use: (i) a lower detection threshold on cell voltage, (ii) the rate of change / slope in cell voltage, or (iii) a combination of these. Some smelters already apply similar strategies for detecting 'Near-AE' or pre-AE periods [30 - 31] and then trigger extra feed or automatic beam movements as a response action (similar to those for automatic AE treatment).

*A lower detection threshold on cell voltage* – for instance a systematic ΔV ~ 150 – 300 mV rise above normal operating or target voltage levels – would provide an earlier trigger for AEs and lead to a more accurate accounting period encompassing all PFC emissions. Furthermore, it would advance the remediation actions and minimise the duration of any PFCs. Considering that at normal operating voltage ~4V modern cells are likely operate at anode potentials closer to ~ 1.75 V [1], an increase of only ~80-150mV is required to enable PFC coevolution (~ 1.83 - 1.89 V), equations 3 - 4). Note that this would already be an average across all anodes, not just on an individual anode. Irrespective, this approach would need to exclude 'noisy' cells and consider normal pot voltage variations over the operational cycle of the cell, e.g. from alumina overfeed / underfeed cycles (perhaps ± 50 mV), ACD changes from beam movements (voltage changes not related to anode potential but a change in electrolyte resistance), additional voltage for anode change, etc.

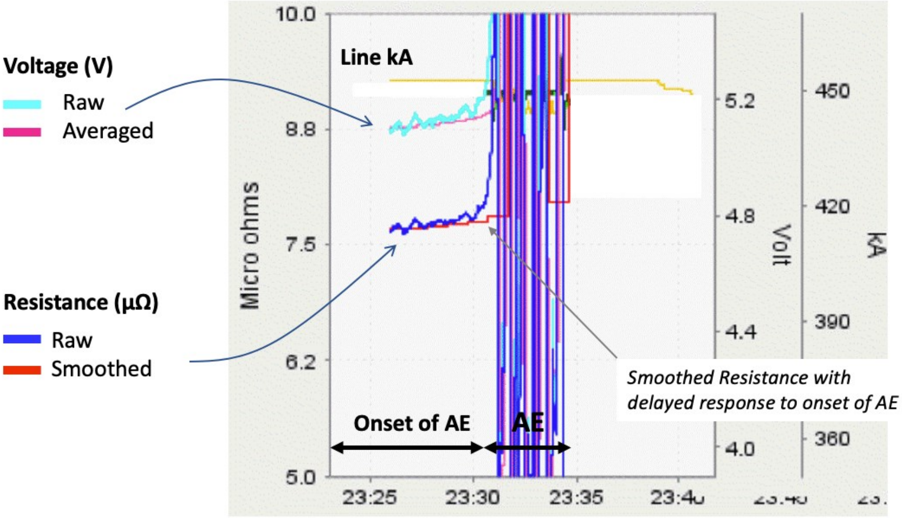

**Figure 8. Cell voltage and resistance signals on a cell prior to, during and after an AE, showing raw (blue, light blue) and smoothed signals typically used for control (red, rose).**

The *rate of change* or *'slope'* in cell voltage (d*V*/d*t*) would also provide an early warning of spatial imbalances in alumina levels overall in the cell. This was illustrated clearly in Figure 1 where well prior to the AE the voltage rise (dV/dt) from ~ 4.5 V to 5 V initially was slow (region "A") and then rapidly increased in the seconds just prior an AE (region "B"). For detecting changes in voltage slope on modern cells – as shown in Figure 8 – the use of raw voltage (light blue) or resistance (blue) signals is recommended because many cell technologies use heavily smoothed or averaged resistance or voltage signals for automatic pot control (red, rose lines). This delays the signal response and takes away the opportunity to pick up the rapid voltage rise approaching an AE (and hence trigger a control response).

If such strategies are applied more universally across the industry, the 'industry-consensus' definition of an AE could be revised – and IPCC Slope factors and emissions coefficients for AE-emissions accounting refined accordingly they then can more accurately capture emissions from all 'anode effects', versus other LV emissions that occur without any observable change in cell voltage levels.

### 4.4. Detecting Low Voltage PFCs – Using Individual Anode Sensors

For high performing facilities where AE-emissions are already comparatively low, the low voltage emissions become the next challenge. As discussed, this is not only a matter of environmental performance, but also for further gains in cell performance KPIs. Unfortunately, cell voltage signals – which represent the overall or *average* condition of the cell – are still incapable of providing information on spatial differences, particularly as reduction cells become larger with more anodes.

This has led to the introduction of individual anode current monitoring as the 'next-generation' sensors for spatial variations in cells (example output in Figure 2). As well as facilitating easier diagnosis of anode issues and anode change quality, they have the ability to sense when individual anodes are undergoing PFC co-evolution long before this progresses to an anode effect (if at all) thereby providing time for control systems and potline operators to respond. Success in doing this would not only minimise LV emissions but also AE emissions. This shows the potential of individual anode current monitoring.

Anode current measurements are certainly not new to the industry – patents have existed since the 1980s [32] and Figure 9 shows a system that has been in operation for over 30 years on an older cell where sensors were conveniently installed on copper flexes that connected individual anodes to the anode beam. In modern smelters, variants of anode sensor systems now include direct voltage drop (mV) measurements and magnetic field sensors [33] connected to pot control systems by wired or wireless communications. These can be installed either directly on anode rod stems (wireless example in Figure 10) or installed along an anode beam (at multiple points to sense current flow to individual anodes, less practical issues with anode change if wired).

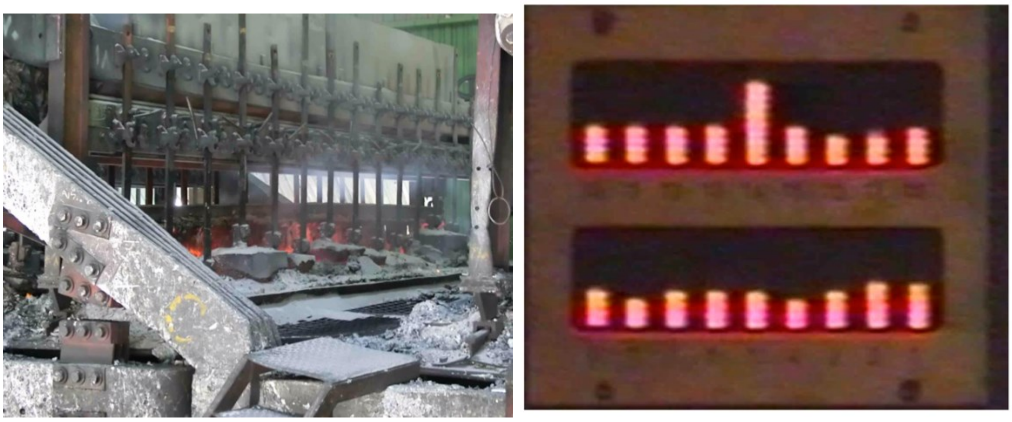

**Figure 9. Old cell technology (left) with system showing anode currents (right) at the cell.**

Anode sensors provide the ability to quickly detect passivation (loss of current) on individual anodes that are likely co-evolving PFCs thereby triggering a control response. They also lead to the ability to predict PFC co-evolution, particularly low voltage emissions (as demonstrated by Dion et al. [35] in Figure 11). Other approaches include (i) using the anode data to model alumina concentrations around specific feeders [36], or (ii) alternatively anode 'pseudo-resistance', effectively allowing alumina feed control by regions in a cell [37]. A further extension of this would be to model individual anode potentials $E_{\text{anode}}$ and therefore identify anodes when PFC co-evolution is likely to be enabled (when $E_{\text{anode}} > 1.83 - 1.89$ V), *before* anodes are passivating from PFC generation.

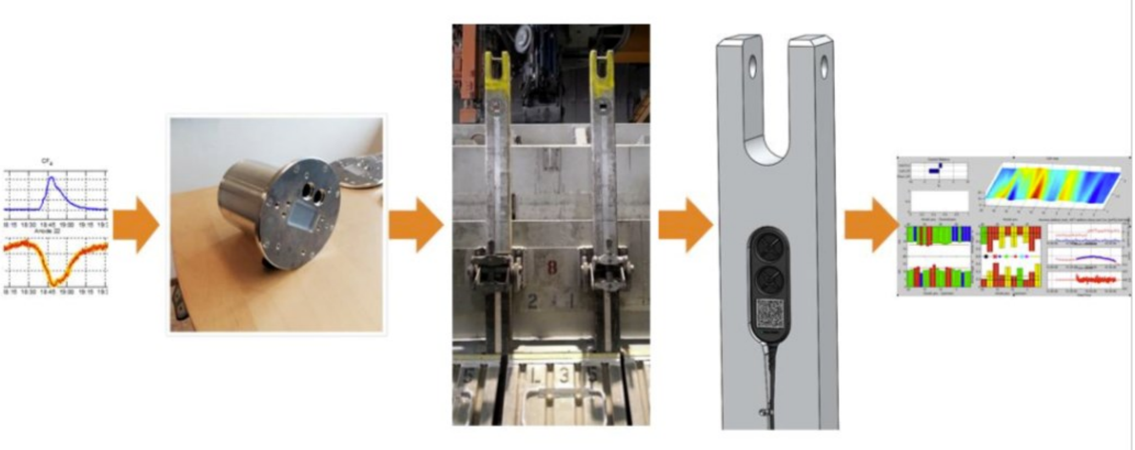

**Figure10. Modern example of anode current measurements for detecting PFC coevolution and other cell diagnostics, reproduced from Norsk Hydro [34].**

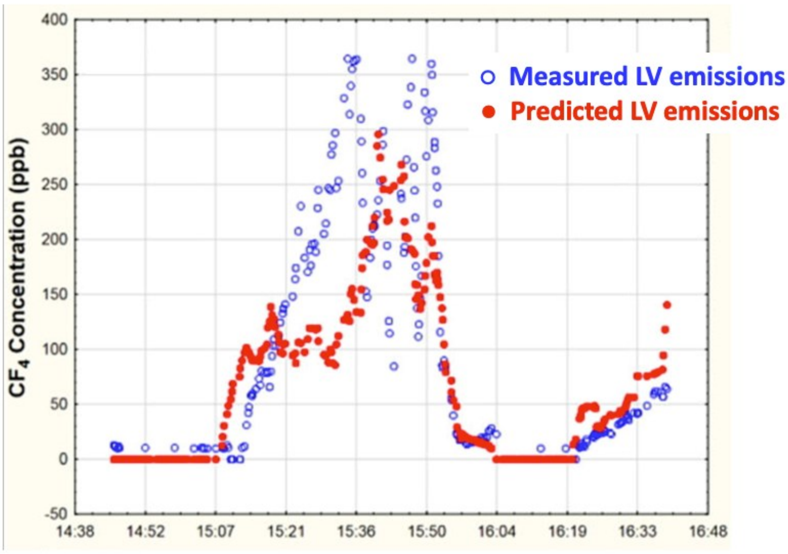

**Figure11. Measured (blue) low voltage CF4 emissions vs. those predicted (red) using models based on anode current data, reproduced from Dion et al. [35].**

These approaches all allow targeted control responses in the cell to address spatial variations, e.g. through automated additional feeds of alumina targeted to specific feeders and anodes that need it. However, in fully automating responses smelters would need to proceed with caution in not just compensating for spatial issues without addressing the root causes – e.g., additional feeds targeted at a point feeder are unhelpful if the cause of spatial issues is a blocked feeder hole.

Furthermore, if such anode sensors (and associated models) were further refined and more widely used by the industry, they could provide the means to introduce a new process-performance based method to account for LV-emissions. This would be a major improvement over the statistical based methods outlined in the IPCCs *2019 Refinements* where emissions are correlated only to technology/amperage, metal production or AE-related emissions.

While the cost of anode monitoring systems is often deemed prohibitive, individual anode sensors might not be as hugely expensive as one might think. The cost is perhaps not more than 1.5 % to the cost of relining a modern large cell or less than 0.2 % of the CAPEX of a new plant, without considering the benefits to process control and ultimately potline KPIs. Indeed, there are smelters already rolling out individual anode monitoring as a full-plant solution whereas others are looking at this for smaller groups of trial or booster cells.

### 4.5. Detecting Low Voltage PFCs – using Low Cost Sensors

An alternative to using anode current sensors for sensing / detecting low voltage PFCs could be to use continuous PFC gas sensors. Direct PFC gas measurement is already an alternative Tier 3 IPCC method for accounting a smelter’s total emissions (section 3.8). However, when the measurement point is the potline scrubber stack, there is a loss of individual cell-to-cell resolution that prevents control actions being taken. In general, continuous gas monitoring technologies are too expensive to apply on individual cells.

The question is therefore, following the trend of ‘low cost sensors’ for ambient air quality (e.g. for particulates/PM$_{2.5}$, NOx, ozone, etc) – can *affordable PFC gas detection sensors could be developed and installed in the exhaust duct of individual cells? Or even in the interconnecting ducts of sections of cells* compatible with the potroom design of cells (e.g., 6 - 12)?

Such sensors do not need to be highly accurate (e.g. on the same level as an FTIR measurement), they only need to indicate when individual cells are generating PFCs. This could be on a binary level (yes/no) or just qualitative levels (0-none, to 5-high). A trigger could then set off further control actions – either by automatic pot controllers, or by operators investigating at the cell.

Figure 12 shows a ~ 10 h period of PFC monitoring (by FTIR) where low voltage emissions were monitored in the gas duct for that section of cells. The highlighted increase in LV-emissions (and the individual jumps up in emissions, marked by arrows) correlates well with the timing of sequential and progressive anode changes on 5 cells. Connecting a ‘low-cost’ PFC sensor in place of the FTIR would still allow identification of these periods for either the control system or an operator to address. Here action is still needed irrespective of the precise amplitude of the PFC coevolution and therefore precision is a lower priority than detection.

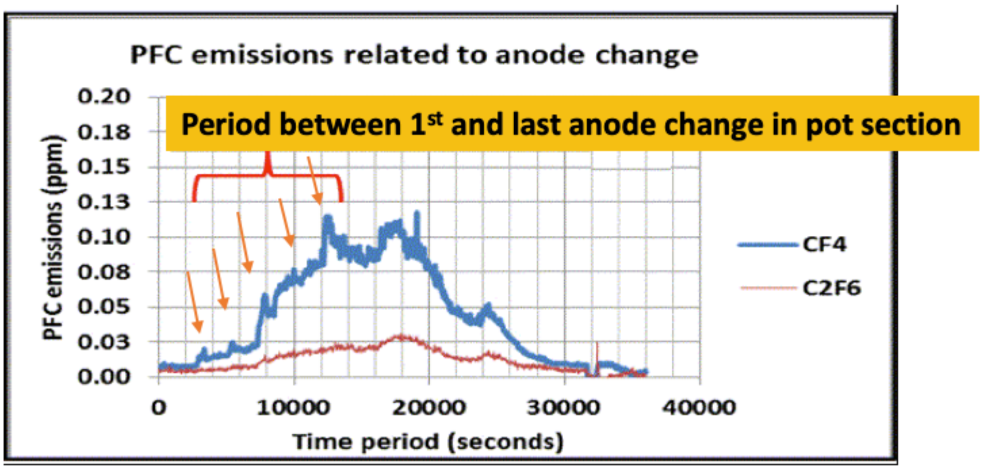

**Figure12. Low voltage PFC emissions measured in the duct of multiple cells.**

## 4.6. Further Process / Technology Divisions for PFC Accounting

The previous sections describe approaches by which AE and low voltage emissions could be better detected by control systems, providing additional process parameters and data that can be used to improve accounting of total PFC emissions.

In terms of technology divisions, the current IPCC approach of dividing by anode technology (prebake vs Søderberg), alumina feed systems (point-fed vs. side/centre-worked) and amperage (greater or less than 350 kA) is limited in its ability to capture the fundamental factors that lead to greater or lesser emissions, particularly low voltage emissions.

Additional factors that could be considered (if data was captured by industry bodies such as the IAI) for further refinements of the technology divisions could include:

- Anode current density (A/cm$^2$ of anode surface)
- Bath levels – or more precisely immersion depth of anodes in the electrolyte – which reflects actual anode current densities.
- Specific electrolyte volume per unit kA
- Specific point-feeder loading, e.g. feeders per unit kA, or kg $Al_2O_3$ demand/per second per feeder?
- No. of anodes, or maximum anode distance serviced per feeder?
- Use of slotted anodes?
- Typical duration for new anodes to reach operational kA draw or temperatures?
- Bath chemistry (xs $AlF_3$, LiF% levels, etc)?

## 5. Conclusions

Recent developments in modern aluminium cells means that the past definitions and assumptions of when PFCs are generated in cells have had to be challenged and re-assessed. The knowledge that PFCs can be generated during normal operating voltages (< 8 V) is now being taken into account in the latest 2019 IPCC guidelines for GHG accounting (now accepted by the IPCC, but yet to be adopted by the UNFCCC for implementation by governmental bodies). As anode effect emissions are better addressed, low voltage emissions will pose the next challenge to the smelting industry.

This all points to an industry need for:

- A new approach to signal processing to achieve optimum benefit of modern cell technologies and for better scientific understanding of the process.
- Faster response to indicators of potential approach to PFC coevolution (such as EGA's 'near-AE' logic) in order to prevent, or shorten the duration of the occasional AEs,
- Implementation of advanced control logic that accounts for and minimises the impact of spatial variations in the cell that are inevitable.
- Redesign of equipment and layout used for alumina feeding to increase their reliability and flexibility.

These will all drive reductions in total PFC emissions with further benefits to cell performance and smelter KPIs.

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## 7. References

1. Barry Welch, Mark Dorreen and David Wong, 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. Paper to be presented at the *37th Conference and Exhibition ICSOBA 2019*, September 16-20, 2019, Krasnoyarsk, Russia.
2. Barry Welch and David Wong, Linking electrochemistry, modern aluminium cell design and operating conditions, for a better understanding of anode reactions and various levels of PFC co-evolution, Part 2: The impact of cell design and process conditions on energy utilization and PFC emissions, Paper to be presented at the *37th Conference and Exhibition ICSOBA 2019*, September 16-20, 2019, Krasnoyarsk, Russia.
3. G.D. Myhre et al., Anthropogenic and natural radiative forcing, in *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (AR5)*, ed. T.F. Stocker et al., (2013), Cambridge University Press: Cambridge, UK & New York, USA.

4. J. Mühle et al., Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane, *Atmospheric Chemistry and Physics*, Vol. 10, pp. 5145–5164, (2010).
5. IPCC Task Force on National Greenhouse Gas Inventories, *Report of IPCC scoping meeting for a Methodology Report(s) to refine the 2006 IPCC Guidelines for National Greenhouse Gas Inventories*, Report of the IPCC Scoping Meeting, ed. S. Ngarize et al. 2016, IGES: Japan.
6. Alton Tabereaux, Nolan E. Richards and C.E. Satchel, Composition of reduction cell anode gas during normal conditions and anode effects, *Light Metals* 1995, 325-333.
7. R. Bunsen, *Annag.*, Vol. 92, p. 251, (1854).
8. International Aluminium Institute, *Results of the 2017 Anode Effect Survey: Report on the aluminium industry's global perfluorocarbon gas emissions*, London, (2018).
9. Jerry Marks and Chris Bayliss, GHG measurement and inventory for aluminum production, *Light Metals*, 2012 805-808.
10. Wangxing Li et al., Latest results from PFC investigation in China. *Light Metals* 2012, 619-622.
11. Jerry Marks and Pernelle Nunez, Updated factors for calculating PFC emissions from primary aluminum production, *Light Metals* 2018, 1519-1525.
12. David Wong et al., PFC emissions from detected versus nondetected anode effects in the aluminum industry. *JOM* 2015, Vol 67, Issue 2, 342-353.
13. Jooil Kim et al., Quantifying aluminum and semiconductor industry perfluorocarbon emissions from atmospheric measurements, *Geophysical Research Letters*, Vol 41, 4787–4794, (2014).
14. Intergovernmental Panel on Climate Change (IPCC), Volume 3 - Industrial Processes and Product Use, Chapter 4, Section 4.4 - Primary Aluminium Production, in *2006 IPCC Guidelines for National Greenhouse Gas Inventories*, ed. A.R. Jamidu H. Y. Katima, IGES: Hayama, Japan, 4.49-4.57, (2006).
15. Intergovernmental Panel on Climate Change (IPCC), Volume 3 - Industrial Processes and Product Use, Chapter 4, Section 4.4 - Primary Aluminium Production, in *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories*, pp. 4.40-4.64, available: https://www.ipcc-nggip.iges.or.jp/public/2019rf/index.html, accessed July 1, 2019, (2019).
16. Lukas Dion et al., Evaluation of time consistency when quantifying emissions of perfluorocarbons resulting from low voltage anode effects, *Light Metals* 2018, 1457-1462.
17. David Wong et al., PFCs from the chinese aluminium sector—Challenges in emissions accounting and further characteristics. *Light Metals* 2018, 1527-1535.
18. Lukas Dion et al., Quantification of perfluorocarbons emissions during high voltage anode effects using non-linear approach, *Journal of Cleaner Production*, 2017, 164, 357-366.
19. Jerry Marks and Pernelle Nunez, New algorithm for calculating $CF_4$ emissions from high voltage anode effects. *Light Metals* 2018, 1479-1485.
20. Lukas Dion et al., Universal approach to estimate perfluorocarbons emissions during individual high-voltage anode effect for prebaked cell technologies. *JOM*, 2018, Vol 70, Issue 9, 1887-1892.
21. US Environmental Protection Agency & International Aluminium Institute. Protocol for measurement of tetrafluoromethane ($CF_4$) and hexafluoroethane ($C_2F_6$) emissions from primary aluminum production, 42 pages, (2008).
22. Luis Espinoza-Nava et al., QCL-based perfluorocarbon emission monitoring, *Light Metals* 2016, 541-544.

23. Paul Fraser, Paul Steele and Mark Cooksey (CSIRO), PFC and carbon dioxide emissions from an Australian aluminium smelter using time-integrated stack sampling and GC-MS, GC-FID analysis, *Light Metals* 2013, 871-876.
24. Eliezer Batista et al., Low voltage PFC measurements and potential alternative to reduce them at Alcoa smelters, *Light Metals* 2018, 1463-1467.
25. David G.E. Davies et al, Practical approach of detecting bath in a reduction cell, Proceedings from the *11th Australasian Aluminium Smelting Technology Conference*, Dubai, 6 - 11 December 2014, Paper 17T2.
26. Barry A. Sadler, Anode manufacturing technology: improvements since 2004 and implications of potential changes in the next 10 years. Proceedings of the *11th Australasian Aluminium Smelting Technology Conference*, Dubai, UAE, 6 - 11 December, 2014, Paper 02Key1.
27. Otavio Fortini, Hall cell energy recovery and anode pre-heating, gauging the opportunity, *JOM*, 2011, Vol 63, Issue 8, 127-131.
28. M. Dupuis and B. Welch, Designing cells for the future – Wider and/or even higher amperage?, *ALUMINIUM*, 1 - 2, 2017.
29. David Wong, Alton Tabereaux and Pascal Lavoie, Anode effect phenomena during conventional AEs, low voltage propagating AEs and non-propagating AEs, *Light Metals* 2014, 529-534.
30. Abdalla Zarouni et al., A study of low voltage PFC emissions at DUBAL, *Light Metals* 2013, 859-863.
31. Andrew Wilson, Mark Illingworth, Mike Pearman, Anode effect prediction and pre-emptive treatment at Pacific Aluminium, Proceedings of the *12th Australasian Aluminium Smelting Technology Conference*, Queenstown, New Zealand, 2018, Paper 4c3.
32. Jeffrey Keniry and Eugene Shaidulin, Anode signal analysis – the next generation in reduction cell control, *Light Metals* 2008, 287-292.
33. Daniel A. Steingart et al. Experiments on wireless measurement of anode currents in Hall cells, *Light Metals* 2008, 333-338.
34. Hans Erik Vatne (Norsk Hydro ASA), Smelter of the Future, Presentation at the *TMS Annual Meeting: 2019 Light Metals Keynote Session*, 11th March 2019, San Antonio, Texas.
35. Lukas Dion et al., Prediction of low-voltage tetrafluoromethane emissions based on the operating conditions of an aluminium electrolysis cell, *JOM*, 2016, Vol 68, No 9, pp. 2472-2482.
36. Yuchen Yao et al., Estimation of spatial alumina concentration in an aluminum reduction cell using a multilevel state observer, *AIChE Journal*, 2017, Vol. 63, No. 7, 2806-2818.
37. Jing Shi et al. Advanced feeding control of the aluminium reduction process, *Proceedings of the 12th Australasian Aluminium Smelting Technology Conference*, Queenstown, New Zealand, 2018, Paper 4c2.